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# An electronic structure study of H<sub>2</sub> and CH<sub>4</sub> interactions with MgO and Li-doped MgO clusters

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An *ab initio* study is presented concerning the chemisorption of hydrogen on a model of the (100) surface of MgO and Li-doped MgO. The local surface environment was modeled employing cubic and tetragonal clusters composed of 8 and 12 atoms, respectively. The lattice constant for the clusters was fixed at the experimentally determined value for bulk MgO and the geometry of the adsorbate was optimized at the unrestricted Hartree–Fock (UHF) level of theory. Correlation energy was treated at the second-order unrestricted Møller–Plesset (UMP2) level at the UHF optimized geometry. It was found that H<sub>2</sub> undergoes heterolytic dissociation at neighboring three-coordinated Mg and O sites (denoted Mg<sub>3c</sub> and O<sub>3c</sub>) in MgO with activation energies of 4.2 and 2.4 kcal/mol at the UHF and UMP2 levels, respectively. Li-doped MgO did not support heterolytic dissociation at neighboring Mg and O sites. Instead H<sub>2</sub> was found to dissociate homolytically without barrier at two O<sub>3c</sub> sites and to undergo hydrogen atom abstraction at O<sub>3c</sub> and O<sub>4c</sub> sites. At the UHF/UMP2 level, it was found that at O<sub>3c</sub> sites, abstraction occurs with a 17.9/3.0 kcal/mol barrier, and at O<sub>4c</sub> sites, abstraction occurs with a 15.7/0.6 kcal/mol activation energy.

## I. INTRODUCTION

Magnesium oxide is known to catalyze a variety of reactions involving hydrocarbons. Some examples of these reactions are the H<sub>2</sub>/D<sub>2</sub> exchange reaction,<sup>1</sup> methanol and ethanol decomposition,<sup>2,3</sup> alkene hydrogenation,<sup>4</sup> the water–gas shift reaction,<sup>5</sup> and isomerization of *cis*-2-butene.<sup>6,7</sup>

In addition, Li-doped (hereafter referred to as Li/MgO) MgO is known to increase the activity of the MgO catalyst with respect to the high temperature conversion of methane to higher order alkanes<sup>8,9</sup> and oxidation of C<sub>2</sub> hydrocarbons to form carbon oxides.<sup>10</sup> In this study, *ab initio* molecular orbital methods are applied to clusters of (MgO)<sub>n</sub> and LiMg<sub>n-1</sub>O<sub>n</sub> (*n*=4 and 6), and a comparative investigation is made of the energetics and chemistry of hydrogen and methane interactions on local surface sites of MgO and Li/MgO.

Because of its industrial importance, and because it is a computationally tractable system at relatively sophisticated levels of theory, numerous theoretical investigations have been carried out on the MgO and Li/MgO systems. Colbourn and Mackrodt<sup>11</sup> used self-consistent field (SCF) molecular orbital methods to study the effect of H<sub>2</sub> chemisorption on single ion and six atom clusters of MgO in a finite point ion field chosen to give the correct Madelung potential at the surface. Their calculations predicted that the dissociative chemisorption of hydrogen cannot take

place at a nondefective (001) surface of MgO.

The results of thermal programmed desorption (TPD) experiments,<sup>12</sup> IR spectra of hydrogen adsorbed on alkaline–earth oxides,<sup>13,14</sup> and theoretical investigations<sup>12,15,17</sup> has shown that, on the surface of MgO, H<sub>2</sub> dissociates heterolytically at adjacent, low coordinated Mg<sup>2+</sup> and O<sup>2-</sup> sites. For brevity, we will use the notation site1–site2 to refer to adjacent sites on the surface on which H<sub>2</sub> dissociates.

From the results of the TPD study cited above, Ito *et al.* concluded that the activity of the available surface sites increases as

$$\text{O}_{4c}\text{--Mg}_{3c} < \text{O}_{3c}\text{--Mg}_{4c} < \text{O}_{3c}\text{--Mg}_{3c},$$

where the subscripts refer to the coordination number of the atom. In subsequent work, Ito *et al.*<sup>18,19</sup> showed that methane also dissociates heterolytically at low coordinated Mg–O sites, where CH<sub>3</sub><sup>+</sup> is bound to Mg, and H<sup>+</sup> is bound to O.

Kobayashi and Yamaguchi<sup>16</sup> and later Sawabe *et al.*<sup>15,17</sup> carried out *ab initio* molecular orbital studies on an eight atom (MgO)<sub>4</sub> cubic cluster to represent the local structure of the (100) surface. Møller–Plesset perturbation through second order was used to treat correlation effects. They found that H<sub>2</sub> readily undergoes heterolytic dissociative chemisorption at neighboring Mg<sub>3c</sub>–O<sub>3c</sub>. Depending on the size of the basis set employed, this process was found to be exothermic by approximately 30 kcal/mol at the SCF level and proceeded with an activation barrier of about 5 kcal/mol. Although homolytic adsorption at nearest O<sub>3c</sub>–O<sub>3c</sub> sites was also found to be exothermic, it is less favorable kinetically, as the SCF estimate of the activation barrier is 68 kcal/mol. A positive cooperativity effect was

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found with respect to the adsorption of a second H<sub>2</sub> molecule to the cubic cluster—an important consequence with respect to the ability of MgO to catalyze the H<sub>2</sub>/D<sub>2</sub> exchange reaction. Although correlation energy was found to alter the energetics considerably (inclusion of correlation often changed the calculated energies by as much as 50%), the qualitative findings regarding H<sub>2</sub> chemisorption onto MgO were unchanged.

With respect to the study of methyl radical formation over Li/MgO, ultrahigh vacuum (UHV) experiments were carried out by Lunsford and co-workers on methane gas passed over MgO and Li/MgO at 500 °C.<sup>20</sup> Using an electron paramagnetic resonance (EPR) spectrometer to detect methyl radical formation, they determined that lithium doping increased the catalytic activity of MgO by a factor of 2.6 to 3.5 depending on the surface area of their MgO sample.

Rodriguez *et al.*<sup>21</sup> used *ab initio* SCF methods to study hydrogen atom abstraction from methane by the MgO and LiO diatomic molecules. They found that the process of hydrogen atom abstraction by either MgO or LiO was exothermic by 3 and 1 kcal/mol, respectively, and that the activation barriers were 36 and 25 kcal/mol, respectively. They ascribed the observed enhancement of the activity of the MgO catalyst upon lithium doping to this reduced barrier.

