Acitve Sites for Methane Activation in MgO and Li doped MgO

zur Erlangung des akademischen Grads
Doctor rerum naturalium (Dr. rer. Nat.)
im Fach Chemie

eingereicht an der
Mathematisch-Naturwissenschaftlichen Fakultät I
Humboldt-Universität zu Berlin

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Datum der Promotion: 19.12.2011
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*The universe is made of stories, not of atoms.*
Muriel Rukeyser
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Chapter 1

Introduction

The transformation of abundant stable hydrocarbons into useful chemicals is a major task of today’s basic research in catalysis. In particular, methane activation has recently received considerable attention. Methane is the main component of natural gas, which reserves are estimated to exceed those of crude oil in the future. Therefore this is not surprising that there are many attempts to convert methane into more valuable chemicals and fuels.

The thermodynamic stability of methane with its noble-gas-like electron configuration makes the activation of this smallest hydrocarbon difficult. Its tetrahedral structure with strong C-H bonds offers no polar electron distribution to undergo chemical attack. Thus, methane is less reactive than nearly all its conversion products, which limits efficient utilization of natural gas.

The oxidative coupling of methane (OCM) to ethane and ethene is an attractive alternative for the existing processes based on crude oil. OCM is a reaction discovered in the 1980s for the direct conversion of methane into C₂ products:

\[
2 \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}. \quad (1.1)
\]

In this reaction methane is activated heterogeneously on the catalyst surface, forming methyl free radicals which then couple in the gas phase and form ethane. Ethane subsequently undergoes dehydrogenation to ethylene. The yield of the desired C₂ products is reduced by non-selective reactions of methyl radicals with the surface and oxygen in the gas phase and also by competitive combustion reactions to CO and CO₂.

The principal product of OCM is ethylene, which is a fundamental building block of chemical industry therefore this process is highly attractive from the economic point of view. Unfortunately, thirty years of research failed to produce a commercial OCM catalyst, preventing this promising process from advancing beyond experimental stage. Many different catalytic materials have been investigated for the OCM reaction (Table 1.1), however they are...
characterized by low yield of the desired C₂ products (not exceeding 30%), poor selectivity towards ethylene and also require quite high temperature (700-900°C). Therefore they still need some improvements before they could be used in large-scale processes. In order to understand in detail the underlying mechanism of the reaction – as a basis for possible improvements of the OCM catalyst, we have studied the simplest one, Li doped MgO.

Table 2.1. OCM performance over selected catalytic materials (table adopted from ref. [4]).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T [K]</th>
<th>X(CH₄) [%]</th>
<th>S(C₂)ᵃ [%]</th>
<th>Y(C₂)ᵇ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/MgO</td>
<td>1013</td>
<td>37.8</td>
<td>50.3</td>
<td>19</td>
</tr>
<tr>
<td>30% BaO/Ga₂O₃</td>
<td>1023</td>
<td>32</td>
<td>54</td>
<td>17.3</td>
</tr>
<tr>
<td>95 mol% BaF₂/Y₂O₃</td>
<td>1023</td>
<td>36.1</td>
<td>62.1</td>
<td>22.4</td>
</tr>
<tr>
<td>La/MgO</td>
<td>1073</td>
<td>29.3</td>
<td>58.8</td>
<td>17.2</td>
</tr>
<tr>
<td>Rb₂WO₄/SiO₂</td>
<td>1123</td>
<td>32</td>
<td>78</td>
<td>25</td>
</tr>
<tr>
<td>Bi₁.₅Y₀.₃Sm₀.₂O₃₋₁₂</td>
<td>1223</td>
<td>43.5</td>
<td>62</td>
<td>27</td>
</tr>
<tr>
<td>La₂O₃-CeO₂</td>
<td>1048</td>
<td>22.3</td>
<td>66</td>
<td>14.7</td>
</tr>
<tr>
<td>Na₂WO₄/SiO₂</td>
<td>1123</td>
<td>44</td>
<td>52</td>
<td>22.9</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>1053</td>
<td>20</td>
<td>65.4</td>
<td>13.1</td>
</tr>
</tbody>
</table>

ᵃ S(C₂) = selectivity towards C₂H₆ and C₂H₄  
ᵇ Y(C₂) = yield of C₂H₆ and C₂H₄

For this simple catalyst there is a mechanism proposed by Lunsford,⁷ which involves Li⁺O⁻ sites. In the first step of the catalytic cycle two surface OH⁻ groups and two •CH₃ radicals are formed. The radicals couple together in the gas phase and form ethane:

\[
2 \text{[Li}^+\text{O}^-\text{]} + 2 \text{CH}_4 \rightarrow 2 \text{[Li}^+\text{O}^-\text{]}\text{H} + 2 \text{ } \cdot \text{CH}_3 \quad (1.2)
\]

\[
2 \text{ } \cdot \text{CH}_3 \rightarrow \text{C}_2\text{H}_6. \quad (1.3)
\]

The second step involves the dissociation of one surface OH⁻ group into lattice O²⁻ and a mobile proton, which migrates to another OH⁻ group yielding water. Water desorbs from the surface leaving an anion vacancy:

\[
2 \text{[Li}^+\text{O}^-\text{]}\text{H} \rightarrow \text{[Li}^+\text{O}^2^-\text{]} + \text{[Li}^+\text{V}_a\text{]} + \text{H}_2\text{O}. \quad (1.4)
\]

In the last step, the active site is regenerated by electron transfer to the anion vacancy and dissociative chemisorption of O₂:

\[
\text{[Li}^+\text{O}^2^-\text{]} + \text{[Li}^+\text{V}_a\text{]} \rightarrow \text{[Li}^+\text{O}^-\text{]} + \text{[Li}^+\text{V}_a^-\text{]} \quad (1.5)
\]

\[
\text{[Li}^+\text{V}_a^-\text{]} + \frac{1}{2} \text{O}_2 \rightarrow \text{[Li}^+\text{O}^-\text{]} \quad (1.6)
\]

When in solid MgO a magnesium ion is substituted by a lithium ion the Li⁺O⁻ site is formed. Such a substitution is possible because the sizes of these ions are similar, 66 pm and 68 pm for Mg²⁺ and Li⁺, respectively. As a result, an O⁻ radical is formed, which is believed to be the oxidizing active species responsible for H abstraction from methane and the
formation of methyl radicals. The same type of oxygen radical species is likely to be formed on ionization of MgO gas phase clusters yielding MgO gas phase cationic clusters.

The main objective of this work has been to study in detail the elementary steps of the oxidative coupling of methane by $O^-$ sites. The idea was to start with small gas phase clusters in order to learn more about the mechanistic behavior of these sites. The study of small size clusters is important because it enables application of more accurate methods (like MP2 and CCSD(T)) to verify the performance of DFT. Moreover, the comparison with gas phase reactivity experiments determines the reliability of computational results. The next steps of this work have involved larger models that mimic Li doped MgO surface, like non-embedded and embedded clusters and slab models.

For gas phase reactivity studies small cationic MgO and Li doped MgO clusters were used to represent $O^-$ radical sites in Li doped MgO surface. Instead of choosing arbitrarily the shape of the clusters we determined their global minimum structures for both sets of clusters (chapter 3.4 and 3.6) and used them in subsequent reactivity studies. To check if there are any structural differences between neutral and cationic MgO clusters we studied the neutral species as well (chapter 3.3). After structure determination we investigated the activation of methane by $O^-$ radicals (chapter 4.2). Due to the small cluster sizes we were able to study the reaction in detail and compare different methods of calculations. However unexpected results for the Li$^+O^-$ sites led us to consider additional types of sites in MgO that may be active for OCM – such as low-coordinated $O^{2-}$ sites, O vacancies with different charge and impurity defects. We were particularly interested in morphological defects and different types of F centers. The methane activation by defective MgO surface was studied by a cluster approach (chapter 4.3.1) and then followed by periodic calculations on periodic slab models (chapter 4.3.2). The results were compared to existing experimental data.
Chapter 2

Theoretical Background

2.1. Density Functional Theory

Density functional theory (DFT) is based on the assumption that the electron density can replace the wave function which describes a chemical system in Schrödinger quantum mechanics. Within this theory, the properties of a many-electron system can be determined using functionals, i.e. functions of another function, which in this case is the energy as a functional of the electron density.

Two Hohenberg-Kohn theorems\cite{8} are the basics of DFT. First of them says that the mapping between the electron density and the wave function of a non-degenerate ground state is reversible. It means that the ground state density uniquely determines the potential and thus all properties of the system, including the many-body wave function. Therefore instead of using wave function (dependent on 3N spatial coordinates for N electrons) one can alternatively use much simpler electron density which depends only on 3 variables and determines the system explicitly.

The second Hohenberg-Kohn theorem defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional. This is equivalent to the variational principle in quantum mechanics. From the variational principle the Kohn-Sham equations are derived.

Within Kohn-Sham method\cite{9} the many body problem of interacting electrons in a static external potential is reduced to a much simpler problem of non-interacting electrons moving in an effective potential (called the Kohn-Sham potential). The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, i.e. the exchange and correlation interactions. Non-interacting systems are relatively easy to solve as the wave function can be represented by Slater determinant of orbitals. Further, the kinetic
energy functional of such a system is known exactly. The exchange-correlation part of the
total energy functional remains unknown and must be approximated.

The Kohn-Sham equations are analogous to the Hartree-Fock equations and they are
solved in the same way, self-consistently (using iterative method). As a result the Kohn-Sham
orbitals which represent correlated electrons are obtained.

The exact exchange-correlation energy functional is not known. However there are
approximations which provide moderate accuracy for ground state structures of molecules
and solids. The simplest one is a local density approximation (LDA) which assumes that
density can be treated locally as a uniform electron gas (the density is a slowly varying
function). Local spin density approximation (LSDA) is an analogous to the LDA but
considers also electron spin (usually for open shell systems). Although LDA gives
surprisingly good predictions for solid state physics, it is not an useful model for chemistry
due to its severe overbinding of chemical bonds.\cite{10}

The second generation of density functionals is called generalized gradient approximation
(GGA) and assumes that the energy is not only a functional of the electron density but also of
the density gradient. There are several specific expressions proposed within GGA, e.g.
Becke's 1988 functional (B88),\cite{11} Perdew-Wang functional from 1991 (PW91)\cite{12} and a
version proposed Perdew, Burke and Ernzerhof (PBE).\cite{13} GGA functionals greatly reduce the
bond dissociation error and generally improve transition state barriers.\cite{10} In this work the
PBE functional was used for periodic calculations.

The next class of functionals is represented by hybrid functionals, which include in the
exchange part the exchange energy calculated as in Hartree-Fock theory. The most popular
hybrid functional is Becke 3 term with Lee, Yang, Parr correlation (B3LYP)\cite{14,15} whose
appearance caused the widespread application of DFT. Despite the progress in the field and
development of several new functionals every year, B3LYP continues to dominate. The
number 3 in the functional name is because B3LYP consists of three components. The
coefficients weighing the various components are empirically optimized to the calculated
atomization and ionization energies of a standard set of molecules. The good performance of
B3LYP has been demonstrated in a large number of studies and proven to give accurate
molecular structures, vibrational frequencies and bond energies.\cite{16} However, the energy
barrier heights obtained by B3LYP are systematically underestimated.\cite{17} In principle B3LYP
is better for main group chemistry than transition metals and it has difficulties to describe
properly van der Waals complexes.\cite{18} Although B3LYP is not perfect, it was applied in this
work while extra attention was paid to those of its weak points which are crucial for this study
(e.g. by checking the energy barriers by more accurate methods and including dispersion correction).

Hybrid functionals give a significant improvement over GGA for many molecular properties. They have been more slowly adopted in solid state chemistry than in the molecular calculations due to the difficulty of computing the exact exchange part within the plane wave basis set approach. However, they give an improvement in relative energies and have advantages in problems for which electron localization has to be described. The standard DFT functionals neglect the long-range part of dispersive interaction. This problem is usually solved by adding a damped dispersion term to standard density functionals calculated from parametrised atom-atom $C_6$ contributions.\(^{[19,20]}\) This kind of approach was used in this work.

There are many other approximations for exchange-correlation functionals and this causes the problem of a reasonable choice. The selection of the functional to use depends on the problem one would like to solve, i.e. on both the property and the type of system under study, and also on the availability of computational resources. The benchmarking studies of density functionals against experimental data or higher-level methods for different physical properties and chemical reactions as regards their credibility and a scale of application are the main guide in this matter.

The application of density functional theory, or rather the Kohn-Sham method based on DFT, has many advantages. First of all it radically decreases the computational cost compared to other quantum chemical methods which include electron correlation (i.e. MP2, coupled cluster methods etc). Of course using DFT it is not possible to systematically improve the accuracy of calculations like in case of traditional ab initio methods (based on wave function) but for solid state such an alternative does not exist at all. The simplification of electronic structure calculation for extended molecular and periodic systems is for sure a significant success of DFT, because the calculations can be scaled linearly with the number of electrons.

2.2. Second Order Møller-Plesset Many Body Perturbation Theory

The idea in perturbational approach is that the problem we want to solve differs only slightly from the unperturbed problem for which the solution is known. Since the perturbation is small (that is the principal assumption for all perturbational methods) the resulting wave function and the corresponding energy differ only little from the known problem. The whole perturbational procedure aims at finding these tiny changes with satisfactory precision.
Mathematically it is done by applying a Hamilton operator which consists of two parts, a reference Hamilton operator and a perturbation Hamilton operator. The latter is multiplied by parameter $\lambda$ which determines the strength of the perturbation. The equations for the first-, second- ect. order corrections are derived by expanding the energy and the wave function into Taylor series and collecting the terms with the same power of $\lambda$.

MP2 is a perturbational method of Møller and Plesset\textsuperscript{[21]} in which only the second-order corrections to the energy are taken into account. The expression for the second-order correction to energy involves matrix elements of the perturbation operator between the Hartree-Fock reference state and all possible excited states. The single excitations, however, give no contribution due to Brillouin theorem so they can be excluded. The same applies to triple and higher excitations because they differ by more than two excitations from the reference wave function and according to Slater-Condon rules their input equals zero. Therefore only the sum over doubly excited determinants is considered.

The results obtained by Møller-Plesset method are usually characterized by oscillating behavior (Figure 2.1).\textsuperscript{[22]} The MP2 energy improves over HF considerably though it overestimates the correlation effect. However, very often it gives better answer than MP3, which is much closer to HF result. MP4 again improves, this time even over MP2. Higher orders of corrections are usually not calculated, therefore there is not much known about their performance. The right answer is typically somewhere between MP3 and MP4.

![Figure 2.1](oscillating_behavior.png)

*Figure 2.1.* Oscillating behavior of MP methods (figure adopted from ref. [22]).
MP2 is usually the first method of choice for including electron correlation (it typically accounts for about 80-90% of correlation energy). To improve the MP2 result MP4 could be considered, however this is not done very often. Instead the CCSD(T) energy is calculated, because it includes all the contributions from MP4 (singles, doubles, triples and quadruples) plus selective sum of all the single and double corrections to infinite order. The computational cost of both methods is similar, therefore CCSD(T) is more often used than MP4.

2.3. **Coupled Cluster Method**

Contrary to the perturbation methods which add all types of corrections (single, double, triple etc.) to the reference wave function to a given order (1st, 2nd etc.) the coupled cluster method includes all corrections of a given type to infinite order.\(^{[23]}\)

Coupled cluster method takes the basic Hartree–Fock molecular orbital method and constructs multi-electron wavefunctions using the exponential cluster operator to account for electron correlation. The exponential cluster operator acting on a reference wave function generates all excited Slater determinants. Considering all of them would lead to full CI method which is impossible for all but the smallest systems. Therefore the cluster operator has to be truncated at some excitation level. Single excitations do not improve over Hartree-Fock due to the Brillouin theorem, so again the lowest level of approximation includes doubles (CCD). Usually doubles are used together with singly excited states which gives more complete model (CCSD). The next level of excitation lead to CCSDT, however these calculations are computationally too expensive to be done in practice. Alternatively the triples can be calculated in a perturbational way and added to CCSD results. Several such hybrid methods exist,\(^{[24]}\) and one of them (CCSD(T)) is used in this work.

2.4. **Exploration of the Potential Energy Surface**

2.4.1. **Potential Energy Surface**

Potential energy surfaces are very complicated due to their multi-dimensional character. There are two types of chemically interesting points on the potential energy surface: local minima, which correspond to stable configuration of nuclei and represent reactants, products and intermediate structures for a reaction, and first-order saddle points which represent transition structures.
2.4.2. Local and Global Optimization

To find a minimum on the potential energy surface a procedure called optimization is used. Optimization methods are used to find stationary points of a function (in this case multidimensional potential energy surface), i.e. points where the first derivative is zero. To confirm that the stationary point found is a minimum, the matrix of second derivatives has to be calculated and all eigenvalues have to be positive.

There are three classes of commonly used optimization methods for finding minima: steepest descent, conjugate gradient and Newton-Raphson methods. In this work conjugate gradient and quasi Newton methods were used.

Usually the number of minima grows exponentially with the number of variables therefore the global optimization is an extremely difficult task for a multidimensional function. Since the final structure depends on the initial geometry the systematic search is only possible for small molecules. For larger systems there are methods for automatic perturbation of geometry from one local minimum to another. Recently, several techniques for automatic determination of the most stable molecular and surface structures have been proposed (for example Monte Carlo Methods, Molecular Dynamics, Simulated Annealing and Genetic Algorithm) among which the genetic algorithm (GA) appears particularly efficient.\(^{25,26}\) In this work for structure determination a Hybrid Ab Initio Genetic Algorithm\(^{27}\) was applied.

The Hybrid Ab Initio Genetic Algorithm (HAGA) following the idea of Deaven and Ho\(^{28}\) is based on the evolutionary approach in which different cluster structures form a population. In the starting population \(M\) initial clusters are obtained by a random distribution of atoms. The atoms are distributed in space in such a way that there are no disjoined atoms of fragments, which prevents problems with the convergence of the self consistent field (SCF) procedure for initial configurations.

After structure optimization (using a conjugate-gradient technique) there is a fitness evaluation for each individual in the current population. The fitness function used in HAGA is based on the total energy of a given cluster. The fitness function is used to select two clusters from the population to be parents for crossover according to a roulette wheel selection.

The crossover operation (that makes the evolution from one generation to the next) adapted in HAGA implementation is similar to the one used by Daeven and Ho.\(^{28}\) The resulting child is rejected if the number of atoms of each type is lower than the target composition. If the number of corresponding atoms is higher then the composition is adjusted by deleting randomly selected atoms. The resulting children structures are then locally minimized.
In order to prevent premature convergence of the GA and provide additional structural diversity the mutation operation is performed by random changes in the structure of randomly chosen parents. Mutated structures are locally minimized and added to the population.

New population is formed out of the parent structures of the current generation, minimized children structures obtained by the crossover operations, and mutated structures. The new population is then sorted into groups of similar structures by comparing topologies of clusters which keeps a maximum diversity during the GA runs. Then the structures are ordered in a list according to the energy. The next generation of parent structures is created by choosing $M$ topmost structures from the list.

2.4.3. Transition State Search

Locating minima on a potential energy surface is straightforward. Finding the first-order saddle point, which corresponds to a transition state structure, is however much more difficult. There are no general methods which guarantee to work. Usually there are two general categories of methods to find transition structure. The first one is based on interpolation between two minima (reactant and product structures). The transition structure is localized somewhere in between these two points. The interpolation can be done in different ways (different methods). These methods however do not find the actual transition structure, they only locate a point close to it. Therefore after using one of the interpolation methods the second way of finding transition structure (which is based on local information only) has to be applied.

Usually a good guess for transition structure is needed to start optimization. It is often difficult to guess the structure, therefore either one of the interpolation method is used or a constrained minimization of an approximate transition structure is applied. The latter is done by freezing internal coordinate that changes the most during the reaction and performing minimization for a couple of points. The maximum energy structure is usually a good guess for transition structure. After that a vibrational analysis is performed in order to identify the index of transition vector (imaginary frequency) to follow during optimization. At the end the vibrational analysis has to be done again, to confirm that the found structure is actually the first-order saddle point (only one imaginary frequency along the reaction coordinate, the others have to be all positive). If that is not the case the optimized structure has to be distorted along the wrong imaginary mode and reoptimized.
Chapter 3

Structure Determination of Gas Phase Clusters

3.1. Introduction

Clusters are aggregates of between a few to thousands of atoms or molecules. Interest in clusters emerges because they often have properties that are intermediate between those in atoms or molecules and in the bulk matter. Atomistic simulations play an important role in cluster science, since many properties, particularly geometrical structures of clusters are difficult to measure experimentally. Additionally, experimental data of clusters often requires interpretation in terms of theoretical models. In contrast to metallic or semiconducting clusters, theoretical studies of the structural and electronic properties of insulating clusters, particularly metal oxides clusters are much less advanced.

Magnesium oxide, MgO, is a prototype material of (simple) metal oxides. For bulk MgO the rock salt structure is the only phase observed in experiments up to the pressure of 227 GPa.\cite{29,30} This indicates an inherent structural stability of MgO which can be expected to persist when passing from the bulk solid to molecular clusters. Indeed, mass spectra of (MgO)$_n^+$ and (MgO)$_n$Mg$^+$ cluster ions along with calculations using rigid ion pair and polarizable ion shell model potentials indicated compact cubic structures similar to fragments of the MgO crystal lattice\cite{31,32} with the most abundant clusters that are based on a (MgO)$_3$ subunit.\cite{33,34} The spectra and cluster compositions observed in IR resonance-enhanced multiphoton ionization experiments on large neutral (MgO)$_n$ ($n \geq 15$) clusters also gave indications for cubic structures.\cite{35} Up to now, computational studies have almost exclusively investigated neutral MgO clusters,\cite{32,36,37,38,39,40,41,42,43,44,45,46} despite the fact that most experiments were performed on cationic clusters. The structures of the clusters were usually assumed to be either cubic or in form of tubes (made of rings) according to the experimental findings.\cite{31,32,33,34} The main conclusion from these studies has been that for a given value of $n$ the most stable structures are cube-like, except for (MgO)$_3n$ clusters for which rings and
stacks of rings are preferred. The geometric structures of the cationic MgO clusters have been assumed to be the same as for neutral ones (vertical ionization approximation),\textsuperscript{[38]} and no systematic theoretical studies of these cationic clusters have been reported so far.