Using semiempirical methods, Mehandru *et al.*<sup>22</sup> estimated the energies involved in hydrogen atom abstraction from methane on a Mg<sub>21</sub>O<sub>20</sub><sup>2+</sup> cluster. Their study indicated that abstraction proceeded without barrier at three-, four-, and five-centered sites, and that these reactions were exothermic by 6.5, 2.5, and 2.5 kcal/mol, respectively.

In this study, we employ *ab initio* all-electron methods to investigate the chemisorption and transition state energies of hydrogen bound to three coordinate and four coordinate sites of MgO and Li/MgO clusters. These calculations are intended to provide a semiquantitative evaluation of the energetics involved in hydrogen atom abstraction from methane on local defects sites on the surface of MgO and Li/MgO. By comparison of the two systems, the results obtained give an indication of how lithium doping affects the chemistry (e.g., mapping of active sites, electron populations, and reaction mechanisms) of the MgO catalyst.

## II. METHOD

Four clusters have been incorporated in this investigation. These included two cubic clusters (MgO)<sub>4</sub> and LiMg<sub>3</sub>O<sub>4</sub>, and two tetragonal clusters (MgO)<sub>6</sub> and LiMg<sub>5</sub>O<sub>6</sub>. These clusters are shown in Fig. 1 and 2.

In all the calculations presented, the Mg–O distance was fixed at its bulk value of 2.106 Å.<sup>23</sup> The relaxation of the distance between the first and second topmost layers of the (100) surface has been studied theoretically via finite cluster<sup>24</sup> and infinite slab methods,<sup>25</sup> and has been estimated to deviate 1%–2% from the bulk value. Experimental investigations of the same phenomenon predict that the relaxation is from 0% to 3%.<sup>26–28</sup> As the purpose of employing the MgO cluster is to model the local environment of a surface defect on MgO, we did optimize the cluster as

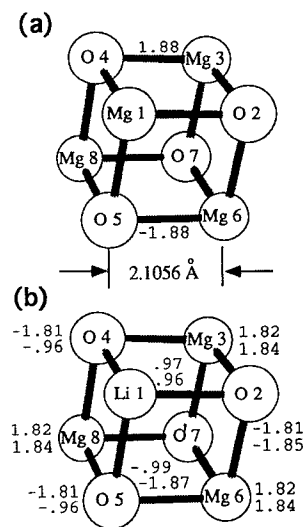


FIG. 1. (a) (MgO)<sub>4</sub>. The numbers shown are the natural populations of symmetry inequivalent atoms. (b) LiMg<sub>3</sub>O<sub>4</sub>. Populations of all the atoms are given. The upper set of numbers are the populations for the <sup>2</sup>A<sub>1</sub> state of the cluster and the lower set are for the symmetry broken <sup>2</sup>A' state.

is the case in other studies in which the relevant issue is the investigation of the electronic and geometric structure of gas phase (MgO)<sub>n</sub> clusters.<sup>29</sup>

For Li/MgO, the lithium atom was assumed to occupy the position of the magnesium atom that it replaced without relaxation. UHF calculations<sup>30</sup> on the lithium trapped-hole center predicted that the Li<sup>+</sup>–O<sup>2–</sup> distance expands by about 10%, and that the Li<sup>+</sup>–O<sup>–1</sup> center contracts by about 8% relative to the bulk Mg–O distance. As these calculations were carried out on small clusters without the rigid environment of neighboring bulk atoms, we presume that these expansions are representative of an upper bound to any actual geometrical distortions.

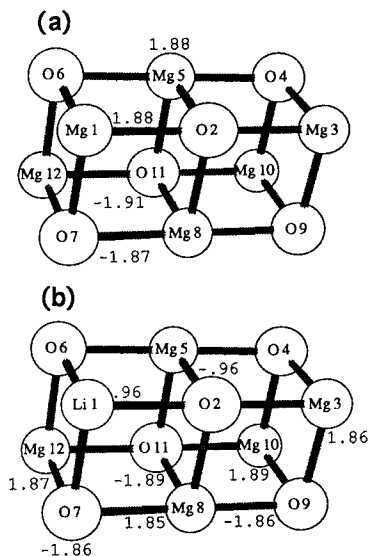
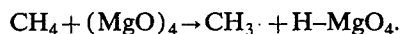


FIG. 2. (a) (MgO)<sub>6</sub>; (b) LiMg<sub>5</sub>O<sub>6</sub>. The numbers shown are the natural populations of symmetry inequivalent atoms.

In Sec. III C, we evaluate the energetics for the process of hydrogen atom extraction from H<sub>2</sub> or CH<sub>4</sub> by various sites of the different model clusters. An example of such a reaction is



The evaluation of the reaction energy requires the calculation of energies for all the products and reactants in the above equation. However, the computation of the optimized geometries and energies of the reactants and CH<sub>3</sub>· needs to be carried out only once for the many different reactions. The product H-Mg<sub>4</sub>O<sub>4</sub> only requires optimizing the three degrees of freedom of the hydrogen atom relative to the cluster.

For the study of chemisorption of CH<sub>4</sub> on MgO and Li/MgO and related transitions states, which involve the breaking of the C-H bond (Sec. III B), we used H<sub>2</sub> as the probe molecule rather than CH<sub>4</sub>. The justification for this computationally less expensive approximation is that the C-H and H-H bonds are similar in nature. They are both nonpolar covalent and have similar bond strengths [103.3 kcal/mol for H<sub>2</sub> (Ref. 31) and 103.2 kcal/mol for CH<sub>4</sub> (Ref. 32)]. Additionally, in their study of the chemisorption of methane on the surface of MgO, Ito *et al.*<sup>18</sup> found that for both the transition and product states, the structure of the CH<sub>3</sub> group was essentially unchanged.

An investigation of the basis set dependence of H<sub>2</sub> chemisorption on (MgO)<sub>4</sub>, including split valence (3-21G and 6-31G), polarized split valence (6-31G\*\*), and triple split valence basis sets (6-311G),<sup>33</sup> was carried out by Sawabe.<sup>15</sup> It was found that the calculation of H<sub>2</sub> adsorption energies and optimized geometries derived from the 3-21G basis set were qualitatively the same as the results for larger basis sets. However, for some weakly physisorbed configurations of H<sub>2</sub> on (MgO)<sub>4</sub>, diffuse *s* and *p* functions on oxygen ( $\alpha_{\text{O}}=0.0845$ ) and diffuse *s* functions on hydrogen ( $\alpha_{\text{H}}=0.036$ ) were necessary to accurately describe the optimized geometries.<sup>34</sup> Hence, the basis employed in these calculations is a 3-21G type augmented with the diffuse functions described above.

The correlation energy of systems involving hydrogen interactions with (MgO)<sub>4</sub> and LiMg<sub>3</sub>O<sub>4</sub> was treated at the second-order unrestricted Møller-Plesset (UMP2) level at the unrestricted Hartree-Fock (UHF) optimized geometry. Preliminary calculations indicated that the difference in the geometries and energies obtained from full UMP2 optimizations did not, for our purposes, differ significantly from the MP2 single-point method.<sup>15</sup> For the remainder of this paper, we will use the notation  $E_{\text{UHF}}/E_{\text{UMP2}}$  to report optimized UHF and single-point UMP2 energies for a given system. All energies are expressed in kilocalories per mole and distances are given in Angstroms.

These calculations were carried out using the software package GAUSSIAN 90.<sup>35</sup>

### III. RESULTS

Section III is divided into three parts. In Sec. III A, we give a description of the electronic states of the bare clusters employed in this study. This is necessary for pedagogical

reasons and also to facilitate the efforts of those who may want to try to reproduce these results. In Sec. III B, we present results for the chemisorption of H<sub>2</sub> onto the cluster surfaces, and in Sec. III C, we discuss the abstraction of H from H<sub>2</sub> and CH<sub>4</sub>.

In each of the sections III A, III B, and III C, we discuss results for each of the clusters employed in this study in the following order: (MgO)<sub>4</sub>, LiMg<sub>3</sub>O<sub>4</sub>, (MgO)<sub>6</sub>, and LiMg<sub>5</sub>O<sub>6</sub>. (MgO)<sub>4</sub> and LiMg<sub>3</sub>O<sub>4</sub> are employed to directly compare the effect of clusters with and without lithium. (MgO)<sub>6</sub> and LiMg<sub>5</sub>O<sub>6</sub> are included to assess the cluster size effect on our results and to explore the chemistry of four-coordinate sites that are not present in the smaller clusters.

#### A. Bare clusters

The symmetry of (MgO)<sub>4</sub> belongs to the *T<sub>d</sub>* point group. The ground state for this system was found to be <sup>1</sup>A<sub>1</sub>.

A Mulliken population analysis of this cluster assigns a  $-1.30|e|$  charge to the oxygen atoms and a  $1.30|e|$  charge to the magnesium atoms. The natural population analysis (NPA) of Weinhold and co-workers,<sup>36</sup> which is a population analysis based on a localized orbital scheme, assigns a charge of  $-1.88|e|$  to the oxygen atoms and  $1.88|e|$  to the magnesium atoms [see Fig. 1(a)]. Mulliken populations are known to give physically unreasonable results for ionic compounds<sup>37</sup> as the off-diagonal elements of the density matrix can contribute “shared” electron density to the cations, thereby assigning too much electron density to cations and too little electron density to the anions. Therefore, all populations reported in the remainder of this paper are derived from the NPA.

The symmetry of LiMg<sub>3</sub>O<sub>4</sub> is classified by the *C<sub>3v</sub>* point group. For this cluster, the lowest energy eigenstate was found to be of broken symmetry in which the wave function was a <sup>2</sup>A' state belonging to the *C<sub>s</sub>* subgroup. The lowest doublet state of nonbroken symmetry was found to be the <sup>2</sup>A<sub>1</sub> state, which lies 29.5/16.9 kcal/mol higher in energy than the <sup>2</sup>A' state. The valence electronic configuration of this state is

$$^2A_1: a_1^2 a_1^2 e^4 a_1^2 e^4 a_1^2 e^4 a_2^2 e^4 a_1^1 e^4.$$

The symmetry broken state arises when the half-filled *a*<sub>1</sub> orbital accepts an electron from the filled degenerate highest-occupied molecular orbital (HOMO). A natural population analysis of the <sup>2</sup>A' state of LiMg<sub>3</sub>O<sub>4</sub> showed that the hole created by the lithium resides on one of the symmetry equivalent oxygens [O5 in Fig. 1(b); charge =  $-0.96$ ]. For the <sup>2</sup>A<sub>1</sub> state, the hole is found on the symmetry unique oxygen [O7 in Fig. 1(b); charge =  $-0.99$ ].  $\langle S^2 \rangle$  for these systems is 0.75, but due to spin contamination inherent in the UHF wave function,  $\langle S^2 \rangle$  was 0.762 and 0.758 for the <sup>2</sup>A<sub>1</sub> and <sup>2</sup>A' states, respectively.

The tetragonal cell (MgO)<sub>6</sub> has *D<sub>2h</sub>* symmetry, and the ground electronic state was found to be <sup>1</sup>A<sub>1g</sub> [see Fig. 2(a)].

For the Li-doped analog to (MgO)<sub>6</sub>, LiMg<sub>5</sub>O<sub>6</sub>, one may consider substituting a lithium atom for a three-

TABLE I. The energy of chemisorption of H<sub>2</sub> onto various neighboring sites in (MgO)<sub>4</sub>, LiMg<sub>3</sub>O<sub>4</sub>, MgO<sub>6</sub>, and LiMg<sub>5</sub>O<sub>6</sub>. NI=not investigated; NTF=no transition state found.

Cluster	Pair site	Chemisorption energy (kcal/mol)	Transition state energy (kcal/mol)
(MgO) <sub>4</sub>	O <sub>3c</sub> -O <sub>3c</sub>	-33.5/-22.5	71.7/59.5
	O <sub>3c</sub> -Mg <sub>3c</sub>	-30.4/-13.8	2.4/4.2
LiMg <sub>3</sub> O <sub>4</sub>	O <sub>3c</sub> -O <sub>3c</sub>	-114.2/-98.5	NTF
	O <sub>3c</sub> -O <sub>7c</sub>	-100.8/-93.5	NI
	O <sub>3c</sub> -Li <sub>3c</sub>	-35.2/-39.3	NI
	O <sub>3c</sub> -Mg <sub>3c</sub>	Not bound	
	O <sub>7c</sub> -Mg <sub>3c</sub>	Not bound	
(MgO) <sub>6</sub> <sup>a</sup>	O <sub>3c</sub> -Mg <sub>3c</sub>	-34.3/-16.6	NI
	O <sub>3c</sub> -Mg <sub>4c</sub>	1.8/14.3	NI
	O <sub>4c</sub> -Mg <sub>3c</sub>	-4.0/9.5	NI
LiMg <sub>5</sub> O <sub>6</sub>	O <sub>2c</sub> -O <sub>6c</sub>	-89.6/-90.5	NTF

<sup>a</sup>From Ref. 15.

coordinate magnesium atom Mg<sub>3c</sub>, or a four-coordinate magnesium atom Mg<sub>4c</sub>. The ground electronic state for a cluster in which Mg<sub>3c</sub> was replaced by Li was <sup>2</sup>A' (C<sub>s</sub> symmetry), and it was found to be 61.6 kcal/mol more

stable than the C<sub>2v</sub> structure obtained by substituting Li for Mg<sub>4c</sub>. Although it is not unreasonable to expect Li substitution at four-coordinate sites, we have limited this study to the more stable situation in which Li is three coordinate. For the <sup>2</sup>A' state of this cluster, the hole was located at the four-centered oxygen site [O6 in Fig. 2(b); charge = -0.96] and ⟨S<sup>2</sup>⟩ was equal to 0.755.