In this chapter systematic studies of neutral, cationic and Li doped MgO clusters are presented. In particular we focused on finding the lowest energy structure for a given chemical composition of the cluster, i.e. the global minimum. The underlying assumption is that the global minima found correspond to the clusters observed in the experiments. Comparison of theoretical results with the experimental IR spectra led us to structural assignments, for the first time based on direct experimental data on the internal cluster structure.

### 3.2. Computational Details

All DFT calculations were performed using the TURBOMOLE program package.\textsuperscript{[47]} To determine the global minimum structures the hybrid ab initio genetic algorithm (HAGA)\textsuperscript{[27]} in combination with density functional theory (DFT) was applied. The global optimizations of cluster structures employed the B3LYP hybrid exchange-correlation functional\textsuperscript{[14,15]} and triple zeta valence plus polarization (TZVP)\textsuperscript{[48,49,50]} basis set. To speedup DFT calculations the multipole accelerated resolution of identity (MARI-J) method\textsuperscript{[51]} for Coulomb interactions was used. The auxiliary basis sets used for MARI-J were of TZVP\textsuperscript{[49]} quality. For a final set of the lowest energy structures of each cluster type structure optimizations and harmonic frequency calculations were performed using the B3LYP functional and a more extended TZVP\textsuperscript{[50]} basis set for all atoms. To verify all minima as well as stability analysis of their wave functions the vibrational analysis was performed.

The B3LYP calculations were followed by MP2 optimizations with TUBROMOLE and then by CCSD(T) single point calculations with MOLPRO.\textsuperscript{[52]} For (MgO)\textsubscript{3}\textsuperscript{+} and (MgO)\textsubscript{4}\textsuperscript{+} CCSD(T) structure optimizations and subsequent numerical frequency calculations were performed. For all MP2 and CCSD(T) calculations the same TZVP basis as for B3LYP was applied.

### 3.3. Neutral (MgO)\textsubscript{n} Clusters

#### 3.3.1. Computational Results

Figure 3.1 presents the structures of (MgO)\textsubscript{n} clusters with $n = 2\text{-}16$. In general, the most stable configurations of neutral clusters distribute the atoms in cage-like structures instead of
pieces of the MgO crystal lattice (except for \( n = 4 \)). The cubic structures are also present among the isomers but with higher energy (Table 3.1).

The \((\text{MgO})_n\) clusters are usually characterized by high symmetry (at least the small ones), however for some of them the lack of a mirror plane, a center of inversion and an improper axis of rotation \((n = 7, 10, 11, 13, 14 \text{ and } 15)\) indicates the existence of enantiomers. As a result of high symmetry the neutral clusters seldom reveal non-zero dipole moment.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure31a.png}
\caption{Low energy isomers for \((\text{MgO})_n\) clusters with \( n = 2-10 \). Black – Mg, red – O.}
\end{figure}
One can easily recognize the building blocks of the structures, which are usually the rhombic and hexagonal rings connected in different ways. For larger cluster sizes sometimes the isomers look very similar (for example for $n = 11$ the lowest energy cage structure is very similar to more layered structure 3).

Figure 3.1.b. Low energy isomers for (MgO)$_n$ clusters with $n = 11-16$. Black – Mg, red – O.
Since the structures for small \((\text{MgO})_n\) clusters are usually different than the MgO crystal lattice, there should be somewhere a transition from the cage-like structures to the cubic ones. The calculations presented here show the preference to form hexagonal tubes for \((\text{MgO})_3\) cluster size. This is in agreement with the experimental data\[^{31,32,33,34}\] and also with some previous calculations.\[^{39,40,41}\] The structural transition of hexagonal tube to rocksalt structure for \((\text{MgO})_3\) neutral clusters has been investigated theoretically and determined to take place at \(k = 6\)\.\[^{46}\]\ Unfortunately the cluster sizes studied here are too small to verify this result.

**Table 3.1.** Relative energies for low energy isomers of \((\text{MgO})_n\) clusters at the B3LYP level of theory. Point group symmetries are given for each isomer.

<table>
<thead>
<tr>
<th>Cluster size ((n))</th>
<th>Relative energy [kJ/mol] for isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2 (D_{2h})</td>
<td>0.0</td>
</tr>
<tr>
<td>3 (D_{3h})</td>
<td>0.0</td>
</tr>
<tr>
<td>4 (T_d)</td>
<td>0.0</td>
</tr>
<tr>
<td>5 (C_s)</td>
<td>0.0</td>
</tr>
<tr>
<td>6 (D_{3d})</td>
<td>0.0</td>
</tr>
<tr>
<td>7 (C_{3v})</td>
<td>0.0</td>
</tr>
<tr>
<td>8 (S_4)</td>
<td>0.0</td>
</tr>
<tr>
<td>9 (D_{3h})</td>
<td>0.0</td>
</tr>
<tr>
<td>10 (C_2)</td>
<td>0.0</td>
</tr>
<tr>
<td>11 (C_s)</td>
<td>0.0</td>
</tr>
<tr>
<td>12 (T_h)</td>
<td>0.0</td>
</tr>
<tr>
<td>13 (C_1)</td>
<td>0.0</td>
</tr>
<tr>
<td>14 (C_1)</td>
<td>0.0</td>
</tr>
<tr>
<td>15 (D_{3h})</td>
<td>0.0</td>
</tr>
<tr>
<td>16 (C_{2})</td>
<td>0.0</td>
</tr>
</tbody>
</table>
In general, the global minima of neutral clusters are energetically well separated from the next lowest energy structures (Table 3.1). Only for \( n = 12 \) and 14 the relative energy between the first and the second isomer is within 10 kJ/mol. Therefore for these cluster sizes the definite answer about the global minimum cannot be given (based on the calculations only). For \( n = 10 \) and 13 this difference is 13.3 and 18.0 kJ/mol, respectively, which makes them also problematic cases.

The comparison with previous calculations of MgO neutral clusters shows that there is a general agreement for ring structures of \( n = 2 \) and 3 to be the lowest energy structures.[36,37,38,39,40,41,42,43,44,46]

The cubic structure of (MgO)_4 (1) was usually found to be the most stable configuration,[37,38,39,41,42,43,44,46] however some calculations predicted ring geometry (2) to be lower in energy.[32,40] Additionally Moukouri and Noguera[36] indicated that dimerization decreases the energy in all type of the structures.

For \( n = 5 \) the global minimum (1) was usually found to be less stable than the ring structure[37,39] (2) however for GA[46] and DFT[41,44] calculations there is an agreement with the results presented here. The structure 3 for this cluster size was also reported as a result of bulk-like structures studies.[43]

For \( n = 6 \) the structure consisting of two stacked hexagonal rings (1) is generally considered to be more stable than the cubic one (2).[36,37,39,40,41,46]

The global minimum structure (1) found for (MgO)_7 was usually reported to be the most stable configuration[40,45] for this cluster size, however the Hartree-Fock calculations show other structures (2, 3, 4) to be energetically more privileged.[39] The ring geometry (not found in our calculations) is the most stable structure calculated with the rigid ion model.[37]

For \( n = 8 \) and 9 the most symmetric structures (D_{4d} and D_{3h} for \( n = 8 \) and 9, respectively) considered here were found in the literature to be the most stable ones.[37,39,40,45] The cubic structures (D_{2d} and C_{4v} for \( n = 8 \) and 9, respectively) were also reported in the literature[39,40,43] when considering the convergence from the cluster to the bulk. In these studies only cube-like structures have been taken into account. The GA calculations by Roberts and Johnston[45] predicted all the structures for this cluster size depending on the charge. On the other hand for \( n = 9 \) they found only one structure consisting of three stacked hexagonal rings (1) which does not vary with the charge of the ions.[45] The structure 2 of (MgO)_9 was also predicted by Dong et al.[46] to be the second stable structure for this cluster size (right after the tube structure (1)).
Among the structures for \( n = 10 \) found by HAGA only two of them were mentioned in the literature\(^{37,39,40,43,45} \) (the global minimum and the most symmetric structure) with the cubic structure \((3)\) as the most stable one. Only the rigid ion model calculations\(^{37} \) and GA results\(^{45} \) indicated the cage-like structure \((1)\) as a global minimum.

For the next cluster size, \( n = 11 \), most of the isomers are known \((1, 3, \text{ and } 4)\) and usually the cage structure \((1)\) is considered to be the global minimum.\(^{37,45,46} \) The Hartree-Fock calculations indicate structure \(4\) to be the most stable configuration.\(^{40} \)

The B3LYP calculations for \((\text{MgO})_{12}\) give five low energy isomers. Usually in the literature two of them are mentioned: the lowest energy cluster \((1)\) with a fullerene-like structure consists of rhombic and hexagonal rings,\(^{37,40,45} \) and the hexagonal tube \((2)\) which has only slightly higher energy (1.8 kJ/mol).\(^{37,46} \) The structure \(4\) for this cluster size was also reported in studies of bulk-like structures.\(^{43} \)

Among the isomers for \( n = 13 \) and 14 only one is known (from each cluster size) namely structure \(3\), for both \((\text{MgO})_{13}\) and \((\text{MgO})_{14}\).\(^{39,40,45} \)

For \( n = 15 \) the hexagonal tube \((1)\) was also predicted by Dong et al.\(^{46} \) to be the global minimum. The cage structure \((2)\) was found as a result of GA with variation of the formal charges \((\pm q)\).\(^{45} \) For \( q = \pm 1 \) the tube structure is the lowest energy one, for \( q = \pm 2 \) the cage structure is more stable.

For \((\text{MgO})_{16}\) only two isomers are found within the relative energy lower than 200 kJ/mol and only these two structures were mentioned in the literature as well. They were found as GA results\(^{45} \) with stability dependent on the charge. Similar as in case of \((\text{MgO})_{15}\) for smaller charge the cube-like structure is privileged while for larger charge the cage-like one.

The comparison with previous calculations of MgO neutral clusters shows that all the structures for \( n = 2-9 \) reported here have already been found. Starting with \( n = 10 \) some new structures appear. However previous ab initio calculations were restricted to a number of assumed geometries (usually cubic and tube-like structures) due to excessive computational requirements for exploration of the whole conformational space. There have been only two attempts to optimize MgO clusters by means of GA so far where the variation of the structures was investigated as a function of the formal charges.\(^{45,46} \) Almost all the structures (except for \( n = 13 \) and 14) predicted using this method were also found in the HAGA calculations.
3.3.2. Comparison with Experiment*

A tunable IR-UV (infrared-ultraviolet) two-color ionization scheme, recently used to obtain far-IR spectra of neutral silicon clusters,[53] was applied to obtain vibrational spectra of $(\text{MgO})_n$ clusters. The technique used here does not use any messenger which might perturb the cluster structure. The two color ionization scheme relies on the absorption of a single or few IR photons prior to interaction with a UV photon to lift the total internal energy of the species above the ionization threshold. The direct photoionization generally prevails over the slower statistical fragmentation process. The formed ions can be detected with high level of sensitivity by means of mass spectrometry. By scanning the energy of the IR photons the ionization efficiency changes and the recorded ion intensity reflects the IR absorption spectrum of the corresponding neutral species.

Figure 3.2 presents a comparison between the experimental IR spectra and the calculated linear IR absorption spectra for the $(\text{MgO})_n$ gas phase clusters ($n = 3-16$). In general the agreement is quite impressive, most of the calculated spectra for the lowest energy structures fit very well with the measured ones. Nevertheless there are some exceptions.

The first one is for $(\text{MgO})_4$, where there is a missing band at about $820 \text{ cm}^{-1}$ in a calculated spectrum. This is the frequency characteristic of a peroxo mode. Therefore we additionally investigated the binding of molecular oxygen to $\text{Mg}_4\text{O}_2$ cluster. Instead of peroxo complexes superoxo species were obtained. They are however very high in energy, the lowest one with $+560.1 \text{ kJ/mol}$ compared to the cubic structure. We also run GA for $\text{Mg}_4\text{O}_4$ in a triplet spin state instead of a singlet spin state, but this attempt resulted in much higher energy structures (more than $200 \text{ kJ/mol}$) compared to the singlet spin state. This led us to consider the second isomer, a ring structure with relative energy $+64.2 \text{ kJ/mol}$. It turns out that the spectrum for the ring structure has all the bands which were missing in the spectrum for the cubic structure ($200-300 \text{ cm}^{-1}$ and $800-900 \text{ cm}^{-1}$). For the band with $800-900 \text{ cm}^{-1}$ range the calculated spectrum has two degenerate frequencies, which are visible as two peaks in the measured spectrum. Therefore the possible explanation could be that in the experimental spectrum two isomers are observed, the cube and the ring.

Another cluster size for which the calculated spectrum for the lowest energy structure does not fit completely to the measured one is $(\text{MgO})_{12}$. For the second energy isomer with $D_{3d}$ symmetry the agreement is very nice, all bands present in the experimental spectrum are

* The experiments were performed by Marko Haertelt and Dr. André Fielicke from the Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Molecular Physics (headed by Prof. Gerard Meijer) within the UniCat collaboration.
predicted in the calculations as well. Since the energy difference between these two isomers is only 1.8 kJ/mol (which is within accuracy of the method) the tube structure is assumed to be the global minimum for this cluster size.

For larger cluster sizes the number of bands in the vibrational spectra increases and leads to the observation of rather broad absorptions. At the same time the potential energy surface becomes more complicated which results in many isomers with similar energies. Therefore also in the experiment multiple isomers might be observed (e.g. $n = 13, 14$ and $16$).

Figure 3.2.a. Vibrational spectra of $(\text{MgO})_n$ clusters with $n = 1-10$ (blue line) compared to the calculated linear absorption spectra (black and gray) along with their geometrical structures. The calculated spectra are convoluted with Gaussian functions. Black – Mg, red – O.
3.3.3. Summary

In this study we demonstrated that the structures of small \((\text{MgO})_n\) gas phase clusters differ from the bulk MgO material, with the exception for \(n = 2\) and \(4\). The hexagonal and rhombic rings are the building blocks for these clusters. Additionally for \((\text{MgO})_{3k}\) composition with \(k = 1\) to 5 hexagonal tubes are formed, while the intermediate sizes prefer cage like structures.

Although many of the structures presented here (but not all of them) have already been found using other theoretical techniques, our calculations reveal the global minima among all these configurations. Comparison with experimental gas phase IR spectra confirms (in most cases) the structures predicted in the calculations.
3.4. Cationic (MgO)$_n^+$ Clusters$^\dagger$

3.4.1. Computational Results

Figure 3.3 presents the global minimum structures together with low energy isomers of (MgO)$_n^+$ clusters with $n = 2$-10. The cationic clusters show the preference to cage-like structures over the cubic ones, similar as neutral MgO clusters. The cations usually have lower symmetry than their neutral counterparts because of the presence of an unpaired electron and the Jahn-Teller effect. For vanadium oxide clusters, it has also been found that addition or removal of an electron lowers the symmetry of the cluster anions or cations, respectively, compared to the neutral systems.[54,55,56] Nevertheless, many of the cationic clusters are similar to their neutral counterparts, however not all the lowest energy structures for (MgO)$_n^+$ are the same as for neutral species (e.g. $n = 5$, 7 and 10). The global minima of the cationic clusters usually have delocalized spin density between two oxygen atoms (for $n = 9$ it is more delocalized), only for $n = 7$ and 10 the ground state structures have localized spin density on one O site which is of particular interest for reactivity studies.

As has already been mentioned, the neutral MgO clusters have already been investigated using many different theoretical methods, which is not the case for cationic MgO clusters. So far they were considered only by applying the vertical ionization potential to the optimized structures of neutral MgO clusters.[38] As a result the geometries for these cationic species were the same as for neutral ones. Calculations presented here are the first (to our knowledge) report about the structure determination of (MgO)$_n^+$ species. Therefore the cationic clusters are described in detail. Due to the small energy differences between the isomers more accurate MP2 and CCSD(T) calculations had to be performed to verify the B3LYP results.

For $n = 2$ only one structure was found, which is the rhombic ring similar to the geometry of the neutral species. A ring structure was also found for (MgO)$_3^+$, however for this cluster size removing of an electron from the neutral cluster leads to a $C_{2v}$ symmetric structure with two different electronic states ($^3B_1$ and $^2A_1$). The energy difference between these two spin states depends on the method used in the calculations. For B3LYP and CCSD(T) the separation is much smaller than for MP2. Additionally, MP2 indicates structure 2 as the lowest energy structure, while for structure 1 gives an unstable solution for the reference wave function. The B3LYP results are consistent with CCSD(T), but only the latter describes the wave function properly. The difference in energy between $^2B_1$ and $^2A_1$ states is too small to conclude which one is the global minimum.

$^\dagger$ This work has been published: Structural diversity and flexibility of MgO gas phase clusters, K. Kwapien, M. Sierka, J. Döbler, J. Sauer, M. Haertelt, A. Fielicke, G. Meijer, Angew. Chem. Int. Ed. 2011, 50, 1716.
Figure 3.3. Low energy isomers for (MgO)$_n^+$ clusters with $n = 2$-10. Black – Mg, red – O, blue – spin density.

The (MgO)$_4^+$ lowest energy isomers are represented by four clusters: the cubic structures (1 and 2), the flat structure that consists of three square rings (3) and the octagonal ring (4). The energy differences between the cubic structures (1 and 2) and the two others clusters (3 and 4) are about 100 kJ/mol (Table 3.2), therefore MP2 and CCSD(T) calculations were only performed for the cubes. The situation here is similar as for (MgO)$_3^+$. Again the Jahn-Teller distortion leads to two almost degenerated states. The energy difference between these two
states decreases when going from B3LYP through MP2 to CCSD(T). For B3LYP and MP2 calculations the wave function for structure 2 is unstable. Since the $^2\text{B}_2$ (C$_{2v}$) and $^2\text{A}_1$ (C$_{3v}$) electronic states separated only by 2.2 kJ/mol (at CCSD(T) level of theory) there is no clear answer about the global minimum.

Table 3.2. Relative energies for low energy isomers of (MgO)$_n^+$ clusters at the B3LYP, MP2 and CCSD(T) level of theory. Point group symmetries are given for each isomer.

<table>
<thead>
<tr>
<th>Cluster size ($n$)</th>
<th>Method</th>
<th>Relative energy [kJ/mol] for isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>B3LYP</td>
<td>D$<em>{2h}$B$</em>{3u}$</td>
</tr>
<tr>
<td>3</td>
<td>B3LYP</td>
<td>C$_{2v}$B$_1$</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>12.3*</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>B3LYP</td>
<td>C$_{2v}$B$_2$</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>B3LYP</td>
<td>C$_s$A$'$</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
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</tr>
<tr>
<td>6</td>
<td>B3LYP</td>
<td>C$_2$B</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
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</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
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</tr>
<tr>
<td>7</td>
<td>B3LYP</td>
<td>C$_s$A$'$</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
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</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
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</tr>
<tr>
<td>8</td>
<td>B3LYP</td>
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</tr>
<tr>
<td></td>
<td>MP2</td>
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<tr>
<td>9</td>
<td>B3LYP</td>
<td>C$_{2v}$B$_1$</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
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<tr>
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<td>B3LYP</td>
<td>C$_s$A$''$</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*not stable HF reference wave function

Among (MgO)$_5^+$ isomers three relevant structures were found: 1, 2 and 3, all have C$_s$ symmetry. B3LYP yields 1 as global minimum structure, 2 (10.6 kJ/mol) and 3 (13.0 kJ/mol) are slightly less stable (Table 3.2). Reoptimization of the structures at the MP2 level (UHF
reference) confirms these results. At this level of theory again 1 corresponds to the global minimum, while 2 (14.4 kJ/mol) and 3 (12.0 kJ/mol) are less stable. These two methods of calculations though indicate the same structure as a global minimum, but the resulting spin localization differ. B3LYP yields delocalized spin density over two inequivalent oxygen sites, while MP2 mainly localizes spin density at the oxygen atom with the lower coordination. To further verify the performance of the methods, CCSD(T) calculations were performed, with UHF as well as ROHF reference functions. The results confirm the B3LYP and UHF-MP2 results and the difference between the two reference functions is small and we will use ROHF-CCSD(T) in larger clusters. The results indicate that for Mg₅O₅⁺ 1 is the global minimum and both B3LYP and MP2 give reliable results, despite different electron localization and hence structures.

For n = 6 the global minimum structure at the B3LYP level is a hexagonal prism with alternating Mg and O atoms 1 and C₂ symmetry. In addition two rod shaped structures with Cᵥ structures exist, 2 that can be seen as a double cube (+11.8 kJ/mol), and a variant 3 in which the atoms in the middle of the rod are displaced away from the central axis (+25.1 kJ/mol). The two other isomers (4 and 5) have much higher energy (92.6 kJ/mol and 146.4 kJ/mol). Reoptimizations at the MP2 level yield a substantially different result. At this level 2 (-1.0 kJ/mol) as well as 3 (-9.2 kJ/mol) are more stable than 1 (Table 3.2). The different stabilities are connected to different localization of spin densities. In 2 the spin density is delocalized over two symmetry equivalent oxygen atoms and the difference between B3LYP and MP2 in relative stability is 13 kJ/mol. In contrast, 3 has localized spin density at a single oxygen atom. Consequently, UHF wavefunction is stable only for 3 and this ion is strongly stabilized with MP2 compared to B3LYP (34 kJ/mol). To check the performance of B3LYP and MP2 additional CCSD(T) calculations were performed. At the CCSD(T) level 2 is the global minimum structure, but it is only slightly more stable than 1 (+1.8 kJ/mol) and 3 (+3.3 kJ/mol). Thus in this case three different structures exist with almost identical stabilities. However, only coupled cluster gives the right result, while B3LYP as well as MP2 fail in this case. The probable cause is the different electron localization in the different isomers, for all isomers the localization is determined by symmetry, and no compensation effects can occur. As the energy differences are small, we cannot give a definitive answer about the global minimum.

The B3LYP calculations for (MgO)⁷⁺ show that in addition to the global minimum 1 the structures 2 (+13.4 kJ/mol) and 3 (+19.3 kJ/mol) exist, which are close in energy. In this case the MP2 results are similar (Table 3.2). The main difference is found for 3 which is predicted
to be considerably less stable by MP2 (+48.7 kJ/mol). This is understandable, because $3$ is the only ion with delocalized spin density. The MP2 results are confirmed by CCSD(T) calculations, at this level $3$ is 44.8 kJ/mol less stable than the global minimum structure $1$. However, this difference has no consequence on the global minimum, because $3$ is less stable than the global minimum in the first place.

For $n = 8$ two structures with small energy difference are found at the B3LYP level, $1$, a hexagonal prism with an added Mg$_2$O$_2$ unit, and $2$, a rodlike cluster composed of three joined cubes (+16.8 kJ/mol). At the MP2 level the stabilities are very similar to the B3LYP result, $2$ is 12.5 kJ/mol less stable. In this case both structures have delocalized spin density, in $1$ it is delocalized over two oxygen atoms and in $2$ over four oxygen atoms. Despite the more extensive delocalization in $2$, the MP2 stabilities are similar to the B3LYP results (Table 3.2). This indicates that $1$ can indeed be expected to be the global minimum structure.

The (MgO)$_9^{+}$ lowest energy isomers are represented by four structures at the B3LYP level. The global minimum $1$ is a double hexagonal prism with $C_{2v}$ symmetry and delocalized spin density over almost all oxygen atoms. The second structure $2$ is 11.9 kJ/mol higher at this level, it is a slablike ion consisting of two square layers with alternating Mg and O atoms. The third structure has a spherical shape with rhombic and hexagonal rings ($3$, +14.6 kJ/mol, $C_{4v}$), and finally $4$ also made of rhombic and hexagonal rings ($C_s$, +44.4 kJ/mol). At the MP2 level the stabilities differ considerably, although $1$ persists as the global minimum (Table 3.2). With MP2 the spin density in $1$ is fully localized on a single oxygen atom, which is possible because one O atom is located on the twofold rotation axis. The second most stable structure at this level is $4$ (+6.0 kJ/mol), however, a major structure relaxation compared to the B3LYP structure occurs so that the spin density is localized on a single oxygen atom in the MP2 structure. A reoptimization of the MP2 structure at the B3LYP yields an energy of +14.8 kJ/mol above the global minimum. The other two structures $2$ and $3$ are strongly disfavored by MP2 and are +49.2 kJ/mol and +41.4 kJ/mol above the minimum, respectively. Since considerable differences between the B3LYP and the MP2 results appear again CCSD(T) calculations have to be performed, this is feasible due to the relatively high symmetry of the structures. At this level again $1$ is found to be the global minimum, followed by $4$ (+7.3 kJ/mol), $2$ (+20.0 kJ/mol) and $3$ (+55.0 kJ/mol). This indicates that B3LYP and MP2 at least give the correct global minimum in this case, although they predict different electron localizations. The stability of the less stable structures is not correct with either B3LYP or MP2. While B3LYP predicts a similar stability of the three remaining structures, MP2 favors $4$ and incorrectly describes the stability of $2$. This is the same effect as for Mg$_3$O$_5^{+}$ and
Mg$_6$O$_6^+$ – different localizations (and thus structures) and incorrect stabilities with B3LYP as well as MP2. Still, the energy difference between the global minimum structure and the next stable structure is large enough in this case, to be confident that 1 is the global minimum.

For the largest cationic cluster size considered here ($n = 10$) three relevant structures at the B3LYP level were found. The global minimum 1 is an elongated ion consisting of hexagonal and rhombic rings. The second structure 2 (+5.9 kJ/mol) is a distorted, less symmetrical variant of 1, and the third structure 3 is a rod structure of joined cubes (+27.4 kJ/mol). At the MP2 level 3 is disfavored (+50.1 kJ/mol), while 2 is predicted to be even closer to 1 (3.1 kJ/mol) (Table 3.2). The differences are so small that they are well within the uncertainty limit of MP2, while CCSD(T) calculations are prohibitively expensive in this case due to size and low symmetry of the structures. Therefore a definitive answer about the most stable structure cannot be given in this case.

To sum up, the global minima structures of cationic clusters determined by HAGA in combination with DFT are mostly in agreement with MP2 and CCSD(T) calculations. Only for $n = 6$ and 10 there is no clear answer about the geometry of the most stable structure. The calculations are verified by comparison with the experimental gas phase IR spectra in the following section.

### 3.4.2. Comparison with Experiment‡

IR-MPD (infrared multiple photon dissociation) spectra of the complexes of (MgO)$_n^+$ with Ar and O$_2$ were measured in the gas phase using the Free Electron Laser for Infrared eXperiments (FELIX).

When FELIX is resonant with an IR-allowed vibrational mode of a cluster, multiple absorption of single photons can take place. If the cluster gains enough energy to overcome its barrier for dissociation, cluster fragmentation becomes possible, leading to intensity changes in the mass spectrum. The mass spectra are averaged and recorded as a function of FELIX wavelength. For the weakly bound Ar and O$_2$ complexes very similar IR spectra were measured. The O$_2$ complexes are shown in this work as these species are more pronounced in the mass spectrum, leading to a better signal-to-noise ratio in the spectra.

Figure 3.4 shows a comparison between the experimental IR-MPD spectra and the calculated linear IR absorption spectra for the (MgO)$_n^+$ gas phase clusters. For $n = 2$, 5 and 7

‡ The experiments were performed by Marko Haertelt and Dr. André Fielicke from the Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Molecular Physics (headed by Prof. Gerard Meijer) within the UniCat collaboration.
there is an excellent agreement with the experiment, which confirms the calculated global minima for \((\text{MgO})_2^+\), \((\text{MgO})_5^+\) and \((\text{MgO})_7^+\) species.

Figure 3.4. Vibrational spectra of \((\text{MgO})_n^+\) clusters with \(n = 2-10\) (red line) compared to the calculated linear absorption spectra (black, gray and dark blue) along with their geometrical structures. The calculated spectra are convoluted with Gaussian functions. Black – Mg, red – O, blue – spin density.

For \(n = 3, 4\) and 6 removing an electron from the neutral clusters results in a Jahn-Teller (JT) distortion leading to the appearance of two or more nearly degenerate lowest energy states which differ by spin localization. For \((\text{MgO})_3^+\) a proper description of this cluster ion could only be achieved at the CCSD(T) level. Only for the lowest energy \(^2\text{B}_1\) state with the
spin density delocalized over two oxygen sites the calculated spectrum shows satisfactory agreement with the IR-MPD spectrum (Figure 3.4).

For \( n = 4 \) the Jahn-Teller distortion leads to \( C_{2v} \) and \( C_{3v} \) symmetric structures with the lowest \( ^2B_2 \) (\( C_{2v} \)) and \( ^2A_1 \) (\( C_{3v} \)) electronic states separated only by 2.2 kJ/mol (at CCSD(T) level of theory). Figure 3.4 shows that for both isomers the calculated spectra would reproduce the experimental one, except for the weak band at about 750 cm\(^{-1}\). A band at such a frequency could be due to a peroxide species. However, formation of peroxide from the \( O_2 \) messenger can be ruled out as the feature is reproduced in the IR spectrum obtained for the Ar complex. Possible other sources for this band could be the presence of isomers (like \( \text{Mg}_4\text{O}_2(\text{O}_2)^+ \)) or of a different species with the same mass/charge ratio.

For the \( (\text{MgO})_6^+ \) cluster ion the structural assignment is more challenging. The global optimizations yield three low lying structures with similar energies (Figure 3.4 and Table 3.2). In fact, different quantum chemical methods predict different energy orderings of the three structures. Figure 3.4 shows also that the calculated spectra for all three isomers reproduce some features of the experimental spectrum. This may indicate that the IR-MPD spectrum for the \( (\text{MgO})_6^+ \) cluster ion reflects the presence of a mixture of all three isomers. As the experiment has been performed at ambient temperature (~30 °C), the population of high lying isomers, as well as an isomerisation on the time scale of the experiment cannot be ruled out.

For the \( n = 8 \) the calculated spectrum almost reproduces all the experimental bands. After addition of the second energy isomer (2) to the spectrum small improvement can be seen but there is still a missing band at 850 cm\(^{-1}\) (similar as for \( (\text{MgO})_4^+ \)).

The \( (\text{MgO})_9^+ \) is much more problematic, however in this case the CCSD(T) optimization is out of the question due to the cluster size. One can try again with the second isomer (2) but it does not help much. The fourth one (4), which is close in energy at the CCSD(T) level (+7.3 kJ/mol), however reproduces missing band at about 700 cm\(^{-1}\) and some in the 300-500 cm\(^{-1}\) range.

For \( (\text{MgO})_{10}^+ \) both calculated spectra are similar. This is due to the similarity between these two structures (2 is a distorted, less symmetrical variant of 1). The spectrum of the second isomer fits better to the experiment reproducing the peaks above 600 cm\(^{-1}\) which are missing in the spectrum for its symmetric counterpart. Since the energy difference between these two isomers is only 3.1 kJ/mol (which is within uncertainty limit of the method) the structure 2 is assumed to be the global minimum for this cluster size.
3.4.3. Summary

In this study the structures of cationic \( \text{(MgO)}_n^+ \) \((n = 2-10)\) clusters were determined by combining quantum chemical calculations with infrared multiple photon dissociation (IR-MPD) experiments. The structures of small cationic MgO clusters form cage like configurations instead of a simple cubic MgO phase. Moreover our calculations show that even for such a prototype oxide as MgO the structures of cationic clusters may differ significantly from their neutral counterparts. Therefore, the vertical ionization approximation does not seem to be generally applicable to metal oxide clusters.

From all the cluster sizes considered here for \( (\text{MgO})_4^+ \), \( (\text{MgO})_6^+ \), \( (\text{MgO})_8^+ \) and \( (\text{MgO})_9^+ \) cluster ions small energy differences between low energy isomers and close similarities of calculated IR spectra prevent unequivocal structure assignment.

3.5. Comparison Between Neutral and Cationic \( \text{(MgO)}_n^{0/+} \) Clusters

3.5.1. Structure

Figure 3.5 presents the comparison between neutral and cationic \( \text{(MgO)}_n^{0/+} \) clusters for the most stable structures of each cluster size. In general, the most stable configurations show the preference to more open structures over the cubic ones, except for \( n = 4 \). Most of the lowest energy structures of cationic clusters are similar to their neutral counterparts. Totally different structures are observed for \( n = 5, 7 \) and \( 10 \). For these cluster sizes however, the cationic

![Figure 3.5](image-url)  

**Figure 3.5.** The most stable B3LYP structures for a) neutral and b) cationic \( \text{(MgO)}_n^{0/+} \) clusters. For cations with \( n = 5, 7 \) and \( 10 \) also structures that originate from the lowest energy neutral cluster are shown (together with their relative energies in kJ/mol). Black – Mg, red – O, blue – spin density.
structures that originate from the most stable neutral cluster were found as well among the low energy isomers (also shown in Figure 3.5). For (MgO)$_5^+$ it is a second lowest energy structure, for (MgO)$_7^+$ the third one and for (MgO)$_{10}^+$ the fifth one.

The cationic clusters usually have lower symmetry than their neutral counterparts because of the presence of an unpaired electron and Jahn-Teller effect. The removal of one electron from the neutral species leads to delocalization of the spin density in cationic form of the clusters. The spin density is delocalized over two equivalent oxygen sites for the cluster sizes for which the structures of neutral and cationic species are similar (with exception for $n = 9$ for which the spin density is much more delocalized). The rest of the cationic structures have spin density either entirely localized on one oxygen site or distributed over two inequivalent oxygen sites ($n = 5, 7$ and $10$).

### 3.5.2. Stability

To compare the stabilities of different cluster sizes the binding energy is usually considered, which is defined as $E_{\text{atom}}/n$, where $E_{\text{atom}}$ (atomization energy) is the energy of the following reaction:

\[
(MgO)_n \rightarrow n \text{Mg} + \frac{1}{2} n \text{O}_2. \tag{3.1}
\]

However the analysis of the binding energy defined in this way is possible only for neutral clusters. Since we would like to compare the stabilities of neutral and cationic clusters we will use another definition of binding energy with a MgO monomer as a reference (hereafter called fragmentation energy):

\[
(MgO)_n \rightarrow n \text{MgO} \tag{3.2}
\]

\[
(MgO)_n \rightarrow (n-1) \text{MgO} + \text{MgO}^+ \tag{3.3}
\]

for neutral and cationic species, respectively.

Figure 3.6 presents all three equations: (3.1), (3.2) and (3.3) as a function of the cluster size. The dashed dark blue line represents the calculated heat of formation for the bulk MgO at the B3LYP level.\[^{[60]}\] This value (6.15 eV) is in excellent agreement with experimental heat of formation for MgO (6.19 eV).\[^{[61]}\] However the calculated heat of formation can not be a reference for the fragmentation energy because the heat of formation is calculated with respect to the atomization energies while the fragmentation energy with respect to the energy of MgO monomer. Therefore the bulk limit for the fragmentation energy has to be recalculated. Since the binding energy and the fragmentation energy of neutral clusters give the same relative values (the latter is just shifted by a constant number) the corresponding
bulk limit should be shifted as well. The energy shift is equal to the binding energy of MgO monomer.

![Figure 3.6](image.png)

**Figure 3.6.** Binding and fragmentation energies of the most stable configurations of \((\text{MgO})_n^{0/+}\) clusters as a function of the cluster size.

In general, the binding and fragmentation energies increase with the cluster size to reach the calculated value for the bulk (dashed line in Figure 3.6). The local maxima \((n = 6, 9, 12\) and 15) indicate enhanced stabilities of the corresponding clusters. The same stable cluster sizes were found in previous HF, MP2 and DFT-LDA calculations.[39,40,41]

Another way to compare the cluster stability, for both neutral and charged species, is considering dissociation and disproportionation energy. The dissociation energy corresponds in this case to the loss of MgO monomer (because this fragmentation path has been observed to be a major dissociation channel in collision-induced-fragmentation studies of small MgO clusters),[33,34] according to the following reactions:

\[
\text{(MgO)}_n^{0/+} \rightarrow (\text{MgO})_{n-1}^{0/+} + \text{MgO}.
\] (3.4)

The calculated values are presented in Figure 3.7, only the most stable structures of each cluster size have been taken into account. The most stable cluster sizes (pointed out by the local maxima) are 3, 6, 8, 9, 12 and 15 for neutral clusters, whereas 2, 4, 6, and 9 for cations. The previously calculated dissociation energies for cationic clusters[39] are in agreement with our results. For neutral clusters our calculations indicate an additional local maximum for \(n = 9\), and one peak for \(n = 3\) instead of two maxima for \(n = 2\) and 4, compared to previously reported results.[38,39,41]
Figure 3.7. Dissociation energies of the most stable configurations of (MgO)$_n$ and (MgO)$_n^+$ clusters ($n = 2$-$16$) as a function of the cluster size assuming fragmentation by the loss of a MgO monomer.

Figure 3.8 presents the disproportionation energy as a function of the clusters size, which is defined as:

\[
2(MgO)_n^{0+} \rightarrow (MgO)_{n-1}^{0+} + (MgO)_{n+1}^{0+}
\]

for the neutral (0) and cationic (+) clusters, respectively. The calculated disproportionation energies indicate the same most stable cluster sizes ($n = 4, 6, 9, 12$ and $15$) for both, neutral and cationic species.
To sum up these three ways of stability analysis, the most stable clusters usually appear at the same cluster size for both, neutral and cationic species. Thus, the magic numbers seem to be \( n = 4, 6, 9, 12 \) and 15. These numbers are in excellent agreement with the experimental data from mass spectrometry of clusters produced in a gas aggregation source \( (n = 2, 4, 6, 9, 12, 15) \)\(^{31,32}\) and by sputtering \( (n = 6, 9, 12) \)\(^{33,34}\).

However one has to remember that the magic numbers inferred from the analysis of abundances maxima observed in mass spectra depend on the fragmentation process. If the fragmentation occurs before ionization it will enhance the abundances of stable neutral clusters, whereas fragmentation after ionization will enhance the abundances of stable cations. Since the point of time when fragmentation takes place is not exactly known, it is difficult to say whether the magic numbers actually apply to charged or neutral clusters.

### 3.5.3. Ionization Potential and Electron Affinity

The structures of neutral species are usually investigated indirectly from mass spectrometry experiment of their ionized forms, where the more abundant species are interpreted as the more stable. The ionization process is described by the ionization potential which is the value of the energy that is needed to remove one electron from a neutral cluster in the gas phase, according to the reaction:

\[
(MgO)_n \rightarrow (MgO)_n^+ + e^-.
\]

Thus the larger value of the ionization potential, the more difficult it is to remove an electron and form a cation.

There are two types of ionization potential – a vertical and an adiabatic one. The former assumes no change of molecular geometry during ionization process. The adiabatic ionization potential, on the other hand, considers the equilibrium structures for both, neutral and cationic species. Since the ionization of molecules often leads to changes in molecular geometry the adiabatic ionization potential would be a reasonable choice. However, according to the Franck-Condon principle, vertical ionization is the most probable, since electrons move much more rapidly than nuclei and the ionized electron departs before the nuclei have time to adjust their position. Therefore here the vertical ionization potential is considered.

The ionization potential, plotted in Figure 3.9 (dark blue line), shows a decrease with the cluster size. For \( n = 3, 7, 9, 12 \) and 15 (maxima in Figure 3.9) it is much more difficult to obtain the cationic form than for \( n = 2, 5, 8, 10 \) and 13 (minima in Figure 3.9). The maxima indicate more stability of the neutral clusters and therefore in mass spectrometry experiment less cations should be produced for these cluster sizes resulting in lower peaks in
experimental spectra. However, as mentioned in previous section, the resulting peaks intensity in mass spectra depends on the fragmentation process which can occur before or after ionization.

The ionization potential can also predict reactivity of neutral clusters. The low values of ionization potential (minima in Figure 3.9) indicate that the ionization occurs quite easily and therefore these neutral clusters are supposed to be reactive in reactions where they play the role of an electron donor.

Figure 3.9 shows also the electron affinity (green line) of the cationic clusters as a function of the cluster size. The electron affinity is the energy released when an electron is attached to the cationic cluster according to the reaction:

\[
(MgO)_n^+ + e^- \rightarrow (MgO)_n.
\]  

The comparison between Figures 3.7, 3.8 and 3.9 indicates that for maxima of the electron affinity the values of dissociation and disproportionation energies for \((MgO)_n\) clusters are below the corresponding energies for \((MgO)_n^+\) species. On the other hand for \(n = 3, 6, \) and 9
the dissociation and disproportionation energies of neutral clusters are larger than for cationic ones (which corresponds to the minima on the electron affinity plot). Thus, the maxima of electron affinity indicate lower stability of the ionized structures than the respective neutral ones, the minima – the opposite.

The electron affinity can be also used to consider the reactivity of single-ionized clusters. The lower value of the electron affinity of the cationic cluster (minima in Figure 3.9) the more reactive the cluster e.g. towards a metal. The maxima indicate resistance of the cationic clusters as electron acceptors.

Besides ionization potential (of neutral clusters) and electron affinity (of cationic clusters), a third line is plotted in Figure 3.9 (red line). This is a sum of equations (3.6) and (3.7). The line is different than zero because the structures for neutral and corresponding cationic species differ. Thus, the values represent the relaxation energy when going from neutral cluster to the cationic form. The line has three maxima which indicate the largest relaxation energy for \( n = 5, 7 \) and 10. These cluster sizes are special because their neutral structure is totally different than the cationic one (which reflects in high relaxation energy above 2.4 eV). For the rest of the cluster sizes the relaxation energies are similar (about 1.5 eV), except for \( n = 9 \) for which the value is 0.6 eV. \((\text{MgO})_9^+\) is the only cationic cluster with spin density delocalized over seven oxygen sites, therefore the relaxation energy for this cluster is so small. The rest of the clusters have spin density delocalized over two oxygen sites. The localization of the spin density is correlated with structural relaxation, leading to similar values of the relaxation energy.

### 3.5.4. Electronic Gap

The frontier energy levels, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), are important for the reactivity of the system. When considering the cluster properties as a function of the cluster size one should remember that their reference system is an infinite MgO crystal, resulting from extrapolation. In this sense the HOMO-LUMO gap of the cluster becomes the gap between the valence and conduction band of the metal oxide.

Table 3.3 displays the electronic gap values of neutral and cationic MgO clusters for the various geometries: rings, stacks of rings (tubes) and cube-like structures. For the neutral clusters the results are presented in Figure 3.10. For cationic clusters two different gap values are reported (GAP 1 and GAP 2). The first one is calculated as a difference between the singly highest occupied molecular orbital (called SOMO) and the corresponding singly lowest
unoccupied orbital. Alternatively one can consider the electronic gap for cationic clusters as a difference between doubly occupied HOMO and LUMO orbitals (excluding the defect states formed after ionization). This can be done because the singly occupied HOMO orbital (SOMO) and doubly occupied HOMO orbital (dHOMO) are close in energy (and for large clusters form a band).

Figure 3.10. Electronic gap values in the various geometries of neutral clusters as a function of the cluster size.

The gap value for neutral clusters increases with the cluster size (for each structural family of clusters) and is supposed to eventually reach the value of the bulk MgO (7.8 eV).[62] On the other hand the cationic clusters have one unpaired electron. Since singly occupied orbitals lead to bands that are half-occupied, there is an overlap of the valence and conduction bands (they behave like metals). The gap value (GAP 1) decreases with the cluster size because the more atoms in the cluster the denser are the energy levels.