For all chemisorption energies reported in this paper, the bare clusters are assumed to be in the lowest energy electronic state that transform as the completely symmetric irreducible representation of that cluster's point group. In every case except for LiMg<sub>3</sub>O<sub>4</sub>, this corresponds to the ground state. An ambiguity that exists in using cluster methods in theoretical chemistry resides in the choice of the electronic state of the bare cluster that best represents the electronic environment on the surface of the infinite solid. Both the <sup>2</sup>A<sub>1</sub> and symmetry broken <sup>2</sup>A' states are symmetry allowed with respect to chemisorption of an S state atom at any of the available three-coordinate sites. However, the choice of <sup>2</sup>A<sub>1</sub> state yielded chemisorption energies that were consistent with surface experiments and were also comparable to results obtained on the larger

TABLE II. Optimized geometries for H<sub>2</sub> chemisorption products, transition states, and physisorbed products on (MgO)<sub>4</sub>, LiMg<sub>3</sub>O<sub>4</sub>, and LiMg<sub>5</sub>O<sub>6</sub>. The dihedral angle atom1-atom2-atom3-atom4 is the angle between the plane defined by atom1, atom2, and atom3 and the plane defined by atom2, atom3, and atom4.

Cluster and symmetry	Adsorbates and site	R <sub>site H</sub> (Å)	Bond angle	Dihedral angle
(MgO) <sub>4</sub> C <sub>2v</sub>	O2-H	0.97	O4-O2-H=148.4	Mg6-O4-O2-H=180.0
	O4-H	0.97	O2-O4-H=148.4	Mg8-O2-O4-H=180.0
(MgO) <sub>4</sub> C <sub>s</sub>	Mg1-H <sup>-</sup>	1.79	O2-Mg1-H=100.6	Mg8-O2-Mg1-H=180.0
	O2-H <sup>+</sup>	0.97	Mg1-O2-H=107.7	O7-Mg1-O2-H=180.0
(MgO) <sub>4</sub> C <sub>s</sub> <sup>a,c</sup>	Mg1-H1	2.13	O2-Mg1-H=66.5	Mg8-O2-Mg1-H=180.0
	O2-H2	1.57	Mg1-O2-H=65.4	O7-Mg1-O2-H=180.0
(MgO) <sub>4</sub> C <sub>2v</sub> <sup>c</sup>	O2-H1	1.39	O4-O2-H1=58.1	Mg6-O2-O4-H1=180.0
	O4-H2	1.39	O2-O4-H2=58.1	Mg8-O2-O4-H2=180.0
LiMg <sub>3</sub> O <sub>4</sub> C <sub>s</sub>	O2-H	0.96	O4-O2-H=136.4	Mg8-O4-O2-H=177.42
	O4-H	0.96	O2-O4-H=136.4	Mg6-O2-O4-H=-177.42
LiMg <sub>3</sub> O <sub>4</sub> C <sub>i</sub>	O5-H	0.96	Li1-O5-H=123.1	Mg3-Li1-O5-H=176.4
	O7-H	0.97	Mg3-O7-H=132.1	Li-Mg3-O7-H=174.3
LiMg <sub>3</sub> O <sub>4</sub> C <sub>s</sub>	Li1-H <sup>-</sup>	2.68	O2-Li1-H=128.2	Mg8-O2-Li1-H=180.0
	O2-H <sup>+</sup>	0.97	Li1-O2-H=114.2	Mg8-Li1-O2-H=180.0
LiMg <sub>3</sub> O <sub>4</sub> C <sub>s</sub> <sup>b</sup>	O2-H1	1.19	Li1-O2-H1=123.3	Mg6-O2-Li1-H1=180.0
	O2-H2	2.11	Li1-O2-H2=123.3	Mg6-O2-Li1-H2=180.0
LiMg <sub>3</sub> O <sub>4</sub> C <sub>s</sub> <sup>b</sup>	O2-H1	2.61	Li1-O2-H=126.9	Mg6-O2-Li1-H1=180.0
	O2-H2	3.34	Li1-O2-H=127.8	Mg6-O2-Li1-H2=180.0
(MgO) <sub>6</sub> C <sub>i</sub> <sup>c</sup>	Mg1 <sub>3c</sub> -H <sup>-</sup>	1.78	O6-Mg1-H=103.3	O7-O6-Mg1-H=137.4
	O5 <sub>3c</sub> -H <sup>+</sup>	0.96	Mg1-O6-H=110.1	Mg12-Mg1-O6-H=137.4
(MgO) <sub>6</sub> C <sub>s</sub> <sup>c</sup>	Mg1 <sub>3c</sub> -H <sup>-</sup>	1.81	O2-Mg1-H=83.5	Mg12-O2-Mg1-H=180.0
	O2 <sub>4c</sub> -H <sup>+</sup>	0.99	Mg1-O2-H=72.1	Mg12-Mg1-O2-H=180.0
(MgO) <sub>6</sub> C <sub>s</sub> <sup>c</sup>	O4 <sub>3c</sub> -H <sup>+</sup>	0.97	Mg5-O4-H=89.6	Mg8-Mg5-O4-H=180.0
	Mg5 <sub>4c</sub> -H <sup>-</sup>	1.94	O4-Mg5-H=74.3	Mg8-O4-Mg5-H=180.0
LiMg <sub>5</sub> O <sub>6</sub> C <sub>i</sub>	O2 <sub>4c</sub> -H	0.97	Li1-O2-H=137.2	O11-Li1-O2-H=181.8
	O6 <sub>3c</sub> -H	0.96	Li1-O6-H=117.8	O11-Li1-O6-H=182.2
LiMg <sub>5</sub> O <sub>6</sub> C <sub>i</sub> <sup>a</sup>	O6-H1	1.20	Li1-O6-H1=125.2	Mg12-O6-Li1-H1=178.2
	O6-H2	2.11	Li1-O6-H2=125.8	Mg12-O6-Li1-H2=182.4
LiMg <sub>5</sub> O <sub>6</sub> C <sub>i</sub> <sup>b</sup>	O6-H1	2.60	Li1-O6-H1=119.0	Mg12-O6-Li1-H1=171.4
	O6-H2	3.34	Li1-O6-H2=119.0	Mg12-O6-Li1-H1=171.4
LiMg <sub>5</sub> O <sub>6</sub> C <sub>i</sub> <sup>a</sup>	O2-H1	1.20	Li1-O2-H1=73.3	O11-O2-Li1-H1=180.0
	O2-H2	2.12	Li1-O2-H1=73.7	O11-O2-Li1-H2=180.0

<sup>a</sup>Transition state.