The neutral clusters are characterized by larger energy gap than the cationic species (GAP 1) because of the different number of electrons. In closed shell systems (neutral clusters) the HOMO-LUMO gap is between the valence and conduction band. In the cationic clusters the gap is between singly occupied alpha orbital and the corresponding virtual beta orbital (which is empty) from the UHF calculations (GAP 1). The gap therefore is close to zero for large clusters.
When considering the electronic gap for cationic clusters without defect states (GAP 2) the gap values change in similar way like for neutral clusters, in general the electronic gap increases with the cluster size. There are some exceptions for the smallest cluster sizes in each structural family because the energy levels are not dense enough for such a small species and the SOMO-dHOMO is not that small any more.

The electronic gap is generally larger for rings and stacks of rings than for cube-like structures (taking into account the same cluster size) which indicates that the electronic properties of the (MgO)$_n$ and (MgO)$_n^+$ clusters depend not only of the clusters size but also on their shape.

### 3.6. Li doped MgO Clusters

#### 3.6.1. Computational Results

Figure 3.11 shows global minima and a few lowest energy isomers of LiO(MgO)$_{n-1}$ clusters ($n = 2-10$) found by HAGA. In general, the most stable configurations of the Li doped MgO clusters consist of either hexagonal prisms (and rings) or cubes (and squares).
Figure 3.11. Low energy isomers for LiO(MgO)_{n-1} clusters with \( n = 2 \) - 10. Black – Mg, red – O, green – Li, blue – spin density.
In addition cage-like structures can be observed. Comparison with pure MgO clusters shows that the structures of LiO(MgO)$_{n-1}$ clusters are based on the structures of (MgO)$_n$ or (MgO)$_n^+$. After doping with lithium two main types of structures (with respect to pure magnesium oxide clusters) are observed – the first group in which Mg is substituted by Li (e.g. for $n = 6$) and the second group in which LiO fragment is attached to the smaller (MgO)$_{n-1}$ cluster (e.g. $n = 10$), according to following equations:

$$(\text{MgO})_n + \text{Li} \rightarrow \text{LiO(MgO)}_{n-1} + \text{Mg} \quad (3.8)$$

$$(\text{MgO})_{n-1} + \text{LiO} \rightarrow \text{LiO(MgO)}_{n-1} \quad (3.9)$$

The energies of the substitution and addition processes are plotted in Figures 3.12 and 3.13.

**Figure 3.12.** The energies of substitution reaction (Mg by Li), according to equation (3.6), for the most stable configurations of LiO(MgO)$_{n-1}$ clusters ($n = 2 - 10$) as a function of the cluster size.

**Figure 3.13.** The energies for addition reaction (LiO fragment), according to equation (3.7), for the most stable configurations of LiO(MgO)$_{n-1}$ clusters ($n = 2 - 10$) as a function of the cluster size.
For the substitution three maxima ($n = 4, 6$ and $9$) can be observed. These cluster sizes are the most stable ones among the pure neutral $(\text{MgO})_n$ clusters (see chapter 3.5.2) and the formation of Li doped analogue is not favourable for them. In case of addition the maxima are for $n = 5, 7$ and $10$, however the corresponding MgO cluster without Li is now $(\text{MgO})_{n-1}$, which at the end gives the same result.

The Li doped MgO clusters usually have lower symmetry than pure MgO clusters because the addition of lithium causes the distortion (usually opening) of the structure. The spin density is usually delocalized between two oxygen atoms in $(\text{MgO})_n^+$, while the clusters containing lithium are characterized by stronger spin localization which may indicate that they are more reactive than cationic MgO clusters.

In contrast to the pure neutral MgO clusters, which have already been investigated using many different theoretical methods, our calculations are the first (to our knowledge) report about the structure determination of LiO$(\text{MgO})_{n-1}$ species. Therefore we describe the Li doped MgO clusters in greater detail.

For the smallest cluster size (i.e. LiO(MgO)) three isomers are found. The 1 is a linear structure with Li at the one end of the cluster and O with an unpaired electron at the other. Then there is a squared structure with $C_{2v}^2B_1$ symmetry (2) which is $43.5$ kJ/mol higher in energy and a rhombic structure (3) with much higher relative energy (84.6 kJ/mol).

The LiO(MgO)$_2$ lowest energy isomers are represented by four clusters: an almost flat structure consists of two squared rings (1), a hexagon (2), a linear structure with Li at one end of the cluster and O with an unpaired electron at the other (3) and a propeller-like structure (4). The energy differences between lowest energy structure (1) and the two other clusters (2 and 3) are about $20$ kJ/mol at the B3LYP level. The MP2 and CCSD(T) calculations reveal the linear structure to be 25 and 30 kJ/mol (MP2 and CCSD(T), respectively) higher in energy than structure 1 while the relative energy for the hexagonal structure increases up to 83 and 60 kJ/mol (MP2 and CCSD(T), respectively). Nevertheless, it does not change the B3LYP indication for structure 1 to be global minimum but only causes the reverse of the stability between the 2 and 3 structures. However, the lowest energy structure at the MP2 level has a different spin localization, instead of A’ type of orbital (as in B3LYP 1 structure) the MP2 gives A” type. In addition the UHF-MP2 wave function for structure 2 is unstable and the reoptimization without symmetry yields structure 1. The propeller-like structure remains at the end of the energy row at both B3LYP and MP2 levels.
Table 3.4. Relative energies for low energy isomers of LiO(MgO)$_n-1$ clusters at the B3LYP, MP2 and CCSD(T) level of theory. Point group symmetries are given for each isomer.

<table>
<thead>
<tr>
<th>Cluster size ($n$)</th>
<th>Method</th>
<th>Relative energy [kJ/mol] for isomers</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>B3LYP</td>
<td>C$_1$</td>
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<td></td>
<td></td>
<td>0.0</td>
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<tr>
<td>3</td>
<td>B3LYP</td>
<td>C$_1$</td>
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<td></td>
<td></td>
<td>0.0</td>
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<tr>
<td></td>
<td>MP2</td>
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<tr>
<td></td>
<td>CCSD(T)</td>
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</tr>
<tr>
<td>4</td>
<td>B3LYP</td>
<td>C$_s$ A$'$</td>
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<tr>
<td></td>
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<td>0.0</td>
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<tr>
<td></td>
<td>MP2</td>
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<tr>
<td></td>
<td>CCSD(T)</td>
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<tr>
<td>5</td>
<td>B3LYP</td>
<td>C$_s$ A$''$</td>
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<td></td>
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<td>0.0</td>
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<td></td>
<td>MP2</td>
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<tr>
<td>6</td>
<td>B3LYP</td>
<td>C$_s$ A$''$</td>
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<td></td>
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<td>0.0</td>
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<td></td>
<td>CCSD(T)</td>
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<td>7</td>
<td>B3LYP</td>
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<td>8</td>
<td>B3LYP</td>
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<td>CCSD(T)</td>
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<td>9</td>
<td>B3LYP</td>
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<td>0.0</td>
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<td>MP2</td>
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*not stable HF reference wave function

For $n = 4$ four different structures are found which are quite close in energy (5-15 kJ/mol). The lowest energy structure (1) can be described as a hat-like structure or open cube structure. The 2 is a flat structure consists of hexagon and square. Then there is a cube structure with $C_s$ A$''$ symmetry (3) and again a flat structure which consists of three squared rings (4). The MP2 calculations indicate structure 2 to be global minimum and cube structure (3) to be the one with the highest relative energy. For this structure the MP2 gives also unstable solution for the reference wave function. After reoptimization with $C_s$ A$'$ symmetry the structure 3 becomes structure 1. The CCSD(T) however confirms the B3LYP global minimum structure, but the
energy difference between 1 and 2 is only 0.8 kJ/mol. As the relative energies are small, there is no definitive answer about the global minimum.

For LiO(MgO)₄ four isomers are found: 1 and 4 with C₅ A” symmetry together with 2 and 3 with C₁ symmetry. After MP2 calculations the relative energies are much higher compared to the B3LYP results, but the sequence of the stability stays unchanged. The agreement between B3LYP and MP2 indicates structure 1 to be global minimum.

For n = 6 three isomers which are very close in energy (see Table 3.4) are found: an open prism structure (1), a double cube structure (2) and an open double cube structure (3). In addition there are a prism structure (4), another open prism structure (5) and a kind of a basket-like structure (6), all with much higher relative energies compared to structure 1. The MP2 calculations indicate structure 3 to be global minimum which is only 1.5 kJ/mol more stable than structure 1. The energy difference between the double cube structure (2) and structure 1 increases from 2.3 at the B3LYP level to 27.7 at the MP2 level. The rest of the isomers have MP2 relative energies much higher compared to B3LYP. For these structures for which we can observe a big change in relative energy going from B3LYP to MP2, the UHF-MP2 wave function is unstable. After reoptimization with lower symmetry the 2 and 4 structures become 3 and 5, respectively. For structure 6 MP2 optimization leads to localization of the spin density on one O site. The CCSD(T) again confirms B3LYP results indicating structure 1 to be global minimum with structure 3 only slightly less stable (1.2 kJ/mol). In this case there is not a definitive answer about the most stable structure.

The LiO(MgO)₆ lowest energy isomers are represented by four clusters: two prism (1 and 2) and two double cube (3 and 4) structures with LiO fragment attached. The difference in energy for the two prism structures is only 1.8 kJ/mol at the B3LYP level, which becomes even smaller for MP2 (0.5 kJ/mol). For the two double cube structures the MP2 relative energies also decrease compared to B3LYP from 12.3 kJ/mol to 2.2 kJ/mol and from 50.6 kJ/mol to 42.8 kJ/mol for the 3 and 4, respectively. The very small energy differences for 1, 2 and 3 led to CCSD(T) calculations which gave similar results as MP2. In this case the three different structures exist with almost identical stabilities.

The B3LYP calculations for LiO(MgO)₇ give five isomers which are close in energy (8-12 kJ/mol). The global minimum structure consists of a prism and a cube (1) and is similar to structure 4 (prism and open cube). Then there is also a triple cube structure (2) and its open analogue (5). The last structure (3) can be describe as an open prism. Reoptimization at the MP2 level changes substantially the order of stability – now the open triple cube structure (5) is the global minimum followed by the open prism structure (3) and the B3LYP lowest energy
structure (1). The highest relative energy is calculated for structure 2 which reveals unstable reference wave function. The optimization without symmetry causes opening of the structure (it becomes 5). CCSD(T) confirms MP2 results indicating structure 5 to be global minimum.

For \( n = 9 \) the global minimum structure at the B3LYP level (1) is a slab structure (\( C_s A' \)) with Li atom at the one corner and O atom with an unpaired electron at the other corner. In addition two prism structures (2 and 3) and another slab structure (4) exist. The prism structures are similar, in the 2 the Li atom is bound into the prism (12.4 kJ/mol) while in the 3 addition of Li causes opening of the ring (20.2 kJ/mol). They differ in spin localization, in the 2 spin is delocalized between two oxygen atoms on both sides of the Li atom, in the 3 spin is localized mostly on the opposite O atom. The least stable isomer (4) is similar to the global minimum, both of them have Li atom at the corner but the unpaired electron is localized on a different oxygen atom causing different distortion of the slab. In this case the MP2 calculations give similar results, they cause only reverse in stability of the two prism structures. The 2 structure has unstable UHF wave function and after reoptimization without symmetry it becomes structure 3. However, this difference has no consequence on the global minimum.

For the largest Li doped MgO cluster size considered here (\( n = 10 \)) eight different isomers are found. All of them are based on the structures of \((\text{MgO})_9\) or \((\text{MgO})^+_9\) (prism, slab and squeezed prism) with LiO fragment attached. At the B3LYP level global minimum is well separated from other isomers (23 kJ/mol). After MP2 calculations the stability sequence does not change, except for structure 3 which becomes 9.6 kJ/mol less stable than the lowest energy structure (1).

To sum up, the global minima structures of Li doped MgO clusters determined by HAGA in combination with DFT are mostly in agreement with MP2 and CCSD(T) calculations. Only for \( n = 8 \) the structure predicted by B3LYP as a global minimum is different than the CCSD(T) result. For three other cases (\( n = 4, 6 \) and 7) a definitive answer about the most stable structure can not be given, due to very small differences in energy between isomers.

### 3.6.2. Stability

To compare the stability of different cluster sizes the dissociation energy which corresponds to the loss of the MgO monomer (because this fragmentation path has been observed to be a major dissociation channel in collision-induced-fragmentation studies of small MgO clusters)\(^{33,34}\) is used, according to following reaction:

\[
\text{LiO}((\text{MgO})_{n-1}) \rightarrow \text{LiO}(\text{MgO})_{n-2} + \text{MgO}. \quad (3.10)
\]
Figure 3.14. Dissociation energies of the most stable configurations of LiO(MgO)\(_{n-1}\) clusters (\(n = 2 - 10\)) as a function of the cluster size assuming fragmentation by the loss of a MgO monomer. The calculated values are presented in Figure 3.14 (only the most stable structures of each cluster size have been taken into account). From the plot the most stable cluster sizes (pointed out by the local maxima) are for \(n = 7\) and 9.

Figure 3.15. Disproportionation energies of the most stable configurations of LiO(MgO)\(_{n-1}\) clusters (\(n = 3 - 9\)) as a function of the cluster size.
Another way to compare the relative cluster stabilities is consideration of the disproportionation energy as a function of the clusters size. The disproportionation energy is defined as a formation of two clusters (one smaller and one bigger) from two clusters of the same size, according to this reaction:

\[
2 \text{LiO(MgO)}_{n-1} \rightarrow \text{LiO(MgO)}_n + \text{LiO(MgO)}_{n-2}.
\] (3.11)

The calculated values of disproportionation energy (plotted in Figure 3.15) indicate the same most stable cluster sizes \(n = 7\) and \(9\) as from dissociation energy analysis.

### 3.6.3. Ionization Potential and Electron Affinity

In order to check the ability of the clusters to take part in different type of reactions one may consider ionization potential and electron affinity. The first one says how easily the cluster is able to remove an electron and create the cationic form:

\[
\text{LiO(MgO)}_{n-1} \rightarrow [\text{LiO(MgO)}_n]^+ + e^-.
\] (3.12)

The lower the value of the ionization potential, the easier the process occurs. The values for ionization potential (see Figure 3.16) are between 8.7 eV and 10.4 eV, and they are higher than for pure MgO clusters (7.6 eV – 8.7 eV). The lowest values are for \(n = 8\) and \(9\), which indicates these cluster to be the best electron donors among the others.

![Ionization potential of the LiO(MgO)\(_{n-1}\) clusters as a function of the cluster size.](image)

**Figure 3.16.** Ionization potential of the LiO(MgO)\(_{n-1}\) clusters as a function of the cluster size.
Figure 3.17 shows the electron affinity of the clusters as a function of the cluster size. The electron affinity is the energy released when an electron is attached to the cluster according to the reaction:

\[
\text{LiO(MgO)}_{n-1} + e^- \rightarrow \text{[LiO(MgO)}_{n-1}]^-.
\] (3.13)

The values now are negative which indicate that it is easier to attach another electron to the clusters than to remove it. This means that Li doped MgO clusters as open-shell systems with one unpaired electron are willing to pair it with another electron. Therefore they will rather behave as electron acceptors than electron donors.

3.6.4. Summary

The global minimum structures of LiO(MgO)\(_{n-1}\) clusters, with \(n = 2-10\), were determined by the hybrid ab initio genetic algorithm (HAGA) in combination with DFT. The most stable configurations of the Li doped MgO clusters consist of either hexagonal prisms (and rings) or cubes (and squares). In principle, the structures of LiO(MgO)\(_{n-1}\) clusters are based on the structures of pure MgO clusters (neutral and cationic). The addition of lithium usually causes distortion of the parent structure, therefore the resulting Li doped MgO clusters have usually more open structures than their undoped counterparts. The LiO(MgO)\(_{n-1}\) clusters are characterized by stronger localization of the spin density compared to MgO cations which may indicate their higher reactivity. The reactivity of these clusters is discussed in the following chapter.
Chapter 4

Reactivity Studies

4.1. Introduction

C-H bond activation is a subject of immense practical and fundamental interest. Particularly conversion of methane into more valuable chemicals and fuels represents a challenge for the future. A chemical of particular importance is ethene, which can be obtained by oxidative coupling of methane (OCM). This reaction involves the breaking of a methane C-H bond and the formation of methyl radicals, which couple together and form an ethane molecule. After that ethane can undergo oxidative dehydrogenation to ethene.

A prototype catalyst for the OCM reaction is lithium doped magnesium oxide. It is believed that the O\(^{-}\) oxygen radical anion is the oxidizing species responsible for hydrogen abstraction from CH\(_4\) and the formation of methyl radicals. To understand the nature of the interaction between CH\(_4\) and MgO, the adsorption and dissociation of CH\(_4\) on MgO and Li doped MgO catalysts have been extensively investigated experimentally and theoretically. The heterolytic dissociation of methane to form CH\(_3\)^- and H^+ is possible to occur on MgO(100) surface even below room temperature, when the active sites are in low-coordination states. Li doped MgO surface does not support heterolytic dissociation due to the presence of O\(^{-}\) oxidizing species which are responsible for hydrogen abstraction from CH\(_4\) and the formation of methyl radicals. Lithium doping enhances the radical production, because it stabilizes O\(^{-}\) states. The addition of lithium was found to enhance not only the catalytic activity of MgO (in reaction with CH\(_4\)) but also the selectivity towards ethane. It is probably due to the Li\(^+\)O\(^{-}\) centers that strengthen the donor-acceptor interaction.
The formation of Li$^+$O$^-$ sites in a solid MgO is possible by substitution of a magnesium ion by a lithium ion. The same type of O$^-$ oxygen radicals can be formed upon ionization of (MgO)$_n$ gas phase clusters yielding (MgO)$_n^+$ ions.

Schröder and Roithova showed by mass spectrometry and in agreement with quantum chemical calculations that the smallest possible species, MgO$^+$, indeed activates methane with hydrogen abstraction as a major pathway.$^{[78]}$ The (MgO)$_2^+$ species was found to activate small hydrocarbon molecules (propane, butane), but not methane. Another joint experimental-computational study has shown that the much larger [(Al$_2$O$_3$)$_4$]$^+$ cluster cation also features O$^-$ and abstracts hydrogen from CH$_4$.$^{[79]}$ For a review of computational studies of anionic, neutral and cationic metal oxide species, see ref. [80].

Based on the hypothesis that Li$^+$O$^-$/MgO is the active site for OCM surface reactions we first study methane activation by small (MgO)$_n^+$ and LiO(MgO)$_{n-1}$ gas phase clusters, to be able to investigate in detail every elementary step of the following reactions,

\[
(MgO)_n^+ + CH_4 \rightarrow [(MgO)_nH]^+ + \cdot CH_3 \\
LiO(MgO)_{n-1} + CH_4 \rightarrow LiO(MgO)_{n-1}H + \cdot CH_3.
\]

(4.1)  (4.2)

For comparison we also consider the reaction with H$_2$, the smallest molecule from which hydrogen can be abstracted,

\[
(MgO)_n^+ + \frac{1}{2} H_2 \rightarrow [(MgO)_nH]^+ + H' \\
LiO(MgO)_{n-1} + \frac{1}{2} H_2 \rightarrow LiO(MgO)_{n-1}H + H'.
\]

(4.3)  (4.4)

Specifically, we are interested in a possible correlation between the energy barriers for the reaction of a given species with CH$_4$ and its hydrogenation (hydrogen attachement) energy,

\[
(MgO)_n^+ + \frac{1}{2} H_2 \rightarrow [(MgO)_nH]^+ \\
LiO(MgO)_{n-1} + \frac{1}{2} H_2 \rightarrow LiO(MgO)_{n-1}H.
\]

(4.5)  (4.6)

The latter has been proposed as a reactivity descriptor for hydrogen abstraction from hydrocarbons$^{[81]}$ and was applied to the oxidative coupling of methane as well.$^{[82]}$

We also discuss the performance and accuracy of DFT method by comparison with MP2 and CCSD(T) calculations.
4.2. (MgO)$_n^+$ and LiO(MgO)$_{n-1}$ Clusters with O$^-$ Sites§

4.2.1. Model systems

To model O$^-$ sites we used the global minimum structures of the (MgO)$_n^+$ and LiO(MgO)$_{n-1}$ clusters determined by the hybrid ab initio genetic algorithm (HAGA) (chapter 3.4 and 3.6). Six different sizes of both cationic MgO and Li doped MgO clusters have been investigated. For (MgO)$_n^+$ there are clusters with $n = 1$-5 and 7, for LiO(MgO)$_{n-1}$ clusters with $n = 2$-6 (Figure 4.1). For LiO(MgO)$_3$ ($n = 4$) we consider two structures (A and B) because of the small energy difference between these two isomers at the CCSD(T) level (0.8 kJ/mol).

![Figure 4.1. Model systems for O$^-$ sites: a) (MgO)$_n^+$ and b) LiO(MgO)$_{n-1}$ clusters. Black – Mg, red – O, green – Li, blue – spin density.](image)

4.2.2. Methods

The calculations consisted of structure optimizations for the relevant intermediates (local minima) and transition structures (saddle points) along the reaction pathway. After each optimization a vibrational analysis was performed to confirm the absence of imaginary frequencies for local minima and the existence of a single imaginary frequency for transition structures. To verify that the transition structures connect the desired minima we slightly distorted these structures along the imaginary frequency mode in both directions and performed optimizations from these two points with a very small step. We also calculated the lowest energy excitations for all the structures to check the stability of their wave functions.

§ Part of this work (concerning cationic MgO clusters) has been published: Reactions of H$_2$, CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ with [(MgO)$_n]$ clusters studied by density functional theory, K. Kwapien, M. Sierka, J. Döbler, J. Sauer, Chem. Cat. Chem. 2010, 2, 819.
DFT calculations were performed using the TURBOMOLE program package.\cite{47} The B3LYP exchange-correlation functional\cite{14,15} and RI-J method\cite{83} were applied for structure optimizations. The basis sets used in the calculations are of triple and quadruple zeta valence plus polarization\cite{50,84} quality (hereafter called TZVP and QZVP, respectively). The structure optimizations were carried out with the [5s,4p,3d/5s,3p,2d,1f/3s,1p] basis set on Mg/C,O/H atoms, followed by single point calculations with the more extended [9s,5p,4d,1f/7s,4p,3d,2f,1g/4s,3p,2d,1f] basis set.

MP2 optimizations were done starting from the optimized B3LYP stuctures. All further calculations were performed based on the optimized MP2 structures as single point calculations. The basis sets used in MP2 and CCSD(T) calculations were the same as for B3LYP results. As the TURBOMOLE standard basis sets are not designed for correlation treatment of inner shells it is recommended to exclude all non-valence orbitals. This procedure is called frozen core approximation and means for Mg\(^{2+}\) that none of its electrons are correlated. Therefore we also performed all electron calculations (for which core electrons are included in the correlation treatment) employing the adequate cc-pCVXZ (X=T and Q) basis sets.\cite{85} To estimate the complete basis set (CBS) limit we used the extrapolation scheme of Halkier et al.\cite{86} and applied correlation consistent triple and quadruple zeta basis sets\cite{85,87} (cc-pVXZ and cc-pCVXZ for frozen core and all electron calculations, respectively). The MP2 calculations were performed with TURBOMOLE\cite{47} using the RI-MP2 approach,\cite{88} followed by CCSD(T) calculations with MOLPRO.\cite{52}

4.2.3. B3LYP Results

4.2.3.1. Energy Profiles

Energy profiles for the reaction of (MgO)\(_2\)\(^{+}\) with H\(_2\) and CH\(_4\) are shown in Figure 4.2. The local minimum and transition structures for other clusters studied here are similar to those with (MgO)\(_2\)\(^{+}\) and therefore they are discussed together. The relative energies (with respect to the separated reactants) of the stationary points along the reaction pathways are listed in Tables 4.1-4.4. Both electronic total energies and the energies at 0 K, including zero point vibrational energies (ZPVE), are given.

The interaction between (MgO)\(_n\)\(^{+}\) and H\(_2\) as well as CH\(_4\) proceeds in a similar way and is consistent with the mechanism proposed by Schröder and Roithova.\cite{78} First, a strong encounter complex is formed. In the transition structure a hydrogen atom of H\(_2\) or CH\(_4\) interacts with an oxygen atom of the cluster. Hydrogen abstraction yields a hydrogen atom or a methyl radical, respectively, attached to [(MgO)\(_n\)H]\(^{+}\) as intermediate. The final products are...
obtained by its dissociation. For all cluster sizes both reactions are exoenergetic and for the same cluster size their reaction energies are similar. The same conclusions apply to the reactions of H2 and CH4 with LiO(MgO)n−1 clusters.

![Energy Profiles](image)

**Figure 4.2.** B3LYP energy profiles (in kJ/mol) for the reaction of (MgO)2+ with H2 (blue line) and CH4 (green line). There are two encounter complexes (EC) for H2 and two reaction intermediate structures (IN) for CH4. Black – Mg, red – O, yellow – C, gray – H, blue – spin density.

The ZPVE changes disfavor the formation of the encounter complexes because of the additional intermolecular vibrations (+5.2 to +9.2 kJ/mol for H2 and +1.8 to +4.2 kJ/mol for CH4). In both reactions an O-H bond is formed, whereas either an H-H or a C-H bond is broken. Since the O-H vibrational frequency is lower than the H-H, but higher than the C-H frequency, the resulting ZPVE changes for the transition structures, products and intermediates are positive for the reactions with H2, but negative for the ones with CH4. This leads to an energy increase along the whole reaction path for H2, but for CH4 the energy is actually lowered starting from the transition structures.
Table 4.1. Hydrogen abstraction from H₂ by (MgO)ₙ⁺. Relative energies (in kJ/mol) with respect to the separated reactants for the encounter complexes (EC), transition structures (TS), intermediates (IN), and products (PR) obtained by B3LYP. Values in parentheses include ZPVE contributions.

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>EC</th>
<th>TS</th>
<th>IN</th>
<th>PR</th>
</tr>
</thead>
<tbody>
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<td>(MgO)+</td>
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<td>-13.5</td>
<td>-78.4</td>
<td>-75.4</td>
</tr>
<tr>
<td>(MgO)₂⁺</td>
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<td>20.0</td>
<td>-32.0</td>
<td>-29.2</td>
</tr>
<tr>
<td>(MgO)₃⁺</td>
<td>-30.6</td>
<td>13.3</td>
<td>-48.1</td>
<td>-44.6</td>
</tr>
<tr>
<td>(MgO)₄⁺</td>
<td>-24.3</td>
<td>13.7</td>
<td>-43.9</td>
<td>-41.2</td>
</tr>
<tr>
<td>(MgO)₅⁺</td>
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<td>13.4</td>
<td>-43.4</td>
<td>-42.2</td>
</tr>
<tr>
<td>(MgO)₇⁺</td>
<td>-18.3</td>
<td>4.3</td>
<td>-66.4</td>
<td>-65.0</td>
</tr>
</tbody>
</table>

a for n = 2, 3, 5, 7 additional stationary points are found at -1 ... -2 kJ/mol that become repulsive on inclusion of the ZPVE.

Table 4.2. Hydrogen abstraction from CH₄ by (MgO)ₙ⁺. Relative energies (in kJ/mol) with respect to the separated reactants for the encounter complexes (EC), transition structures (TS), intermediate (IN), and products (PR) obtained by B3LYP. Values in parentheses include ZPVE contributions.

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>EC</th>
<th>TS</th>
<th>IN</th>
<th>PR</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MgO)+</td>
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<td>-19.7</td>
<td>-194.8</td>
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<td>(MgO)₂⁺</td>
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<td>19.7</td>
<td>-43.7</td>
<td>-20.9</td>
</tr>
<tr>
<td>(MgO)₃⁺</td>
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<td>-61.8</td>
<td>-42.1</td>
</tr>
<tr>
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<td>11.4</td>
<td>-54.7</td>
<td>-39.0</td>
</tr>
<tr>
<td>(MgO)₅⁺</td>
<td>-44.2</td>
<td>21.1</td>
<td>-48.6</td>
<td>-40.0</td>
</tr>
<tr>
<td>(MgO)₇⁺</td>
<td>-33.7</td>
<td>6.1</td>
<td>-72.8</td>
<td>-62.8</td>
</tr>
</tbody>
</table>
Table 4.3. Hydrogen abstraction from H₂ by LiO(MgO)_{n-1}. Relative energies (in kJ/mol) with respect to the separated reactants for the encounter complexes (EC), transition structures (TS), intermediates (IN), and products (PR) obtained by B3LYP. Values in parentheses include ZPVE contributions.

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>EC</th>
<th>TS</th>
<th>IN</th>
<th>PR</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOMgO</td>
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<td>-3.5</td>
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<tr>
<td>LiO(MgO)₂</td>
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<td>-2.8</td>
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<tr>
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<td>-11.0</td>
<td>-5.8</td>
<td>-5.4</td>
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<tr>
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</table>

4.2.3.2. Structures

In the first step of the reaction an encounter complex is formed. With both H₂ and CH₄, two types of the encounter complex structures can be observed for Li doped MgO clusters, while only one for cationic clusters. In the first type the methane C atom or H₂ attach to the Mg²⁺ or Li⁺ site of the cluster, respectively. For H₂ this is kind of a side-on complex (see Figure 4.2). The second type is an end-on complex with an H···O contact to the cluster O site. For larger cluster sizes with more available O and Mg sites more encounter complex structures exist. The stability order is similar in all the reactions studied here – the most stable complex is the one formed with the Mg²⁺ site, followed by Li⁺ and then O²⁻ sites, and finally the O⁻ site with the smallest binding energy. The relative energies for encounter complexes with the Li⁺ and O²⁻ sites are similar and therefore in some cases a reversal in stability takes place. Sometimes the Mg sites are not so easily accessible for molecules which makes some of the Mg-C (or Mg-H₂) complexes not as stable as could be expected.
Table 4.4. Hydrogen abstraction from CH$_4$ by LiO(MgO)$_n$-1. Relative energies (in kJ/mol) with respect to the separated reactants for the encounter complexes (EC), transition structures (TS), intermediates (IN), and products (PR) obtained by B3LYP. Values in parentheses include ZPVE contributions.

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>EC</th>
<th>TS</th>
<th>IN</th>
<th>PR</th>
</tr>
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<tbody>
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<td>(7.4)</td>
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<td></td>
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<td>(-12.9)</td>
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<td></td>
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<td>LiO(MgO)$_5$</td>
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<tr>
<td></td>
<td>-1.2</td>
<td>(0.5)</td>
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</table>

The optimized transition structures for H abstraction from H$_2$ and CH$_4$ are presented in Figure 4.3. They are very similar for both reactions, taking into account the same cluster size. The only difference is for $n = 3$; for methane activation by LiO(MgO)$_2$, the transition structure is planar which is not the case for reaction with H$_2$. The H-H, C-H and O-H bond distances (see Figure 4.3) indicate that the transition structures can be described as “early” (the OH bond is only partially formed). The H-H bonds are much less extended compared with C-H bonds and the O-H distances are larger for interaction with H$_2$ than for methane. The transition structures of the reaction with H$_2$ are therefore even more similar to reactants.
Figure 4.3. Optimized B3LYP transition structures for H abstraction from H\textsubscript{2} and CH\textsubscript{4} by a) (MgO)\textsubscript{n}\textsuperscript{+} and b) LiO(MgO)\textsubscript{n-1}. H-H, C-H and O-H bond distances are given in pm. Black – Mg, red – O, green – Li, yellow – C, gray – H, blue – spin density.
For methane activation two types of intermediate structures are found. The most stable intermediates involve a C-Mg or C-Li interaction between the methyl radical and the Mg or Li site of the cluster. Again for larger clusters more intermediate structures of this type exist. In the second type of intermediates a methyl radical is weakly bound to the OH group of the cluster. This is always the least stable intermediate structure. For the interaction with the H₂ molecule there is only one type of the intermediate but its structure depends on the cluster type. For cationic cluster it is a complex with weak interaction between two hydrogen atoms. The H···H(O) distance is about 210 pm. For Li doped MgO clusters it is a structure in which H atom weakly interacts with O site (from the OH group of the cluster). After dissociation the hydrogenated clusters are obtained. The OH distances in all product structures equal 96 pm.

4.2.3.3. Energy barriers

In single collision gas phase experiments one can observe a reaction if the energy of the transition structure is lower than that of the reactants. Therefore, for gas phase reactions the apparent energy barrier is usually considered and a negative value means that the reaction is likely to occur.

Among the clusters studied here only MgO⁺ exhibits negative apparent energy barriers (Tables 4.1-4.4) in reactions with both H₂ and CH₄. All other reactions have positive apparent energy barriers, and therefore will not occur under single collision conditions. A small negative apparent barrier is also found for CH₄ activation by (MgO)⁷⁺, but in this case the reaction is unlikely to occur because entropy favors dissociation of the encounter complex into the reactants compared to crossing the barrier.

For cationic clusters the apparent energy barriers as a function of the cluster size show a similar pattern for reactions with H₂ and CH₄. The barrier is lowest for MgO⁺ (n = 1), followed by the largest clusters, n = 7, while for all other cluster sizes (n = 2-5) higher barriers are calculated. The highest barrier is found for n = 2 in the reaction with H₂, but for n = 5 in the reaction with CH₄.

For Li doped MgO clusters reacting with H₂ the energy barriers are small, 3.7 – 8.1 kJ/mol, while for CH₄ activation the barriers are larger (4.6 – 20.5 kJ/mol). The clusters 3 and 4B have almost the same apparent energy barriers (with CH₄ and H₂) due to the same geometrical arrangement around the O⁻ active site. In general, the ring planar clusters (2, 3, 4B) are more reactive than the cage-like ones (4A and 6).
4.2.3.4. H attachment energy

The H attachment energy, defined according to the reactions (4.5) and (4.6) for cationic MgO and Li doped MgO clusters, respectively, has been proposed as a reactivity descriptor for hydrogen abstraction from hydrocarbons. The correlation between the energy barriers for the reaction of a given species with CH$_4$ and its hydrogenation energy is given in Figure 4.4. In the plot we also included the data for the [(Al$_2$O$_3$)$_4$]$^+$ gas phase cluster from a previous study.

![Figure 4.4. Apparent energy barrier as a function of the H attachment energy for H abstraction from CH$_4$ by (MgO)$_n^+$ (green dots) and LiO(MgO)$_{n-1}$ (blue squares).](image)

By and large, the apparent barriers follow the trend of the H attachment energies with larger deviations for cationic MgO clusters. For the reaction with MgO$^+$ the barrier is exceptionally low. This is most likely due to the additional Mg-C interaction in the transition structure. This is the only one TS with “side-on” configuration (which is even stronger for MP2, see Figure 4.5 below). For an enforced linear transition structure an apparent barrier of +15.5 kJ/mol is obtained.

For Li doped clusters the points follow the expected trend. This confirms that the H attachment energy can indeed be used as a screening parameter to estimate the H abstraction ability and the barrier height. For example for $n = 4$ both clusters A and B have similar total energies, but the 4A species has a much higher H attachment energy and the calculated barrier is also higher compared to 4B.
4.2.3.5. Spin density distribution

The spin density in the present \((\text{MgO})_n^+\) clusters is the result of an electron hole in the parent \((\text{MgO})_n\) clusters. Among the clusters of this study (Figure 4.1.a), in 1 and 7 the spin density is localized on a single oxygen site, and for the other clusters B3LYP predicts delocalization between two oxygen sites. For 2, 3, and 4 these two oxygen sites are symmetry equivalent, which is not the case for 5.

Most of the \(\text{LiO}(\text{MgO})_{n-1}\) clusters have the spin density totally localized on one oxygen site, only for 2 and 4A there is some delocalization over a second oxygen site (see Figure 4.1.b). In general, Li containing clusters show a stronger spin localization than \((\text{MgO})_n^+\) species. However, this does not mean that they are more reactive. Their calculated energy barriers are higher than for cationic MgO clusters (see Figure 4.4).

For the present study it is of interest how the spin density distributions changes along the hydrogen abstraction path. In the encounter complexes, no change is observed compared to the isolated clusters, whereas in the transition structures the spin density always localizes on the oxygen site to which the H-H or the C-H bond coordinates (Figure 4.3). In the intermediate structures formed upon hydrogen abstraction it is entirely localized on the radical species, i.e. on the hydrogen atom or on the carbon atom of the methyl radical.

For the \((\text{MgO})_n^+\) clusters there is some correlation between the reactivity towards \(\text{CH}_4\) and the localization of the spin density. The monomeric and heptameric cluster cations, which are most reactive (lowest apparent energy barriers) are exactly the species for which the spin density is totally localized on one oxygen site. Clusters with spin density delocalized between two equivalent oxygen sites 2, 3, and 4, are less reactive. Cluster 5 with the spin density delocalized between two inequivalent oxygen sites is the least reactive towards methane among the clusters considered here.

4.2.4. Comparison with MP2 and CCSD(T) calculations

To check the performance of DFT, in particular B3LYP, MP2 and CCSD(T) calculations were performed for the smallest clusters of the cationic and Li doped series. First the B3LYP structures were optimized at the MP2 level using the same TZVP basis set. Figure 4.5 shows the encounter complex and transition structures after B3LYP and MP2 optimizations for cationic and Li doped MgO clusters, respectively. At the optimized MP2/TZVP structures we performed single point MP2 calculations first with QZVP and then with cc-pVXZ (X = T, Q), i.e., triple- and quadruple-zeta basis sets, and extrapolated to the complete basis set (CBS).
limit. For CCSD(T) the same procedure was applied, except for CCSD(T)/TZVP were single point calculations were performed instead of optimization. The results are given in Table 4.5.

Table 4.5. Hydrogen abstraction from CH₄ by MgO⁺ and LiOMgO. Relative energies (in kJ/mol) with respect to the separated reactants for the encounter complex (EC) and the transition structure (TS) obtained by B3LYP, MP2 and CCSD(T).

<table>
<thead>
<tr>
<th>Method</th>
<th>MgO⁺ EC</th>
<th>MgO⁺ TS</th>
<th>LiOMgO EC</th>
<th>LiOMgO TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/TZVP</td>
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<td>-19.7</td>
<td>-13.7</td>
<td>19.1</td>
</tr>
<tr>
<td>B3LYP/QZVP/B3LYP/TZVP</td>
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<td>-20.2</td>
<td>-13.9</td>
<td>18.6</td>
</tr>
<tr>
<td>MP2/TZVP</td>
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<td>-2.4</td>
<td>-14.4</td>
<td>37.4</td>
</tr>
<tr>
<td>MP2/QZVP/MP2/TZVP</td>
<td>-96.4</td>
<td>-8.5</td>
<td>-15.0</td>
<td>32.1</td>
</tr>
<tr>
<td>MP2/CBS</td>
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<td>-10.1</td>
<td>-14.9</td>
<td>30.9</td>
</tr>
<tr>
<td>CCSD(T)/TZVP/MMP2/TZVP</td>
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<td>-14.5</td>
<td>31.8</td>
</tr>
<tr>
<td>CCSD(T)/QZVP/MMP2/TZVP</td>
<td>-96.3</td>
<td>-15.6</td>
<td>-15.3</td>
<td>25.4</td>
</tr>
<tr>
<td>CCSD(T)/CBS</td>
<td>-97.8</td>
<td>-17.4</td>
<td>-14.8</td>
<td>24.0</td>
</tr>
</tbody>
</table>

4.2.4.1. MgO cationic

For the encounter complex (EC), which is dominated by electrostatic and polarization interactions, similar structures were found, only the Mg-C distance is slightly longer (0.5 pm) at the MP2 level. The increased distance with MP2 can be attributed to the frozen core approach, which effectively freezes all electrons on Mg²⁺ and neglects the polarization of the 2p orbitals by the interaction. When considering an all electron calculation with a cc-pCVTZ basis the Mg-C distance is 224.1 pm in the optimized structure and as expected the value is smaller than the B3LYP value. Still, the relaxation upon optimization (starting from the MP2/TZVP structure) is below 0.1 kJ/mol, so the error on the structure due to the frozen core optimization is negligible.

The transition structures (TS) are more different. With B3LYP an early transition structure was found; the C-H bond is only slightly elongated from 109 pm to 118 pm, while the O-H distance is 145 pm. The C-H-O bond is almost perpendicular to the Mg-O bond. With MP2 the carbon atom is much closer to the Mg atom (247 pm compared to 328 pm for B3LYP), the C-H and O-H bond lengths are almost equal (127 and 125 pm, respectively) and the O-H-C angle is more bent. The MP2 interaction energy for the encounter complex (96.4 kJ/mol) differs by less than 2 kJ/mol from the B3LYP result. This rather strong binding is due to the low coordination of the Mg atom.

The single point MP2 and CCSD(T) calculations with correlation consistent basis sets and extrapolation to the complete basis set (CBS) limit lower the energy of the TS by 7.7 and 8.9
kJ/mol at the MP2 and CCSD(T) levels, respectively, and that of the EC by 1.7 and 2.1 kJ/mol, respectively.

Figure 4.5. Encounter complex and transition structures for H abstraction from CH₄ by a) MgO⁺ and b) LiOMgO. Comparison of B3LYP and MP2 results. Bond distances are given in pm. Black – Mg, red – O, green – Li, yellow – C, gray – H, blue – spin density.

4.2.4.2. Li doped MgO

The transition structures obtained by both methods are very similar. The C-H and O-H distances are slightly longer and the Mg-O-H angle is larger for B3LYP results. Despite geometrical similarities of the two structures the difference in their relative energies is quite large though: 19.1 and 37.4 kJ/mol for B3LYP and MP2, respectively. In case of the encounter complex (EC) B3LYP and MP2 structures are more different, but the relative energies are almost the same. The MP2 gives a bent structure whereas B3LYP a linear one. The C-Li bond distances are similar, just a little longer at the MP2 level.
Going from TZVP to QZVP the relative energies for the encounter complexes are slightly higher (within 1 kJ/mol) whereas for the transition structures the values for QZVP basis set are smaller, for B3LYP only 0.5 kJ/mol, for MP2 and CCSD(T) around 5 kJ/mol. The complete basis set (CBS) estimation lowers the relative energies of both TS and EC.

The comparison between our B3LYP/TZVP values and CBS at MP2 and CCSD(T) levels shows that the relative energy for the EC almost does not change. For the TS however the different methods give different results: 19.1, 30.9 and 24.0 for B3LYP, MP2 and CCSD(T), respectively. This is in line with general trends; B3LYP often underestimates barriers, while MP2 usually gives too high barriers.\textsuperscript{[16]} The extrapolated CCSD(T) barrier, which is about 5 kJ/mol above the B3LYP result, is also expected.\textsuperscript{[17]}

### 4.2.4.3. All electron calculations

Because frozen core means for Mg\textsuperscript{2+} that none of its electrons is correlated we also performed all electron calculations employing the adequate cc-pCVXZ (X=T and Q) basis set family.\textsuperscript{[85]} Both MP2 and CCSD(T) consistently predict that core-polarization lowers the EC and TS energies by 3.6 to 4.5 kJ/mol (Table 4.6). Our best estimates for the EC and TS energies, -102 and -21 kJ/mol (all electron CCSD(T)/CBS//MP2/TZVP), are very close to the B3LYP results, -98 and -20 kJ/mol. The close agreement for the TS is somewhat surprising because the structures differ. One possible explanation is that wavefunction based methods include some dispersion interaction between C and Mg, stabilizing the TS. This interaction is missing with B3LYP, but this is compensated by the underestimation of the barrier by the DFT method.