<sup>b</sup>Physisorbed state.

<sup>c</sup>From Ref. 15.



TABLE III. The energy of abstraction of H·, H<sup>+</sup>, and H<sup>−</sup> from H<sub>2</sub> and CH<sub>4</sub> onto various sites of (MgO)<sub>4</sub>, LiMg<sub>3</sub>O<sub>4</sub>, and LiMg<sub>5</sub>O<sub>6</sub>. The binding energy is obtained by subtracting *D<sub>e</sub>* for homolytic or heterolytic dissociation of H<sub>2</sub> from the abstraction energy.

Cluster	Adsorbate	Adsorption site	Abstraction energy (kcal/mol)		Binding energy (kcal/mol)
			H <sub>2</sub>	CH <sub>4</sub>	
(MgO) <sub>4</sub>	H·	O <sub>3c</sub>	79.4/90.1	85.6/100.2	−0.8/−1.0
	H <sup>+</sup>	O <sub>3c</sub>	127.5/146.4	186.1/204.8	−272.8/−256.0
	H <sup>−</sup>	Mg <sub>3c</sub>	337.4/334.1	240.0/247.4	−62.9/−68.3
LiMg <sub>3</sub> O <sub>4</sub>	H·	O <sub>3c</sub>	−34.6/−38.5	−28.4/−28.4	−114.8/−129.6
	H·	O <sub>73c</sub>	−8.9/−23.1	−2.7/−12.9	−89.1/−114.2
	H·	Li <sub>3c</sub>		Not bound	
	H <sup>+</sup>	O <sub>3c</sub>	106.2/113.8	164.7/172.2	−294.1/−288.6
	H <sup>−</sup>	Mg <sub>3c</sub>	314.4/321.2	217.9/234.4	−85.9/−81.2
	H <sup>−</sup>	Li <sub>3c</sub>	350.9/359.4	254.4/272.7	−49.4/−43.0
LiMg <sub>5</sub> O <sub>6</sub>	H·	O <sub>63c</sub>	−42.0/−55.1	−35.8/−44.9	−122.2/−146.2
	H·	O <sub>24c</sub>	−6.0/−21.3	0.1/−11.6	−86.2/−112.4

cluster, the H<sub>2</sub> molecule was absorbed into the interior. In the former case, the transition state search led to the energy of dissociated H<sub>2</sub> unperturbed by MgO, and in the latter case, the transition state search led to the absorption barrier of H<sub>2</sub> through the surface of the cluster. No transition state connecting free H<sub>2</sub> to the homolytic adsorption product was found.

Next, we attempted a search for a local minimum on the potential surface. This time the H<sub>2</sub> bond length was started at the experimental value of 0.741 Å, and the center of mass of the H<sub>2</sub> molecule was placed 1 Å above the surface of the cluster. Again the orientation of H<sub>2</sub> was chosen so as to possess only C<sub>1</sub> symmetry. A geometry optimization, following the gradient of the energy downhill via the Berny optimization algorithm,<sup>40</sup> led directly to the O<sub>3c</sub>–O<sub>3c</sub> adsorption state discussed above. Hence, we conclude that H<sub>2</sub> may dissociate homolytically on LiMg<sub>3</sub>O<sub>4</sub> without a barrier.

### 3. (MgO)<sub>6</sub>

The study of H<sub>2</sub> chemisorption presented here is taken directly from the work of Sawabe<sup>15</sup> and is reproduced here so that the results may be compared to chemisorption of H<sub>2</sub> on LiMg<sub>5</sub>O<sub>6</sub> in the next section.

From Table I, it can be seen that the difference in the calculated chemisorption energy of H<sub>2</sub> at the O<sub>3c</sub>–Mg<sub>3c</sub> site going from the (MgO)<sub>4</sub> to (MgO)<sub>6</sub> cluster is 3.9/2.8 kcal/mol. This represents a 11%/17% change in the calculated energies and gives us some feeling for the magnitude of the cluster size effect.

Also from Table I, we see that when one of the hydrogens is adsorbed at a four-coordinate site, the calculated chemisorption energy is reduced. Compared to chemisorption in which both hydrogens are bonded to three-coordinate sites, chemisorption in which one of the hydrogens is bonded at a four-coordinate site is from 23 to 31 kcal/mol less stable. In fact, this type of chemisorption is predicted to be endothermic except in the case of the SCF evaluation of the chemisorption energy of H<sub>2</sub> at a Mg<sub>3c</sub>–O<sub>4c</sub> site.

A study of homolytic dissociation of H<sub>2</sub> onto neighboring O<sub>3c</sub>–O<sub>4c</sub> sites was not carried out, since even if a stable product were found, it is expected that there would be a large energy of activation. This result is anticipated since, as we have already seen, there exists a large barrier to dissociation on neighboring oxygen sites on (MgO)<sub>4</sub>, and the increase in coordination of one of the oxygens is unlikely to reduce this barrier. Therefore, our conclusion that MgO supports mainly heterolytic dissociation at neighboring Mg and O sites remains the same.

### 4. LiMg<sub>5</sub>O<sub>6</sub>

In LiMg<sub>5</sub>O<sub>6</sub>, it was found that chemisorption involving the O<sub>4c</sub> site reduces the chemisorption energy compared to chemisorption involving only three-coordinate sites by 24.6/8.0 kcal/mol (see Table I). However, in contrast to the results found for the undoped (MgO)<sub>6</sub> cluster, there is still a strongly exothermic chemisorbed product (−89.6/−90.5 kcal/mol) with hydrogens adsorbed at neighboring O<sub>3c</sub> and O<sub>4c</sub> sites.

We were neither able to find a transition state connecting free H<sub>2</sub> and the bare cluster to the chemisorbed product at the O<sub>3c</sub>–O<sub>4c</sub> site, nor did it appear that H<sub>2</sub> could dissociate without a barrier onto this site. Specifically, we began by using the Berny optimization algorithm to search for a transition state to the chemisorption of H<sub>2</sub> to neighboring three-coordinate and four-coordinate oxygen sites. The hydrogen was placed at varying distances away from the cluster with the ends directed towards the three- and four-coordinate oxygen. Likewise, we attempted optimization runs starting from similar initial starting points to determine if simultaneous chemisorption at three- and four-coordinate sites could be obtained without a barrier. These geometry searches led to states involving the abstraction of a single hydrogen from H<sub>2</sub> at either the three- or four-coordinated oxygen site, but not to states connecting free H<sub>2</sub> to a chemisorbed product in which both hydrogens were adsorbed to the surface. Further discussion on hydrogen atom abstraction from H<sub>2</sub> onto the Li-doped clusters will be given in Sec. IV.



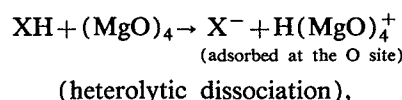
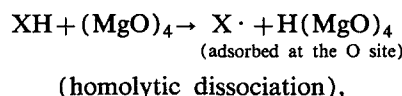
TABLE IV. Optimized geometries for H<sup>•</sup>, H<sup>+</sup>, and H<sup>-</sup> on various sites of (MgO)<sub>4</sub>, LiMg<sub>3</sub>O<sub>4</sub>, and LiMg<sub>5</sub>O<sub>6</sub>. For complexes with C<sub>3v</sub> symmetry, the bond is collinear with the C<sub>3</sub> axis.

Cluster and symmetry	Adsorbates and site	R <sub>site H</sub> (Å)	Bond angle	Dihedral angle
(MgO) <sub>4</sub> C <sub>3v</sub>	O2-H	2.62	...	...
	O2-H <sup>+</sup>	0.97	...	...
	Mg1-H <sup>-</sup>	1.84	...	...
LiMg <sub>3</sub> O <sub>4</sub> C <sub>s</sub>	O2-H	0.97	Li1-O2-H=114.2	O7-Li1-O2-H=180.0
LiMg <sub>3</sub> O <sub>4</sub> C <sub>3v</sub>	O7-H	0.97	...	...
LiMg <sub>3</sub> O <sub>4</sub> C <sub>s</sub>	O2-H <sup>+</sup>	0.98	Li-O2-H=116.0	O7-Li-O2-H=180.0
LiMg <sub>3</sub> O <sub>4</sub> C <sub>3v</sub>	Li1-H <sup>-</sup>	2.84	...	...
LiMg <sub>3</sub> O <sub>4</sub> C <sub>s</sub>	Mg3-H <sup>-</sup>	1.85	O7-Mg3-H=121.6	Li1-O7-Mg3-H=180.0
LiMg <sub>5</sub> O <sub>6</sub> C <sub>1</sub>	O6 <sub>3c</sub>	0.96	Li1-O6-H=116.3	O11-Li1-O6-H=181.8
LiMg <sub>5</sub> O <sub>6</sub> C <sub>s</sub>	O2 <sub>4c</sub>	0.97	Li1-O2-H=69.9	O7-Li1-O2-H=180.0

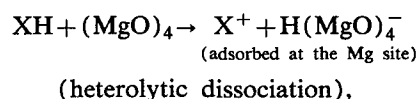
### C. Abstraction of H<sup>•</sup>, H<sup>+</sup>, and H<sup>-</sup> from H<sub>2</sub> and CH<sub>4</sub>

#### 1. (MgO)<sub>4</sub>

In this section, we present a study of the abstraction of hydrogen by MgO from either H<sub>2</sub> or CH<sub>4</sub>. Specifically, we will look at the energetics of reactions of the type



and

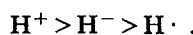


where X=CH<sub>3</sub> or H.

In Table III, results are presented for the abstraction energy (the energy of the products minus the reactants for the equations displayed above) of H<sup>•</sup>, H<sup>+</sup>, and H<sup>-</sup> from both H<sub>2</sub> and CH<sub>4</sub>. The UHF optimized geometries and natural populations for these systems are given in Tables IV and V, respectively.

To evaluate the binding energy of the hydrogen atom adsorbate, one should subtract  $D_e$  for homolytic dissociation of H<sub>2</sub> (80.2/91.1 kcal/mol) from the H<sup>•</sup> abstraction energy given in column four of Table III. Likewise, to estimate the binding energy of either the H<sup>+</sup> or H<sup>-</sup> adsorbate, one should subtract  $D_e$  for the heterolytic dissociation of H<sub>2</sub> (400.3/402.4 kcal/mol) from either the H<sup>+</sup> or H<sup>-</sup> abstraction energy given in the same table and column. (A negative binding energy is indicative of a bound state of the adsorbate.)

As can be seen from the positive values for the energies listed in Table III for (MgO)<sub>4</sub>, the energy given back to the formation of a single adsorbate to cluster atom bond does not compensate for the energy required to homolytically or heterolytically break either the H-H or C-H bond. However, after subtraction of  $D_e$ , we observe that the binding energies for all the species shown in Table III are negative, and the bond strengths follow the order



At the MP2 level, the binding energies are -256.0 kcal/mol (O-H<sup>+</sup>), -68.3 kcal/mol (Mg-H<sup>-</sup>), and -1.0 kcal/mol (O-H).

From Table V, we may observe that this trend in the binding energies varies directly as the amount of electron density donated from the hydrogen species to the cluster.

TABLE V. Natural populations for systems in which H<sup>•</sup>, H<sup>+</sup>, and H<sup>-</sup> are adsorbed onto various sites of (MgO)<sub>4</sub> and LiMg<sub>3</sub>O<sub>4</sub>.