<table>
<thead>
<tr>
<th>Method</th>
<th>EC (kJ/mol)</th>
<th>TS (kJ/mol)</th>
</tr>
</thead>
<tbody>
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<td>-10.1</td>
</tr>
<tr>
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</tr>
<tr>
<td>CCSD(T)/CBS//MP2/TZVP</td>
<td>-97.8</td>
<td>-17.4</td>
</tr>
<tr>
<td>all-CCSD(T)/CBS//MP2/TZVP</td>
<td>-101.8</td>
<td>-21.0</td>
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</table>

\textbf{Table 4.6.} Hydrogen abstraction from CH\textsubscript{4} by MgO\textsuperscript{+}. Relative energies (kJ/mol) with respect to the separated reactants for the encounter complex (EC) and the transition structure (TS) obtained by MP2 and CCSD(T) (all – all electron calculations).
4.2.5. Reactions with higher hydrocarbons

For MgO$^+$ and (MgO)$_2^+$ we also studied reactions with ethane and propane and compared the results with mass spectrometry experiment. The optimized transition structures together with the energy barriers are presented in Figure 4.6.

As has already been mentioned, the smallest possible MgO$^+$ cation activates methane. Larger hydrocarbons, like ethane and propane, react with the cluster as well with much more negative energy barriers. This is due to additional C-Mg interaction for ethane and propane which is not really possible for methane (though the transition structure for methane is already bent instead of being linear). For propane activation the calculations show lower barrier for H abstraction from secondary C atom by 6 kJ/mol compared to the activation of the primary C-

** This work has been published: Preferential activation of primary C-H bonds in the reactions of small alkanes with the diatomic MgO$^+$ cation, D. Schröder, J. Roithová, E. Alikhani, K. Kwapien, J. Sauer, Chem. Eur. J. 2010, 16, 4110.
H bond. The difference is reduced to 2 kJ/mol when the ZPVE are taken into account. The experiment shows however the preferential formation of $n$-$C_3H_7$ instead of $i$-$C_3H_7$. This is due to a pronounced dynamical effect on the course of the reactions, because all stationary points are well below the energy of the entrance channel. Accordingly, the differential accessibility of the hydrogen atoms is expected to be of much larger significance than such a small energy difference for the corresponding barriers.$^{[90,91]}$

For (MgO)$_2^+$ the apparent energy barriers of the reactions with methane and ethane are positive. The structures are also similar in both cases with almost linear C-H-O arrangement. For ethane activation the second carbon atom points away from the cluster which results in a large C-Mg distance (458 pm) and no stabilizing interaction. Concerning reaction with propane one would expect that hydrogen abstraction from the secondary C atom is favoured, because it leads to the more stable secondary propyl radical. However the corresponding transition structure is almost symmetric with two methyl groups pointing away from the (MgO)$_2^+$ (exactly like for ethane). For the H abstraction from the primary C atom the transition structure looks differently. In this case the C-H-O angle is slightly bent which allows simultaneous hydrogen abstraction from one end of the carbon chain and anchoring of the other end on the cluster. This strongly stabilizes the transition structure, it is three times more stable than the one for H abstraction from secondary C atom.

Gas phase experiments have shown that MgO$^+$ abstracts hydrogen from all considered hydrocarbons while (MgO)$_2^+$ only from propane. The agreement with our results is thus excellent. All the reactions for which our calculations predict negative apparent energy barriers were observed to take place in experiment and vice versa. Moreover, our B3LYP predictions for gas phase clusters with O$^-$ sites are in agreement with mass spectrometric experiments, lending credit to the DFT method used.

4.2.6. Comparison with Periodic Models

The calculated H abstraction energy barriers for the global minimum structures of (MgO)$_n^+$ and LiO(MgO)$_{n-1}$ clusters (which model the O$^-$ radical species) are smaller than 32 kJ/mol, while the observed one for solid catalysts is much higher (147 kJ/mol).$^{[92]}$

One could argue that the gas phase models used in this work are much too small and the shape of the clusters has not much in common with the MgO crystal lattice and thus they might not properly describe the reaction on the MgO surface. Therefore we also used a slab LiO(MgO)$_8$ cluster (with Li doping in different positions, labeled Li 1 and Li 2) as a model for a corner site of Li doped MgO surface. The cluster calculations were followed by periodic
electrostatic embedded calculations where the cluster model was embedded in periodic point charges. Finally the LiO(MgO)$_8$ was incorporated into a periodic slab model and periodic calculations were performed. The PBE transition structures for all the models are presented in Figure 4.7 (the computational details for the periodic calculations are given in chapter 4.3.2). The apparent energy barriers are listed in Table 4.7.

![Transition structures for H abstraction from CH$_4$ by Li$^+$/O$^-$ sites on the corner obtained by PBE calculations. The optimized B3LYP (cluster and embedded) transition structure are not shown due to similarity to PBE results. O-H and C-H bond distances are given in pm. Black – Mg, red – O, green – Li, yellow – C, gray – H, blue – spin density.](image)

**Figure 4.7.** Transition structures for H abstraction from CH$_4$ by Li$^+$/O$^-$ sites on the corner obtained by PBE calculations. The optimized B3LYP (cluster and embedded) transition structure are not shown due to similarity to PBE results. O-H and C-H bond distances are given in pm. Black – Mg, red – O, green – Li, yellow – C, gray – H, blue – spin density.

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$^a$ B3LYP

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$^a$ B3LYP

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<tr>
<td>C-H</td>
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</table>

For the Li 1 site the transition structures have a linear O-H-CH$_3$ arrangement. For the periodic models (both, embedded and a slab) CH$_4$ is lower due to the interaction of the methane C atom with Li site on the corner. The transition structures for Li 2 site change depending on the type of the applied model. For cluster and periodic slab model the linear structure is preserved. The embedded calculations for this site result in a transition structure with CH$_4$ tilted towards Li site on the edge. The analysis of O-H and C-H bond distances
together with spin density distribution (see Figure 4.7) indicates majority of the transition structures to be “early”. Only the PBE cluster and embedded results for Li 2 site show that the spin density is partially localized on C atom as well (and not exclusively on the O site on the corner). Additionally H atom is much further from the methyl group, compared to other models, which indicates that these transition structures are more “late”.

While the energy barriers for B3LYP cluster and embedded calculations are very similar for both sites (despite the different structures) they differ much more for PBE results. This is due to the spin density localization for the surface models, which for B3LYP is almost the same in both cases (localized on the O on the corner) whereas for PBE the Li 2 site is delocalized between two O sites on the corners and one on the terrace (see Figure 4.8). The delocalization of the spin density causes almost six times higher energy barrier for Li 2 compared to Li 1. The same situation is observed for PBE periodic calculations. Again, the delocalization of the spin density leads to higher energy barriers. The PBE embedded cluster model is the only one among the PBE results which shows the same spin density distribution for Li 2 site as B3LYP. This is due to the embedding which requires freezing of the border atoms. As a result the opening of the structure is blocked and the spin density localizes on one O site on the corner. The obtained energy barriers for both Li 1 and 2 sites are similar, as for B3LYP embedded models.

![Figure 4.8. Spin density distribution for cluster models of Li$$^+$$O$$^-$$ sites obtained by B3LYP and PBE calculations. Black – Mg, red – O, green – Li, blue – spin density.](image)

The analysis of PBE results (cluster and periodic) shows the same pattern for both sites, the energy barriers obtained by periodic calculations being higher. For B3LYP calculations going from the cluster calculations to embedded models the energy barriers increase by about 10 kJ/mol. For periodic models we were not able to apply B3LYP functional because the calculations of exact exchange (Fock exchange) is computationally very expensive with a plane wave basis set. Therefore the B3LYP barriers for periodic models were estimated using...
high-level correction.\textsuperscript{[93]} This means that no structure optimization was performed, just B3LYP and PBE single point calculation on the structure cut out from the optimized periodic PBE transition structure. The high-level correction was calculated as a difference between B3LYP and PBE cluster results and added to the energy barrier obtained by periodic PBE calculations. Therefore the trends in B3LYP energy barriers (going from cluster to periodic model) are similar to those obtained by PBE. The inclusion of dispersion correction usually lowers the calculated barriers.

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<tr>
<td></td>
<td>periodic\textsuperscript{b}/PBE</td>
<td>+21.8</td>
<td></td>
<td>+42.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Grimme dispersion correction but with Ne parameters for Mg\textsuperscript{2+}.\textsuperscript{[93]}  
\textsuperscript{b} estimated using high-level correction.\textsuperscript{[93]}

Thus, even the application of periodic models shows that the calculated barriers for Li\textsuperscript{+}O\textsuperscript{−} sites are still much too low, compared to the experimental value. However we considered here only the three-coordinated O site on the corner, which probably is more reactive than e.g. five-coordinated O site on the terrace. For the terrace we have only B3LYP results (cluster and periodic embedded calculations). Using PBE we did not succeed to find transition structure for this site independently of the applied model. The results for the terrace site are presented in Figure 4.9.

The energy barrier going from the corner to the terrace site increases to 61 kJ/mol for the cluster model and to 41 kJ/mol for the embedded cluster model. Usually when atoms are frozen (like the border atoms in the embedded cluster model) the energy barriers are higher because the relaxation of the surface is limited. In this case, however, the spin density distribution plays an important role. For the non-embedded cluster model the spin density is delocalized over three oxygen sites, while for the embedded cluster model it mostly localizes on one oxygen site (right above Li site). The same type of active site for the solid MgO catalyst was also studied by Catlow \textit{et al.} and an apparent energy barrier of 74 kJ/mol was
found. This apparent energy barrier is interpreted as the first approximation to the activation energy, because no transition structure optimization was applied. Instead a scan over the potential energy surface was performed for different fixed distances between methane C atom and the O⁻ site on the surface. Moreover, a different exchange-correlation functional was used in these studies (B97-1). This functional includes almost the same amount of Fock exchange (21%) as B3LYP, therefore our embedded calculations show the same spin density distribution as the one obtained by B97-1. Additionally, test calculations for B97-1 show a decrease in accuracy for hydrogen abstraction reaction barriers. Thus, the comparison with our results can be only qualitative, and the value obtained by Catlow et al. (which is still half the experimental value) can be assumed as an upper limit for the energy barrier for H abstraction from methane by Li⁺O⁻ sites.

![Diagram showing surface models and transition structures for the Li⁺O⁻ terrace site, a) cluster calculations, b) periodic embedded model, c) from ref. [94]. Black – Mg, red – O, green – Li, yellow – C, gray – H, blue – spin density.](image)

**Figure 4.9.** Surface models and transition structures for the Li⁺O⁻ terrace site, a) cluster calculations, b) periodic embedded model, c) from ref. [94]. Black – Mg, red – O, green – Li, yellow – C, gray – H, blue – spin density.

### 4.2.7. Summary and Conclusions

The results presented here show that all the calculated barriers for H abstraction by O⁻ radicals differ much from the experimental value. This indicates that the Li⁺O⁻ species are too reactive and are not responsible for the rate-determining step in OCM.

In addition, recent studies could not find evidence for Li⁺O⁻ species under OCM relevant conditions. It was also shown that Li is not necessary for C-H activation, the reaction can be also performed on pure MgO without any Li doping. Addition of Li, however, enhances
the OCM activity most likely by restructuring the material accompanied by creating more defects such as edges, corners and kinks.\cite{98} The presence of low coordinated $O^{2-}$ ions was confirmed by diffuse reflectance UV/Vis spectroscopy.\cite{97} Our calculations, together with experimental results show that the current hypothesis about $Li^+O^-$ sites being responsible for OCM activity of Li doped MgO needs to be revised.

According to the OCM experiment\cite{99} the $C_2$ production starts at the same temperature for MgO and Li/MgO indicating the same active sites in both cases (this rules out the Li$^+O^-$ sites, because they are not present in MgO). Since addition of Li creates more low-coordinated $O^{2-}$ sites, one should take a closer look on the morphological defects. Therefore, in addition to models of $O^-$ radical sites, also different types of defect sites on MgO were considered and their reactivity towards methane was studied.

### 4.3. Cluster Calculations on Defective MgO

From chapter 4.2. we know that the $O^-$ radical sites are too reactive to be responsible for the OCM rate-determining step (which is H abstraction from methane). Moreover we know that addition of Li enhances the activity of MgO catalysts however not because of formation of $O^-$ sites but due to restructuring of the MgO surface and formation of additional low-coordinated $O^{2-}$ sites such as corners, edges, steps and kinks.\cite{98} Therefore one should concentrate first of all on morphological defects of MgO when looking for an active site in OCM. Accordingly, we began our investigation with a corner site.

#### 4.3.1. Model Systems

We concentrated on the low coordinated $O^{2-}$ site on the corner. For that a $(MgO)_9$ cluster model was applied. In addition, we studied also intrinsic (e.g. $O$ vacancies) and impurity defects in MgO. All the models are presented in Figure 4.10.

The $F^0$ center, a neutral $O$ defect, has two electrons trapped in the $O$ vacancy. They can be spin paired (singlet state) or unpaired (triplet state). The singlet spin state has a $62\,kJ/mol$ lower energy. Additionally, experimental studies\cite{100} show no EPR signal which indicates that the singlet state is the ground state for the $F^0$ center. Nevertheless, the triplet spin state was considered as well because a crossover between these two spin states may be possible during the reaction.
The $F^+$ center (O vacancy with one unpaired electron) is represented by three models. The first one is a singly charged $F^+$ center and the two latter are neutral. The formation of such centers is possible by substitution of one divalent Mg ion by one monovalent Li ion close to the $F^0$ center:

\[
\begin{align*}
\text{Mg}^{2+}F^0 & \xrightarrow{\text{Li/Mg}} \text{Li}^+F^+ \\
\text{Mg}^{2+}2e^- & \xrightarrow{\text{Li/Mg}} \text{Li}^+e^-
\end{align*}
\]

Due to different positions of Li atom two models were obtained (labeled Li-$F^0$ 1 and 2). Such centers are likely to be present in Li/MgO since it has been shown that Li ions migrate to the surface $F^0$ centers and interact with electrons trapped in the O vacancies.\cite{96,98}

There are also bare O vacancies in MgO (O vacancies without trapped electrons) called $F^{2+}$ centers. And again we considered two types of $F^{2+}$ centers, a doubly charged one (labeled $F^{2+}$) and neutral ones containing two Li atoms close to the O vacancy (Li$_2$-$F^0$ 1 and 2). We also tried a model with two Li atoms in a top layer of a cluster but this structure was not stable and the slab opened during optimization.

Considering instead of charged $F^+$ and $F^{2+}$ centers the Li doped neutral ones (e.g. Li-$F^0$ instead of $F^+$) is very convenient from the computational point of view, because one does not have to deal with background charges when doing periodic calculations.

\textbf{Figure 4.10.} Model systems for defective MgO (cluster calculations). Black – Mg, red – O, green – Li, blue – spin density, light blue – HOMO orbital.
In order to be able to make a comparison to O$^-$ sites (without considering the cluster shape and size) a LiO(MgO)$_8$ cluster model (with Li doping in two different position, labeled Li 1 and Li 2) was applied as well.

4.3.2. Methods

The calculations performed for defective MgO using the cluster model were done in the same way as for small O$^-$ radicals (cationic MgO and Li doped MgO clusters, chapter 4.2). For the models of defective MgO, besides B3LYP we applied also the GGA type PBE functional\cite{13} to be able to compare our cluster model results to the periodic ones (in chapter 4.3.2).

4.3.3. B3LYP Results

4.3.3.1. Defect formation energy

The extraction of an O atom or ion from a perfect MgO surface involves a high energy cost and has been a subject of several theoretical investigations\cite{101,102,103,104,105,106,107,108} The defect formation energy is defined as the energy required to remove an atom (or ion) from the surface and place it in the infinite distance from it. This value should be always calculated with respect to some reference, which usually is a single O atom (or ion). For us, it makes more sense to calculate formation energies with respect to the energy of $\frac{1}{2}$ O$_2$ molecule, since there are O$_2$ molecules present in the gas phase and only very few O atoms. Therefore our defect formation energies are defined as:

\[
(MgO)_9 \rightarrow Mg(MgO)_8 + \frac{1}{2} O_2 \quad (4.9)
\]

\[
(MgO)_9 \rightarrow [Mg(MgO)_8]^+ + \frac{1}{2} O_2 + e^- \quad (4.10)
\]

\[
(MgO)_9 \rightarrow [Mg(MgO)_8]^{2+} + \frac{1}{2} O_2 + 2e^- \quad (4.11)
\]

for F$^0$, F$^+$ and F$^{2+}$ centers, respectively.

The results presented in Table 4.8 show that the formation of a neutral F$^0$ center has the smallest defect formation energy. This is reasonable since the presence of the two extra electrons in the vacancy gives rise to a strong Madelung stabilization. For the triplet spin state the value is higher by 0.64 eV compared to the singlet spin state. The removal of one electron from the neutral F$^0$ center and formation of a singly charged F$^+$ center costs 4.3 eV. Going further, from F$^+$ center to doubly charged F$^{2+}$ center, an energy more than twice as large is needed. Thus, the order of stability of the F centers in MgO is F$^0$ singlet $>$ F$^0$ triplet $>$ F$^+$ $>$ F$^{2+}$. The same stability order was reported for surface F centers on a terrace and edge\cite{102} and
for bulk F centers. This trend can be explained by electronic structure and the nature of oxygen vacancies in ionic materials like MgO, where the removal of an O atom (or ion) does not result in a formation of new bonds. Instead the cavities are formed which may be filled by electrons trapped by the strong electrostatic potential of the ionic crystal. Therefore neutral vacancies (F\(^0\) centers) are more stable due to the large stabilization arising from the Madelung energy which is gained by the presence of electronic charge in the vacancy. The low stability of F\(^2\+) centers is consistent with the experiment which does not report this kind of species in bulk MgO, since even if they are formed they are extremely short lived.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Defect formation energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(^0) singlet</td>
<td>+4.86</td>
</tr>
<tr>
<td>F(^0) triplet</td>
<td>+5.50</td>
</tr>
<tr>
<td>F(^+)</td>
<td>+9.80</td>
</tr>
<tr>
<td>Li^{-}F(^0) 1</td>
<td>+2.41</td>
</tr>
<tr>
<td>Li^{-}F(^0) 2</td>
<td>+2.26</td>
</tr>
<tr>
<td>F(^2+)</td>
<td>+18.38</td>
</tr>
</tbody>
</table>

According to Pacchioni et al.\(^{[102]}\) the defect formation energy increases with the coordination number of a given site, i.e. it is smaller for the edge site than for the terrace site, because low-coordinated ion is less strongly bound to the rest of the crystal. This is consistent with our calculations for the corner site, for which the defect formation energies are smaller than the reported values for terraces and edges.

Since we also studied Li doped MgO sites, we can calculate defect formation energies of the neutral F\(^+\) centers (Li^{-}F\(^0\) 1 and 2) according to the reaction:

\[
\text{LiO(MgO)}_8 \rightarrow \text{Li(MgO)}_8 + \frac{1}{2} \text{O}_2. \quad (4.12)
\]

These values are about four times smaller than for charged F\(^+\) center which indicates that when Li is present in MgO (close to the O vacancy) the formation of the F\(^+\) centers is much easier. The defect formation energies for neutral F\(^2\+) centers (Li\(_2\)-F\(^0\) 1 and 2) are not reported here because the optimization of the cluster model with two Li atoms, (LiO\(_2\))(MgO)\(_7\), destroyed the slab model and led to the tube structure.

### 4.3.3.2. Energy profiles

Energy profiles for all the model systems are presented in Figure 4.11. The relative energies (with respect to separated reactants) of the stationary points along the reaction pathway are listed in Table 4.9. Both, electronic total energies and the energies at 0 K, including zero point vibrational energies (ZPVE), are given.
c) F° centers (singlet – green, triplet – blue)

Mg(MgO)_8 + CH_4

0.0

RE

EC

+61.9

+58.3

TS

+137.1

INT

+152.8

PR

+173.1

Mg(MgO)_8H + CH_3

0.0

RE

EC

-3.8

INT

-25.2

d) F° center

[Mg(MgO)_8]^+ + CH_4

0.0

RE

EC

-19.2

TS

+129.1

INT

+87.0

PR

+126.6
e) Li-F° 1

Li(MgO)₈ + CH₄
0.0
RE
EC

TS
+122.1

[Li(MgO)₈H] + CH₃
+122.7
PR

INT
+103.7

f) Li-F° 2

Li(MgO)₈ + CH₄
0.0
RE
EC

TS
+132.6

[Li(MgO)₈H] + CH₃
+133.9
PR

INT
+113.5
g) $\text{F}^{2+}$ center

\[ \text{Mg} \left( \text{MgO} \right)_6 + \text{CH}_4 \]

\[ \text{TS} \]

\[ +295.6 \]

\[ \text{PR} \]

\[ +319.3 \]

\[ \text{INT} \]

\[ -76.5 \]

h) $\text{Li}_2\text{F}^0$

\[ \text{Li}_2\text{Mg}_7\text{O}_8 + \text{CH}_4 \]

\[ \text{TS} \]

\[ +402.4 \]

\[ \text{PR} \]

\[ +358.1 \]

\[ \text{INT} \]

\[ -17.4 \]
In general the reaction proceeds in a similar way for all the defective sites. In a first step the CH$_4$ molecule is adsorbed on a cluster (encounter complex). In the transition structure the methane C-H bond splits and the intermediate is formed. After dissociation of the CH$_3$ group the final products are obtained.

Contrary to O$^-$ sites, the methane activation on defective MgO is endoenergetic. The second striking difference between these two types of sites is the desorption energy of CH$_3$ (Table 4.9). This is closely related to the different splitting of the methane C-H bond caused by different types of sites. As already discussed (in chapter 4.2) O$^-$ sites abstract H from methane and form methyl radicals. In this respect the F$^+$ centers (F$^+$, Li-F$^0$ 1 and 2) are similar to O$^-$ radicals. The similar behavior of these two types of sites can be explained by the same electronic spin state. Both, O$^-$ radicals and F$^+$ centers have one unpaired electron which is able to abstract hydrogen from methane. Since F$^0$ center in a triplet spin state has two unpaired electrons, it splits the H-CH$_3$ bond homolytically as well. The CH$_3$ desorption for all these sites (O$^-$ sites, F$^+$ centers and F$^0$ triplet) is about 20 kJ/mol.
Table 4.9. Relative energies (in kJ/mol) with respect to the separated reactants for the encounter complexes (EC), transition structures (TS), intermediates (IN), and products (PR) obtained by B3LYP. Values in parentheses include ZPVE contributions.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Spin multiplicity</th>
<th>EC</th>
<th>TS</th>
<th>IN</th>
<th>PR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li 1</td>
<td>2</td>
<td>-4.5 (-1.5)</td>
<td>18.9 (9.1)</td>
<td>-63.2 (-65.9)</td>
<td>-46.1 (-54.1)</td>
</tr>
<tr>
<td>Li 2a</td>
<td>2</td>
<td>-</td>
<td>21.7 (10.5)</td>
<td>-59.8 (-64.4)</td>
<td>-44.4 (-53.0)</td>
</tr>
<tr>
<td>O2^-</td>
<td>1</td>
<td>-5.1 (-1.8)</td>
<td>86.4 (76.1)</td>
<td>33.0 (32.2)</td>
<td>228.2 (215.3)</td>
</tr>
<tr>
<td>F0 singlet</td>
<td>1</td>
<td>-3.8 (-1.2)</td>
<td>137.1 (122.9)</td>
<td>-25.2 (-34.7)</td>
<td>173.1 (151.7)</td>
</tr>
<tr>
<td>F0 triplet</td>
<td>3</td>
<td>-3.6 (-1.2)</td>
<td>109.4 (93.3)</td>
<td>90.9 (74.3)</td>
<td>111.2 (89.4)</td>
</tr>
<tr>
<td>F+</td>
<td>2</td>
<td>-19.2 (-15.5)</td>
<td>129.1 (112.8)</td>
<td>87.0 (72.0)</td>
<td>126.6 (105.4)</td>
</tr>
<tr>
<td>Li-F0 1</td>
<td>2</td>
<td>-4.0 (-1.4)</td>
<td>122.1 (105.1)</td>
<td>103.7 (86.6)</td>
<td>122.7 (100.9)</td>
</tr>
<tr>
<td>Li-F0 2</td>
<td>2</td>
<td>-9.7 (-6.5)</td>
<td>132.6 (116.6)</td>
<td>113.5 (96.8)</td>
<td>133.9 (112.4)</td>
</tr>
<tr>
<td>F2^+</td>
<td>1</td>
<td>-42.2 (-38.8)</td>
<td>295.6 (286.8)</td>
<td>-76.5 (-73.2)</td>
<td>319.3 (295.0)</td>
</tr>
<tr>
<td>Li2-F0 1</td>
<td>1</td>
<td>-4.8 (-2.2)</td>
<td>402.4 (387.1)</td>
<td>-17.4 (-19.1)</td>
<td>358.1 (330.9)</td>
</tr>
<tr>
<td>Li2-F0 2</td>
<td>1</td>
<td>-15.3 (-12.2)</td>
<td>327.2 (318.4)</td>
<td>48.5 (44.9)</td>
<td>358.3 (330.7)</td>
</tr>
</tbody>
</table>

* for this site an EC was not found, the optimization always destroyed the slab model and led to a tube structure.

The rest of the defective sites are close shell systems. Among them O2^- site and F0 center in a singlet spin state cause heterolytic splitting of the C-H bond and formation of a Grignard type Mg-alkyl complex. This is the reason why the CH3 desorption energies for O2^- site and F0 singlet are so high (about 10 times larger than for O•– sites).

The last class of defects, F2^+ centers (F2^+, Li2-F0 1 and 2), have no trapped electrons in a vacancy (therefore they are called bare vacancies) which can abstract H from methane. There is also no O atom, so proton abstraction is not possible as well. The only way of H-CH3 splitting left is another type of heterolytic splitting into H^- and CH3^+. This type of C-H splitting leads to formation of a methoxy group. As a result the CH3 desorption energies for F2^+ centers are almost twice as large as for O2^- site and F0 singlet (because the O-C(H3) bond needs to be broken).

4.3.3.3. Structures

Only for F0 and Li-F0 1 centers the adsorbat complex has an O-H-CH3 configuration. This is due to the repulsive interaction between the methane molecule and electrons trapped in the vacancy. In the other encounter complexes CH4 is usually adsorbed on the Mg site on the edge close to the O site or vacancy on the corner. Though the Li-F0 1 and 2 models are
similar, the doping of Li in different positions causes different localization of the trapped electron and therefore the encounter complex structures differ.

In the intermediates the methyl group is localized on the Mg site nearby the vacancy, except for F²⁺ centers where a methoxy group on the other O corner is formed.

The transition structures for defective MgO sites differ from those for Li doped MgO. Instead of a linear O-H-CH₃ arrangement (as for O⁻ radicals) the C-H bond activation is taking place rather on the edge of the cluster. This indicates the important role of a stabilizing Mg-C interaction during the whole reaction (see encounter complex and intermediate structures in Figure 4.11). The F²⁺ centers behave differently, in this case the CH₃ group interacts with O site on the other corner and H is abstracted by Mg site. For this type of site it is also possible that both CH₃ and H are attached to Li site (but not Mg), however this type of transition structure is 100 kJ/mol higher in energy.

The transition structures are very similar to the intermediate structures. The C-H bond is already broken and the methyl group is close to a Mg or O site. It is difficult to discuss the O-H distances because for all the F centers there is no O-H bond formed. The comparison can be done only for Li doped models and O²⁻ site and shows that the O-H distance is shorter for O²⁻ site. However the C-H distances can be discussed for all the considered sites and they simply increase going from Li doped models, through O²⁻ site, F⁰ and F⁺ centers to F²⁺ centers (Table 4.10). The only exception is the Li₂-F⁰ 2 site where the C-H distance is similar as for F⁺ centers. Thus, all the transition structures for defective MgO can be described as “late” (they resemble more closely the product structures) which is in contrast to O⁻ radicals where the transition structures were “early”.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Distances [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-H</td>
</tr>
<tr>
<td>Li 1</td>
<td>132.7</td>
</tr>
<tr>
<td>Li 2</td>
<td>129.8</td>
</tr>
<tr>
<td>O²⁻</td>
<td>123.0</td>
</tr>
<tr>
<td>F⁰ singlet</td>
<td>-</td>
</tr>
<tr>
<td>F⁰ triplet</td>
<td>-</td>
</tr>
<tr>
<td>F⁺</td>
<td>-</td>
</tr>
<tr>
<td>Li-F⁰ 1</td>
<td>-</td>
</tr>
<tr>
<td>Li-F⁰ 2</td>
<td>-</td>
</tr>
<tr>
<td>F²⁺</td>
<td>-</td>
</tr>
<tr>
<td>Li₂-F⁰ 1</td>
<td>-</td>
</tr>
<tr>
<td>Li₂-F⁰ 2</td>
<td>-</td>
</tr>
</tbody>
</table>
4.3.3.4. Energy barriers

The apparent energy barriers for all the corner models are listed in Table 4.9. The O\textsuperscript{2-} site is characterized by the lowest energy barrier (+86 kJ/mol) among the defective MgO sites. For the F\textsuperscript{0} center the barrier increases to +137 kJ/mol for a singlet spin state. The triplet spin state has a lower barrier, however the initial state is 62 kJ/mol higher in energy so the overall reaction barrier is anyway more positive (+171 kJ/mol). All the centers with one unpaired electron (F\textsuperscript{+}, Li-F\textsuperscript{0} 1 and 2) have barriers around 130 kJ/mol. Going further to O defects without electrons (F\textsuperscript{2+}, Li\textsubscript{2}-F\textsuperscript{0} 1 and 2), the barriers are even higher, around +300 kJ/mol when the methyl group weakly interacts with the O site on the opposite corner and around +400 kJ/mol when CH\textsubscript{3} is attached to the Li site. This type of transition structure is only possible when the Li\textsuperscript{+} ion is nearby, because when Mg\textsuperscript{2+} ion is present there instead, the methyl group moves further to the O site and does not bind to the Mg site (this is due to the larger charge on Mg\textsuperscript{2+} than on Li\textsuperscript{+}).

4.3.3.5. Splitting of the C-H bond

The height of a barrier is correlated with the type of H-CH\textsubscript{3} bond splitting, – see differential electron density and spin density in Figure 4.12. For the heterolytic splitting (O\textsuperscript{2-} site) the barrier is rather low. For F\textsuperscript{+} and Li-F\textsuperscript{0} centers which cause homolytic splitting of the C-H bond the barrier is around 130 kJ/mol (which is close to the experimental value, 147 kJ/mol).\textsuperscript{[92]} The F\textsuperscript{0} triplet also splits the H-CH\textsubscript{3} bond homolytically with a lower barrier, but it is not the ground state for the F\textsuperscript{0} center. The F\textsuperscript{0} singlet site is interesting because the differential electron density in the transition structure is somewhere between heterolytic and homolytic dissociation. The H atom is located in between regions of positive (dark blue) and negative (light blue) values of the differencial electron density, see Figure 4.12.a. This can be also seen in the charge values from natural population analysis\textsuperscript{[110]} (Table 4.11). The changes (going from encounter complex, through transition structure to intermediate structure) in the charge value on C for the F\textsuperscript{0} singlet are similar as for the O\textsuperscript{2-} site, whereas the H atom behaves like H for F\textsuperscript{0} triplet spin state (the charge value decreases). However one should also take a look at the charge value on Mg on the corner. For F\textsuperscript{0} triplet the charge does not change, one electron is localized on the Mg on the corner in all three stationary points. This means that actually only one electron is taking part in the reaction, exactly like for F\textsuperscript{+} centers, where the trapped electron couples with H\textsuperscript{-} radical forming H\textsuperscript{-}. For the F\textsuperscript{0} singlet Mg on the corner does not share the trapped electrons in intermediate structure, but gives them to the H\textsuperscript{-}, increasing the negative charge on hydrogen and forming a hydride (H\textsuperscript{-}). Thus, the F\textsuperscript{0} singlet causes
heterolytic splitting of H-CH₃. The F²⁺ centers have the highest barriers among all the considered sites and split C-H bond heterolytically but this time hydride (H⁻) and CH₃⁺ group are formed.

Figure 4.12.a. Transition structures for methane activation by O²⁻ site and F⁰ centers in MgO. Differential electron density (calculated as a difference between electron density for transition structure and a sum of electron densities for reactants in geometry of transition structure), HOMO orbitals and spin density are shown. Some bond distances are given in pm.

The analysis of all the different sites in MgO shows that methane is a very flexible molecule and can dissociate in different ways depending on the local environment. For alkaline MgO (without vacancies) H-CH₃ splits heterolytically on the Mg²⁺O²⁻ pair forming a OH⁻ group and a Grignard type Mg-alkyl complex. This type of splitting was confirmed by NMR experiment and calculations for C₂H₂ on MgO clusters¹¹¹ and also was seen for methane activation on alumina.¹¹² When an F⁰ center is formed two electrons are trapped in the vacancy. These electrons interact with a proton of methane and form H⁻. Excitation of one
electron from HOMO to LUMO orbital and formation of a triplet spin state for the $F^0$ center allows for homolytic splitting of H-CH$_3$. For the $F^+$ center one unpaired electron localized in the vacancy abstracts H from methane and a methyl radical is formed. The $F^{2+}$ centers (bare O vacancies) without trapped electrons which can abstract hydrogen or proton from methane, cause another type of heterolytic splitting into H$^-$ and CH$_3^+$ (this type of C-H splitting was also found for 2Zn/HZSM-5 zeolite\textsuperscript{[113]}). Thus, the MgO surface though usually alkaline, can locally have other type of environment (caused by defects and doping) and react in different ways with the same molecule.

Figure 4.12.b. Transition structures for methane activation by $F^+$ centers in MgO. Differential electron density (calculated as a difference between electron density for transition structure and a sum of electron densities for reactants in geometry of transition structure) and spin density are shown. Some bond distances are given in pm.
Table 4.11. Charge values from natural population analysis for methane C atom, abstracted H and corner site of the cluster in different stationary points (encounter complexes, transition structures and intermediates).

<table>
<thead>
<tr>
<th>Site type</th>
<th>Atom</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>EC</td>
</tr>
<tr>
<td>(\text{O}^{2-})</td>
<td>C</td>
<td>-0.87</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.22</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-1.76</td>
</tr>
<tr>
<td>(F^0) singlet</td>
<td>C</td>
<td>-0.84</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.20</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>+0.93</td>
</tr>
<tr>
<td>(F^0) triplet</td>
<td>C</td>
<td>-0.84</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.20</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>+0.93</td>
</tr>
<tr>
<td>(F^+)</td>
<td>C</td>
<td>-0.90</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.17</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>+1.16</td>
</tr>
<tr>
<td>(\text{Li}-F^0) 1</td>
<td>C</td>
<td>-0.85</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.20</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>+0.87</td>
</tr>
<tr>
<td>(\text{Li}-F^0) 2</td>
<td>C</td>
<td>-0.92</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.21</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>+0.98</td>
</tr>
<tr>
<td>(F^{2+})</td>
<td>C</td>
<td>-0.96</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.31</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>+1.82</td>
</tr>
<tr>
<td>(\text{Li}_2-F^0) 1</td>
<td>C</td>
<td>-0.85</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.18</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>+0.94</td>
</tr>
<tr>
<td>(\text{Li}_2-F^0) 2</td>
<td>C</td>
<td>-0.93</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.21</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>+0.94</td>
</tr>
</tbody>
</table>
4.3.3.6. H attachment energy

The H attachment energy can be again considered here, for defective MgO sites, and compared to O$^{-}$ radical sites. When we add points for LiO(MgO)$_{8}$ models to the plot with small cationic MgO and Li doped clusters there will be no change of trend (Figure 4.13.a). After inclusion of data for defective corner sites, their energy barriers are usually above the line, except for O$^{2-}$ site (Figure 4.13.b). However when considering all the points together (Figure 4.13.c) there is a linear correlation for all the sites that split H-CH$_{3}$ bond homolytically (O$^{-}$ sites, F$^{0}$ triplet and all F$^{+}$ centers). The O$^{2-}$ site is beneath the line since it splits the C-H bond heterolytically into H$^{+}$ and CH$_{3}^{-}$. The F$^{0}$ singlet is between O$^{2-}$ and F$^{+}$ centers due to its intermediate character, since it splits H-CH$_{3}$ heterolytically (like O$^{2-}$ site).
but at the end it forms $H^-$ (like $F^+$ centers). Above the line there are $F^{2+}$ centers which cause heterolytic splitting of $H-C(H_3)$ into $H^-$ and $CH_3^+$. This indicates that the simple H attachment reaction can be used not only to estimate the barrier height but also to distinguish between different types of interaction of $CH_4$ molecule with defective MgO sites.

(a) O$^-$ radical sites

![Graph of O$^-$ radical sites](image1)

(b) O$^-$ radicals with defective sites

![Graph of O$^-$ radicals with defective sites](image2)
Figure 4.13. Apparent energy barriers as a function of the H attachment energy for methane activation by a) O$^-$ radicals (cationic MgO and Li doped MgO clusters), b) O$^-$ radicals with defective sites, c) all together.

4.3.3.7. **Mechanism based on heterolytic splitting of the H-C(H₃) bond**

The transition structures for the interaction of CH₄ with O²⁻ and F⁰ singlet sites represent a chemisorbed complex instead of H abstraction (a redox step). The H-C(H₃) bond splits heterolytically on the Mg²⁺O²⁻ pair forming OH⁻ and a Grignard type Mg-alkyl complex. To complete the redox reaction the CH₃ group has to desorb from the MgO cluster. However, as has already been mentioned the CH₃ desorption costs about 200 kJ/mol for O²⁻ and F⁰ singlet sites.

Another way to take out the methyl group from the catalyst surface would be oxidation with O₂. This idea is supported by experiments because the C₂ production stops when O₂ is not provided.[⁹⁹] Thus, when the intermediate structure reacts with molecular oxygen, the (CH₃)$^-$ species can be substituted by the (O₂)$^-$ (superoxo) species (mechanism A, see Figure 4.14), according to the reaction:

\[
(CH₃)^-(\text{Cluster})H^+ + O₂ \rightarrow (O₂)^+(\text{Cluster})H^+ + 'CH₃ .
\] (4.13)
The energy for this reaction step is +4 and +6 kJ/mol for the O$_{2-}$ and F$^0$ singlet sites, respectively, which is a substantial improvement compared to CH$_3$ desorption.

**Figure 4.14.** Mechanism A. Black – Mg, red – O, yellow – C, gray – H, blue – spin density.
However, one has to remember that OCM is a catalytic reaction, which means that the catalyst after reaction has to come back to its initial state. The easiest way to do that and to close the catalytic cycle would be the coupling of the \((O_2^-)\) superoxo species with the proton yielding the \(\text{HOO}^\cdot\) radical, which can react further in the gas phase. Unfortunately, this reaction step costs even more than 200 kJ/mol (+206 and +262 kJ/mol for \(O^2^-\) and \(F^0\) singlet, respectively) making this reaction pathway unlikely. Moreover, after summing up all the reactions for this mechanism the cycle is not closed (Table 4.12).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\text{O}^2^-)</th>
<th>(F^0) singlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cluster} + \text{CH}_4 \rightarrow \text{CH}_4 \cdots \text{Cluster} )</td>
<td>-5.1</td>
<td>-3.8</td>
</tr>
<tr>
<td>(\text{CH}_4 \cdots \text{Cluster} \rightarrow (\text{CH}_3)^- (\text{Cluster})\text{H}^+)</td>
<td>+38.1</td>
<td>-21.4</td>
</tr>
<tr>
<td>((\text{CH}_3)^- (\text{Cluster})\text{H}^+ + \text{O}_2 \rightarrow (\text{O}_2^-) (\text{Cluster})\text{H}^+ + \cdot\text{CH}_3)</td>
<td>+4.2</td>
<td>+6.1</td>
</tr>
<tr>
<td>((\text{O}_2^-) (\text{Cluster})\text{H}^+ \rightarrow \text{Cluster} + \text{HOO}^\cdot)</td>
<td>+206.1</td>
<td>+262.4</td>
</tr>
<tr>
<td>(\text{HOO}^\cdot + \text{CH}_4 \rightarrow \cdot\text{CH}_3 + \text{H}_2\text{O}_2)</td>
<td></td>
<td>+96.1</td>
</tr>
<tr>
<td>(\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_6)</td>
<td></td>
<td>-382.8</td>
</tr>
<tr>
<td>(2 \text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}_2)</td>
<td></td>
<td>-43.4</td>
</tr>
</tbody>
</table>

*Cluster = \((\text{MgO})_9\) for the \(\text{O}^2^-\) site and \((\text{MgO})_8\text{Mg}\) for the \(F^0\) center

Another option would be inserting oxygen instead of replacing \((\text{CH}_3)^-\) by \((O_2)^-\) (mechanism B, see Figure 4.15), according to the reaction:

\[
(\text{CH}_3)^- (\text{Cluster})\text{H}^+ + \frac{1}{2} \text{O}_2 \rightarrow (\text{CH}_3)^- (\text{Cluster})\text{OH}^+. \tag{4.14}
\]

This step is strongly exoenergetic for the \(F^0\) center (-411 kJ/mol), whereas for \(O^2^-\) site it costs +118 kJ/mol, which is more than the calculated barrier for the \(\text{CH}_4\) heterolytic dissociation. For \(F^0\) center oxygen binds into vacancy forming the intermediate \((\text{CH}_3)^- (\text{MgO})_8\text{H}^+\) structure, exactly like the \((\text{CH}_3)^- (\text{Cluster})\text{H}^+\) structure for \(O^2^-\) site (see Figure 4.15). The \(O^2^-\) site has no vacancy therefore the insertion of oxygen results in formation of peroxo unit. Going further the next step would involve a second heterolytic H-C(H) bond splitting,

\[
(\text{CH}_3)^- (\text{Cluster})\text{OH}^+ + \text{CH}_4 \rightarrow \text{CH}_3(\text{CH}_3)(\text{Cluster})\text{OH}_2 \tag{4.15}
\]

which is about +200 kJ/mol for the \(F^0\) center, but still below the energy for the entrance channel. For \(O^2^-\) this step is exoenergetic. The resulting structures for both sites differ again.
Figure 4.15. Mechanism B. Black – Mg, red – O, yellow – C, gray – H.
While for $F^0$ center the structure represents a molecular adsorption of $C_2H_6$ and $H_2O$ on the cluster, for $O^2-$ site water molecule is adsorbed in dissociated form (see Figure 4.15). To close the catalytic cycle $C_2H_6$ and $H_2O$ need to desorb. The desorption of these two molecules costs $+157$ and $+89 \text{ kJ/mol}$ for $O^2-$ and $F^0$ site, respectively. The water desorption is more expensive than the desorption of ethane, independently of the fact which molecule will desorb first (see Table 4.13, the numbers in parentheses show the reverse desorption).