	Adsorption sites for H, H <sup>+</sup> , and H <sup>-</sup>							
	(MgO) <sub>4</sub>			LiMg <sub>3</sub> O <sub>4</sub>				
	O2-H	O2-H <sup>+</sup>	Mg1-H <sup>-</sup>	O2-H	O7-H	O2-H <sup>+</sup>	Mg3-H <sup>-</sup>	Li1-H <sup>-</sup>
Li1	...	...	...	0.97	0.97	0.94	0.96	0.97
Mg1	1.88	1.75	1.75	...	...	...	...	...
O2	-1.88	-1.35	-1.86	-1.45	-1.82	-1.47	-1.82	-1.86
Mg3	1.88	1.76	1.85	1.84	1.82	1.89	1.76	1.84
O4	-1.88	1.70	-1.86	-1.85	-1.82	-1.36	-1.81	-1.86
O5	-1.88	1.70	-1.86	-1.85	-1.82	-1.36	-0.97	-1.86
Mg6	1.88	1.76	1.85	1.84	1.82	1.89	1.78	1.84
O7	-1.88	-1.78	-1.89	-1.87	-1.46	-1.86	-1.84	-1.89
Mg8	1.88	1.78	1.85	1.88	1.82	1.82	1.78	1.84
H	-0.006	0.42	-0.83	0.49	0.50	0.52	-0.84	0.002



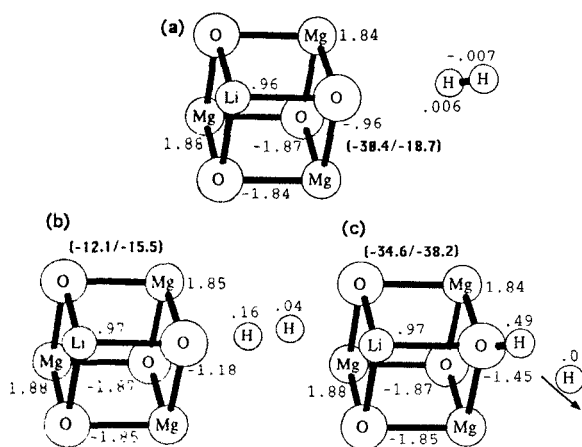
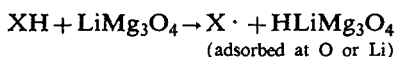


FIG. 4. (a) Physisorbed and (b) transition states of H<sub>2</sub>. (c) H atom abstracted from H<sub>2</sub> and adsorbed at O<sub>3c</sub>. The numbers in parentheses are the SCF/MP2 energies relative to free H<sub>2</sub> and the bare cluster expressed in kilocalories per mole. Other numbers give the the natural populations of symmetry inequivalent atoms. Geometries of these states are given in Table II.

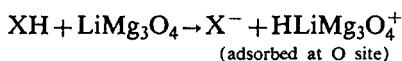
This quantity is given by the difference in the formal charge of the hydrogen species (viz., +1, -1, and 0) from the population of the adsorbed hydrogen species. For (MgO)<sub>4</sub>, the amount of electron density donated is 0.58, 0.17, and -0.006 for H<sup>+</sup>, H<sup>-</sup>, and H<sup>·</sup>, respectively.

## 2. LiMg<sub>3</sub>O<sub>4</sub>

We next consider the hydrogen abstraction reactions for a Li-doped system

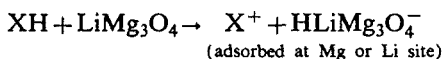


(homolytic dissociation),



(heterolytic dissociation),

and



(heterolytic dissociation)

where X = CH<sub>3</sub> or H.

From Table III, we observe that for the abstraction of H<sup>·</sup> from H<sub>2</sub> or CH<sub>4</sub> and subsequent adsorption of H<sup>·</sup> at O<sub>3c</sub> that the reaction energy is negative. That is, even given the highly reactive hydrogen atom or methyl radical byproduct, these calculations predict that these reactions proceed exothermically.

A search for a transition state to this process was carried out. For the hydrogen molecule, it was discovered that the molecule is first physisorbed at 2.61 Å away from the O<sub>3c</sub> site with an energy of -30.4/-18.7 kcal/mol. A transition state at -12.1/-15.5 kcal/mol was found in which the shortest distance from the H<sub>2</sub> to the O<sub>3c</sub> site was reduced to 1.19 Å and the H-H bond length was stretched to 0.92 Å. A diagram of this process is shown in Fig. 4. The

barrier to abstraction is given by the difference in energy of the physisorbed state from the transition state (i.e., 18.3/3.2 kcal/mol).

As noted in Table III, the hydrogen atom is not bound to the Li<sub>3c</sub> site, but the hydride ion is bound. The binding energy of this hydride is -49.4/-43.0 kcal/mol. However, the population analysis shown in Table V indicates that the charge on the "hydride" is only 0.002. That is, the excess charge initially carried by the hydride ion is completely donated to the LiMg<sub>3</sub>O<sub>4</sub> cluster.

Table III also indicates that chemisorbed states are possible for H<sup>+</sup> bound to O<sub>3c</sub> and H<sup>-</sup> bound to Mg<sub>3c</sub> or Li<sub>3c</sub>. However, as with (MgO)<sub>4</sub>, although the binding energy is positive—294.1/288.6 kcal/mol for H<sup>+</sup>-O<sub>3c</sub>, 85.9/81.2 kcal/mol for H<sup>-</sup>-Mg<sub>3c</sub>, and 49.4/43.0 kcal/mol for H<sup>-</sup>-Li<sub>3c</sub>—the processes of heterolytic abstraction of a single hydrogen ion from H<sub>2</sub> or CH<sub>4</sub> is a highly endothermic process.

## 3. LiMg<sub>5</sub>O<sub>6</sub>

Table III shows that on LiMg<sub>5</sub>O<sub>6</sub>, a hydrogen atom can be abstracted from H<sub>2</sub> or CH<sub>4</sub> exothermically at either an O<sub>6c</sub> or O<sub>4c</sub> site. At the SCF level, the CH bond was found to be nearly equal in strength to the H-O<sub>4c</sub> bond. At the MP2 level, the H-O<sub>4c</sub> bond was somewhat stronger by 11.6 kcal/mol. Transition states for abstraction at both the O<sub>3c</sub> and O<sub>4c</sub> sites were located and are discussed below.

It was found that the process of hydrogen atom abstraction onto an O<sub>3c</sub> site of LiMg<sub>5</sub>O<sub>6</sub> was very similar to the same process for LiMg<sub>3</sub>O<sub>4</sub> depicted in Fig. 4. A bound state of H<sub>2</sub> at a long distance (2.60 Å) from an O<sub>3c</sub> site was discovered with an adsorption energy of -37.1/-34.3 kcal/mol. The geometry optimization of this state was computationally very expensive. In addition to the fact that 158 basis functions were employed, the geometry of this state carried only C<sub>1</sub> symmetry and the potential energy surface for the nuclear coordinates in the region of the energy minimum was relatively flat, so that small steps had to be taken to find the optimized structure. In order to make the problem computationally tractable, it was necessary to only partially optimize the H<sub>2</sub> coordinates. That is, the H<sub>2</sub> center of mass coordinates were optimized, but the H<sub>2</sub> internal coordinates were set equal to those obtained from the optimization of H<sub>2</sub> relative to the O<sub>3c</sub> site in LiMg<sub>3</sub>O<sub>4</sub> discussed above. Specifically, the H-H distance was set to 0.746 Å and the internal, angular coordinates were fixed so that the line of the H<sub>2</sub> molecule was pointed directly at the O<sub>3c</sub> site.

A transition state was located with an energy of -19.2/-31.3 kcal/mol in which the shortest distance from the hydrogen to the O<sub>3c</sub> was 1.20 Å and the H-H distance was stretched to 0.92 Å. The barrier to hydrogen abstraction at an O<sub>3c</sub> site is given by the difference in energy of the physisorbed state discussed in the preceding paragraph and this transition state (i.e., 17.9/3.0 kcal/mol). This is in close agreement to the same barrier determined using LiMg<sub>3</sub>O<sub>4</sub> discussed in Sec. III O 2 (viz. 18.3/3.2 kcal/mol).

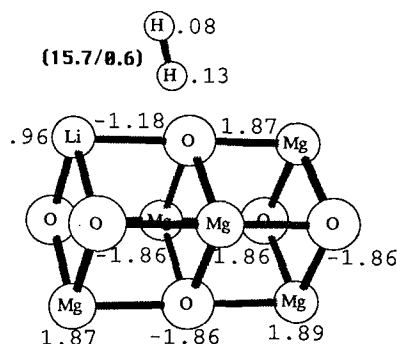


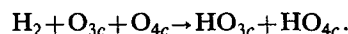
FIG. 5. The transition state for the abstraction of hydrogen from H<sub>2</sub> onto an O<sub>4c</sub> site. The numbers in parentheses are the SCF/MP2 energies relative to free H<sub>2</sub> and the bare cluster expressed in kilocalories per mole. Other numbers give the natural populations of the symmetry inequivalent atoms. The geometry of this state is given in Table II.

At the O<sub>4c</sub> site, the transition state was such that the distance between the O<sub>4c</sub> site and the hydrogen was 1.20 Å, the H-H distance was 0.92 Å, and the barrier height was 15.7/0.6 kcal/mol. No physisorbed state near O<sub>4c</sub> was found, so that this energy directly gives the barrier to hydrogen atom abstraction from H<sub>2</sub> at an O<sub>4c</sub> site. A diagram of this transition state is shown in Fig. 5.

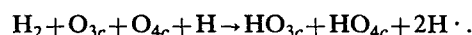
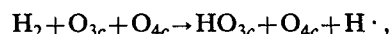
#### IV. DISCUSSION

The chemistry of the MgO catalyst is markedly different from the Li/MgO catalyst. On MgO, we have seen that H<sub>2</sub> dissociates heterolytically on neighboring three-coordinate Mg and O sites, and possibly undergoes heterolytic dissociation at O<sub>3c</sub>-Mg<sub>4c</sub> or O<sub>4c</sub>-Mg<sub>3c</sub> sites. In contrast, no heterolytic dissociation at neighboring oxygen and magnesium sites was observed in Li/MgO. Instead, we found that the H-H bond could be cleaved without a barrier at proximal O<sub>3c</sub>-O<sub>3c</sub> sites and that a hydrogen atom could be abstracted from H<sub>2</sub> or CH<sub>4</sub> at either an O<sub>3c</sub> or O<sub>4c</sub> site.

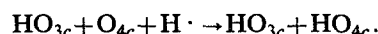
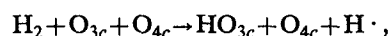
At the end of Sec. III B 4, we noted that no transition state was found for the direct dissociation and subsequent chemisorption of H<sub>2</sub> at an O<sub>3c</sub>-O<sub>4c</sub> site. Nor did we find that H<sub>2</sub> chemidissociated onto these sites without a barrier. That is, the following reaction does not appear to be possible in a single step



From our study of the transition state to abstraction of H· from H<sub>2</sub> or CH<sub>4</sub>, it appears that the pathway to the product found in Sec. III B 4 could result from two separate abstraction events at O<sub>3c</sub> and O<sub>4c</sub>. That is,



Another plausible mechanism is that hydrogen atoms generated as products abstraction could migrate to other three- or four-coordinated sites and be adsorbed. For example,



The increase of the catalytic activity of MgO upon Li doping does not appear to be a consequence of lowering the transition state barrier to C-H or H-H bond breaking, as has been previously suggested.<sup>21</sup> In fact, it was found that the transition barrier to heterolytic dissociation at O<sub>3c</sub>-Mg<sub>3c</sub> was negligibly low at 2.4/4.2 kcal/mol.

We observed that MgO does not support a pathway to hydrogen atom abstraction for either H<sub>2</sub> or CH<sub>4</sub>. Additionally, Ito *et al.*, using theoretical methods similar to the ones presented in this work, concluded that CH<sub>4</sub> dissociates heterolytically on clean MgO with CH<sub>3</sub><sup>-</sup> bound to Mg and H<sup>+</sup> bound to O.<sup>18</sup> A possible mechanism for the formation of higher order alkanes from methane passed over a clean MgO catalyst that is not in disagreement with either of these observations is one in which adsorbed CH<sub>3</sub> groups combine on the surface and deadsorb in the gas phase as C<sub>2</sub>H<sub>6</sub>. For Li/MgO systems, methyl radicals or hydrogen atoms are generated directly into the gas phase via hydrogen atom abstraction and may combine with other radicals so generated. Such a difference in the mechanisms of reaction could account for the observed difference in the activity of Li/MgO relative to MgO.

In our study, we assumed that the Li dopant was located at a three coordinate site. Let us suppose for the moment that the ability of the Li/MgO cluster would still be able to support an abstraction mechanism at O<sub>3c</sub> and O<sub>4c</sub> sites even if Li were situated at a more highly coordinated position. (This is not an unreasonable supposition since the primary function of the Li dopant is to provide reactive Li<sup>+</sup>O<sup>-</sup> centers—a function that it should be able to carry out regardless of its coordination.)

If this is the case, we also note that Li/MgO provides many more sites, whereby the H-H or C-H bond may be cleaved. In MgO, two neighboring sites on the surface had to fulfill the condition that they be triply or quadruply coordinated in order for the site to be active. Whereas for Li/MgO, if a Li atom is proximal, dissociation may occur at an O<sub>3c</sub> or O<sub>4c</sub> site regardless of the coordination of the neighboring atoms. This, then is a second way in which Li doping may increase the catalytic activity of MgO.

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