**Table 4.13. Reaction energies (in kJ/mol) for mechanism B (shown in Figure 4.15).**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>O$^2-$</th>
<th>F$^0$ singlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cluster + CH$_4$ → CH$_4$···Cluster</td>
<td>-5.1</td>
<td>-3.8</td>
</tr>
<tr>
<td>CH$_4$···Cluster → (CH$_3$)$^+$ (Cluster)H$^+$</td>
<td>+38.1</td>
<td>-21.4</td>
</tr>
<tr>
<td>(CH$_3$)$^+$ (Cluster)H$^+$ + $\frac{1}{2}$ O$_2$ → (CH$_3$)$^+$ (Cluster)OH$^+$</td>
<td>+118.0</td>
<td>-410.8</td>
</tr>
<tr>
<td>(CH$_3$)$^+$ (Cluster)OH$^+$ + CH$_4$ → (CH$_3$CH$_3$)(Cluster)OH$_2$</td>
<td>-457.0</td>
<td>+198.0</td>
</tr>
<tr>
<td>(CH$_3$CH$_3$)(Cluster)OH$_2$ → (CH$_3$CH$_3$)(Cluster) + H$_2$O</td>
<td>+152.3 (+1.8)</td>
<td>+91.9 (+3.8)</td>
</tr>
<tr>
<td>(CH$_3$CH$_3$)(Cluster) → C$_2$H$_6$ + Cluster</td>
<td>+4.8 (+155.3)</td>
<td>-3.0 (+85.1)</td>
</tr>
<tr>
<td>2 CH$_4$ + $\frac{1}{2}$ O$_2$ → C$_2$H$_6$ + H$_2$O</td>
<td>-148.9</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Cluster = (MgO)$_n$ for the O$^2-$ site and (MgO)$_n$Mg for the F$^0$ center

Besides substitution and oxygen insertion there is also another way for O$_2$ to interact with the (CH$_3$)$^+$ (Cluster)H$^+$ intermediate, namely hydrogen abstraction (mechanism C, see Figure 4.16):

\[
(CH_3)^-(\text{Cluster})^+ + \frac{1}{2} O_2 \rightarrow (CH_3)^+(\text{Cluster}) + \cdot OH \quad (4.16)
\]

\[
(CH_3)^+(\text{Cluster})^+ + \frac{1}{2} O_2 \rightarrow (CH_3)^+(\text{Cluster}) + \cdot OH \quad (4.17)
\]

for O$^{2-}$ site and F$^0$ center, respectively. The above equations (4.15 and 4.16) show that for each site different product is obtained. For O$^{2-}$ site H abstraction results in formation of $\cdot$CH$_3$ radical while for F$^0$ center CH$_3^-$ is attached to the cationic cluster (see Figure 4.16). The reaction energy for this step is positive, +227 for the O$^{2-}$ site and +77 kJ/mol for the F$^0$ center, which makes this mechanism unlikely for O$^{2-}$ site. After H abstraction $\cdot$OH goes into the gas phase and reacts with a second CH$_4$ molecule, giving $\cdot$CH$_3$ and water. Then $\cdot$CH$_3$ couples with the methyl radical or CH$_3^-$ attached to the surface forming adsorbed ethane. After desorption of the latter (which costs -3 kJ/mol) the catalyst comes back to its initial state. The energies are collected in Table 4.14.
Figure 4.16. Mechanism C. Black – Mg, red – O, yellow – C, gray – H, blue – spin density.
Based on the reaction energy calculations the last mechanism is the most likely for F\textsuperscript{0} center. There are experiments, according to which coupling of methyl radicals takes place in the gas phase, but not on the catalyst surface\textsuperscript{[64,114]} as considered here. However, only microkinetic modelling can show if it is compatible with experimental information.\textsuperscript{[115,116]}

### Table 4.14. Reaction energies (in kJ/mol) for mechanism C (shown in Figure 4.16).

<table>
<thead>
<tr>
<th>Reaction(^a)</th>
<th>Site type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{O}^2)</td>
</tr>
<tr>
<td>Cluster + CH(_4) → CH(_4)···Cluster</td>
<td>-5.1</td>
</tr>
<tr>
<td>CH(_4)···Cluster → (CH(_3))((\text{Cluster})\text{H}^+)</td>
<td>+38.1</td>
</tr>
<tr>
<td>(CH(_3))((\text{Cluster})\text{H}^+) + (\frac{1}{2}) O(_2) → (CH(_3))((\text{Cluster})) + (\text{'OH})</td>
<td>+226.9</td>
</tr>
<tr>
<td>(\text{'OH}) + CH(_4) → (\text{'CH}_3) + H(_2)O</td>
<td>-42.1</td>
</tr>
<tr>
<td>(CH(_3))((\text{Cluster})) + (\text{'CH}_3) → (CH(_3)CH(_3))((\text{Cluster}))</td>
<td>-371.5</td>
</tr>
<tr>
<td>(CH(_3)CH(_3))((\text{Cluster})) → C(_2)H(_6) + Cluster</td>
<td>+4.8</td>
</tr>
<tr>
<td>2 CH(_4) + (\frac{1}{2}) O(_2) → C(_2)H(_6) + H(_2)O</td>
<td>-148.9</td>
</tr>
</tbody>
</table>

\(^a\) Cluster = (MgO)\(_9\) for the \(\text{O}^2\) site and (MgO)\(_8\)Mg for the F\textsuperscript{0} center

#### 4.3.4. Comparison with experiment

Comparison of the calculated apparent energy barriers (see Table 4.9) with the experimental value (147 kJ/mol)\textsuperscript{[92]} shows that F\textsuperscript{0} and F\textsuperscript{+} centers could be the sites responsible for H abstraction from methane in OCM reaction. The two sites cause different type of H-C(CH\(_3\)) bond splitting, heterolytic for F\textsuperscript{0} and homolytic for F\textsuperscript{+}. As a result for F\textsuperscript{0} center (CH\(_3\))\textsuperscript{−} group is formed which binds so strongly to the Mg site that its desorption costs about 200 kJ/mol. Such a problem does not appear for F\textsuperscript{+} centers where the \(\text{\'CH}_3\) desorption energy is 10 times lower. Therefore F\textsuperscript{+} centers as the active sites would be a better choice because they would fit to the Lunsford mechanism,\textsuperscript{[7]} while for F\textsuperscript{0} center a new mechanism would need to be proposed. However the formation energy of a charged F\textsuperscript{+} center is twice larger than of a neutral F\textsuperscript{0} center. Nevertheless neutral F\textsuperscript{+} centers can be created by addition of Li which was found to migrate close to the F\textsuperscript{0} centers (which are present in MgO) and form Li-F\textsuperscript{0} centers.\textsuperscript{[96]} For this type of neutral F\textsuperscript{+} centers the defect formation energy is even smaller than for the F\textsuperscript{0} center (see Table 4.8). The hypothesis that F\textsuperscript{0} centers are responsible for H abstraction in MgO whereas Li-F\textsuperscript{0} together with F\textsuperscript{0} centers in Li doped MgO would be in agreement with experimental findings according to which addition of Li to MgO enhances OCM activity.\textsuperscript{[64,75]} The higher activity would be caused by formation of additional Li-F\textsuperscript{0} centers after Li doping. The only missing part is the catalytic cycle for F\textsuperscript{0} center.
4.4. Calculations with Periodic Boundary Conditions on Defective MgO

Cluster models of limited size have been used. This was motivated by the need to consider many different sites. However, the results have to be checked by comparison with more realistic models. Therefore we performed also periodic calculations with periodic boundary conditions using the periodic electrostatic embedded cluster model\cite{117} and a periodic slab model. F$^{2+}$ centers were not considered since the barriers found in cluster calculations are very high compared to the observed apparent OCM barrier.

4.4.1. Model systems

In principle there are two ways to model periodic systems. One of them is the embedding scheme which embeds the cluster in an array of point charges. For that we used Periodic Electrostatic Embedded Cluster Method (PEECM)\cite{117} with an infinite array of point charges. The PEEC method divides the entire periodic system into two parts. The inner part, the part of interest (reaction site), is treated quantum-mechanically (QM). The outer part describes the environment of the cluster by a periodic array of point charges representing cationic and anionic sites of a perfect ionic crystal. The atoms of the cluster on the boundary between these two parts are replaced by effective core potentials (ECPs) for cations and point charges for anions. This prevents artificial polarization of the electron density. In our calculations we embedded the (MgO)$_{11}$ cluster shown in Figure 4.17. Using exactly the same cluster as for the gas phase calculations would require freezing of the Mg on the corner whose relaxation might play an important role during the reaction. Figure 4.17 shows that in general the spin density and homo orbital (for the F$^0$ singlet) are localized in the same way as for the cluster model (see Figure 4.10). Only for Li-F$^0$ 2 and F$^0$ triplet the spin density is more localized in the O vacancy because the Mg site on the corner is more coordinated compared to the cluster model. Another way to model periodic systems is the slab model, which considers periodically repeated slabs of the material separated by vacuum layers. A pseudo unit cell is built as a slab formed by a certain number of atomic layers and a vacuum region. The vacuum region has to be large enough that opposite surfaces do not interact with each other. The model used for periodic MgO calculations is a slab which consists of a (3x3) surface unit cell with four layers of MgO. One bottom layer was fixed during the optimization. The corner site was modeled by a diatomic step (Figure 4.18), because the monoatomic step does not describe properly the F$^0$ center on the corner. The vacancies were created in the top layer.

Since the cluster results for the charged F$^+$ center and the neutral Li-F$^0$ 1 and 2 centers are similar we can draw conclusions about charged defects based on studies of the neutral ones.
Therefore for periodic calculations only neutral sites were considered to avoid dealing with the background charges (to neutralize the system).

Figure 4.17. Model systems for defective MgO (PEECM calculations). Black – Mg, red – O, green – Li, blue – spin density, light blue – HOMO orbital.
Figure 4.18. Side view of model systems for defective MgO (periodic slab calculations). Black – Mg, red – O, green – Li. O vacancy is marked by a blue crossed circle.

4.4.2. Methods

The periodic embedded cluster calculations employed the TURBOMOLE program package,\(^{[47]}\) in the same way as employed for the cluster models (chapter 4.3.1.2).

Periodic DFT calculations for a slab model were performed with the Vienna Ab initio Simulation Package (VASP).\(^{[118,119]}\) The PBE functional\(^{[13]}\) with dispersion corrections (PBE+D)\(^{[20,120]}\) was applied. For Mg\(^{2+}\) we used the \(C_6\) and \(R_0\) parameters derived for Ne instead of standard parameters for Mg atoms, because for Mg\(^{2+}\) the 3s electrons, which contribute substantially to the polarizability of Mg atoms, are missing.\(^{[93]}\) We applied the projector augmented wave (PAW) method\(^{[121,122]}\) and a plane waves basis set with a kinetic energy cutoff of 400eV. For k-point sampling a \(2\times2\times1\) Monkhorst-Pack\(^{[123]}\) grid was used.

4.4.3. Results

4.4.1. Defect formation energy

The defect formation energy can be again considered here, for periodic models and compared to the cluster calculations for defective MgO. The results presented in Table 4.15 show that calculations for periodic models give the same answer as cluster studies. The largest value of the formation energy for a given type of site is obtained by periodic electrostatic embedded cluster calculations. This is because the model requires freezing of atoms on the border with point charges. Since the cluster relaxation lowers the defect
formation energy the values calculated by PEECM are always higher compared to other models.

Table 4.15. Comparison of the defect formation energies for different sites obtained using cluster, embedded and periodic models.

<table>
<thead>
<tr>
<th>Site type</th>
<th>B3LYP</th>
<th>PBE</th>
<th>PBE+D⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cluster embedded cluster</td>
<td>cluster periodic</td>
<td>periodic</td>
</tr>
<tr>
<td>F⁰ singlet</td>
<td>+4.86</td>
<td>+5.02</td>
<td>+4.47</td>
</tr>
<tr>
<td>F⁰ triplet</td>
<td>+5.50</td>
<td>+6.08</td>
<td>+5.18</td>
</tr>
<tr>
<td>F⁺</td>
<td>+9.80</td>
<td></td>
<td>+9.58</td>
</tr>
<tr>
<td>Li-F⁰ 1</td>
<td>+2.41</td>
<td>+2.47</td>
<td>+2.23</td>
</tr>
<tr>
<td>Li-F⁰ 2</td>
<td>+2.26</td>
<td>+2.48</td>
<td>+2.43</td>
</tr>
</tbody>
</table>

a Grimme dispersion correction but with Ne parameters for Mg²⁺.[⁹³]

4.4.2. Transition structures

The transition structures for defective MgO sites obtained by periodic electrostatic embedded calculations (Figure 4.19) look almost the same as for the cluster models (see Figure 4.12). There are only small differences in bond distances, but they do not change the structures. The only difference is for Li doped sites. The O-H and H-CH₃ distances are almost the same meaning that the H atom is closer to the O⁻ species. The transition structures are therefore more “late” than in gas phase calculations. Moreover for Li 2 no linear O-H-CH₃ arrangement can be observed, instead the methyl group is a little bit aside (see also chapter 4.2.6).

To compare transition structures obtained by PBE periodic plane wave calculations with B3LYP calculations on cluster models, first B3LYP and PBE results on the same system have to be compared. In most cases, the same structures and spin localization are obtained with both functionals. The only exception is for Li 2, where the spin density is more delocalized for PBE than for B3LYP (see also chapter 4.2.6).

Figure 4.20 shows the optimized transition structures obtained by PBE periodic plane wave calculations. They are very similar to those obtained by the PEEC method. Only the transition structures for Li doped sites differ, they are again “early”, exactly like for the cluster studies.

The periodic slab calculations were performed with and without dispersion contributions, but no difference was found for structures. The analysis of bond distances shows the largest deviation for F⁰ singlet (4.9 pm). Inclusion of dispersion only affects the energies, see Table 4.16 below.
Figure 4.19. Transition structures for the reaction of CH$_4$ with different surface sites obtained by PEECM calculations. Black – Mg, red – O, green – Li, yellow – C, gray – H, blue – spin density. Some bond distances are given in pm.
Figure 4.20.a. Transition structures for the reaction of CH$_4$ with Li doped sites (Li 1 and 2, Li-F$^0$ 1 and 2) obtained by periodic slab calculations. Black – Mg, red – O, green – Li, yellow – C, gray – H. Some bond distances are given in pm.
Figure 4.20.b. Transition structures for the reaction of CH₄ with O²⁻ site and F⁰ center obtained by periodic slab calculations. Black – Mg, red – O, yellow – C, gray – H. Some bond distances are given in pm.

4.4.3. Energy barriers

The apparent energy barriers are listed in Table 4.16. In principle the barriers for the embedded models are a bit lower than for the cluster calculations (except for F⁰ in a triplet spin state). This is in contrast to Li⁺O⁻ sites, for which the barriers are higher (discussed in chapter 4.2.6.).

Table 4.16. Apparent energy barriers (in kJ/mol) for H abstraction from methane by defective MgO sites obtained by different models and methods of calculations. For comparison the results for Li⁺O⁻ sites (Li 1 and 2) are included.

<table>
<thead>
<tr>
<th>Site type</th>
<th>PBE cluster</th>
<th>PBE+D³ cluster</th>
<th>B3LYP cluster</th>
<th>B3LYP+D³ cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li 1</td>
<td>+4.7</td>
<td>+8.1</td>
<td>+8.6</td>
<td>+18.9</td>
</tr>
<tr>
<td>Li 2</td>
<td>+28.8</td>
<td>+40.5</td>
<td>+32.5</td>
<td>+21.7</td>
</tr>
<tr>
<td>O²⁻</td>
<td>+61.7</td>
<td>+79.4</td>
<td>+77.8</td>
<td>+86.4</td>
</tr>
<tr>
<td>F⁰ singlet</td>
<td>+117.6</td>
<td>+108.9</td>
<td>+92.0</td>
<td>+137.1</td>
</tr>
<tr>
<td>F⁰ triplet</td>
<td>+103.4</td>
<td>-</td>
<td>+109.4</td>
<td>+112.6</td>
</tr>
<tr>
<td>F⁺</td>
<td>-</td>
<td>-</td>
<td>+129.1</td>
<td>-</td>
</tr>
<tr>
<td>Li-F⁰ 1</td>
<td>+118.3</td>
<td>+113.7</td>
<td>+102.8</td>
<td>+122.1</td>
</tr>
<tr>
<td>Li-F⁰ 2</td>
<td>+127.5</td>
<td>+117.2</td>
<td>+107.5</td>
<td>+132.6</td>
</tr>
</tbody>
</table>

³ Grimme dispersion correction but with Ne parameters for Mg²⁺.[93]

⁴ estimated using high-level correction.[93]
Comparison between B3LYP and PBE cluster results shows lower barriers for GGA functional. For PBE going from cluster to periodic calculations there is a decrease in barriers heights (with exception for O$^{2-}$ site). The barriers are lower when dispersion is included. The estimation of B3LYP energy barriers (using high-level correction)$^{[93]}$ for periodic slab models gives higher values than PBE periodic results, which is expected.$^{[124]}$

4.4.4. Conclusions

The periodic calculations for defective MgO sites lead to the same conclusions as cluster studies for these sites. This confirms that the model we used for the cluster calculations though small is good enough to study OCM on defects in MgO.
Chapter 5

Summary

This work presents a detailed quantum chemical (mostly DFT) study of H abstraction from methane by MgO and Li doped MgO. It is motivated by the UniCat effort to understand the oxidative coupling of methane (OCM). Based on the hypothesis that an Li’O'– species is responsible for the H abstraction step in OCM small cationic MgO and Li doped MgO clusters (which model O'– sites) were investigated. Because we were interested in real gas phase model systems the global minimum structures of (MgO)$_n^+$ and LiO(MgO)$_{n-1}$ clusters were first determined (by means of genetic algorithm) and then used in subsequent reactivity studies. To check if there are any structural differences between neutral and cationic MgO clusters the neutral species were studied as well. After structure determination, the activation of methane by the O'– radical sites was investigated. The small cluster sizes enabled to study the reaction in detail and to compare different methods of calculations. The results were verified by comparison with more realistic models that mimic Li doped MgO surface, like non-embedded and embedded clusters and slab models. However, unexpected results for the Li’O'– sites led to the consideration of additional types of sites in MgO that may be active for OCM – such as low-coordinated O$^{2-}$ sites, O vacancies with different charge and impurity defects. In particular morphological defects and different types of F centers were investigated. Methane activation by defective MgO surface was studied by a cluster approach and then followed by periodic calculations on periodic slab models. The results were compared to existing experimental data.

The results presented here show that structures of small (MgO)$_n$ gas phase clusters ($n = 2$-$16$) differ from the bulk MgO material. In general, the most stable configurations of neutral clusters distribute the atoms in cage-like structures instead of pieces of the MgO crystal lattice (except for $n = 4$). Hexagonal and rhombic rings are the building blocks for these clusters. Additionally, for (MgO)$_{3k}$ composition with $k = 1$-$5$ hexagonal tubes are
formed, while the intermediate sizes prefer cage-like structures. Many of the structures presented here (but not all of them) have already been found using other computational techniques, however these calculations reveal the global minima among all the configurations. Comparison with experimental gas phase IR spectra confirmed (in most cases) the structures predicted by the calculations.

The structures of small \((\text{MgO})_n^+\) clusters \((n = 2-10)\) show similar features as their neutral counterparts, i.e. the preference to cage-like structures over the cubic ones. The cations usually have lower symmetry than the neutral MgO clusters due to the presence of an unpaired electron and the Jahn-Teller effect. Nevertheless, many of the cationic clusters are similar to their neutral counterparts, however not all the lowest energy structures for \((\text{MgO})_n^+\) are the same as for neutral species (e.g. \(n = 5, 7\) and 10). The removal of one electron from the neutral species leads to delocalization of the spin density in the cationic form of the clusters. For the lowest energy structures the spin density is usually delocalized over two equivalent oxygen sites (for \(n = 9\) it is more delocalized), only for \(n = 7\) and 10 the ground state structures have localized spin density on one O site which is of particular interest for reactivity studies. Comparison of theoretical results with the experimental IR spectra led to structural assignments, for the first time based on direct experimental data on the internal cluster structure.

The most stable isomers of Li doped MgO clusters form cage-like structures which consist of either hexagonal prisms (and rings) or cubes (and squares). Comparison with undoped MgO clusters shows that the structures of \(\text{LiO}(\text{MgO})_{n-1}\) clusters \((n = 2-10)\) are based on the structures of \((\text{MgO})_n\) or \((\text{MgO})_n^+\). After doping with lithium two main types of structures (with respect to pure magnesium oxide clusters) are observed – the first group in which Mg is substituted by Li (e.g. for \(n = 6\)) and the second group in which the LiO fragment is attached to the smaller \((\text{MgO})_{n-1}\) cluster (e.g. \(n = 10\)). The Li doped MgO clusters usually have lower symmetry than pure MgO clusters because the addition of lithium causes a distortion (usually opening) of the structure. The lithium containing clusters are characterized by stronger spin localization than the cationic MgO species. The global minima structures of Li doped MgO clusters determined by HAGA in combination with DFT are mostly in agreement with MP2 and CCSD(T) calculations. For some cases \((n = 4, 6\) and 7) a definitive answer about the most stable structure can not be given, due to very small differences in energy between isomers.

The reactivity studies of small cationic and Li doped MgO clusters show that the H abstraction from methane proceeds in a similar way for all the clusters and is consistent with
the mechanism proposed by Schröder and Roithova. First, an encounter complex is formed which is based on the interaction between methane C atom and the Mg or Li site of the cluster. In the transition structure a hydrogen atom of CH₄ interacts with an O⁻ species of the cluster, created upon ionization or substitution of one Mg ion by Li ion. After H abstraction from methane a methyl radical is formed which is attached to a hydrogenated cluster as an intermediate. The final products are obtained by its dissociation. For all clusters methane activation is exoenergetic.

The \textbf{H abstraction energy barriers} for global minimum (MgO)$_n^+$ and LiO(MgO)$_{n-1}$ clusters (which model the O⁻ radical species) are smaller than 32 kJ/mol. For slab LiO(MgO)$_n$ models with O⁻ site on the corner the values are around 20 kJ/mol. Going from the corner site to the terrace site the energy barrier increases to 61 kJ/mol for the cluster calculations. The periodic calculations usually give larger values but still much smaller than the observed one for solid Li/MgO catalyst (147 kJ/mol).\cite{92} This indicates that the Li\(^+\)O⁻ species are too reactive and are not responsible for the rate-determining step in OCM. Additionally, recent studies could not find evidence for Li\(^+\)O⁻ species under OCM relevant conditions.\cite{96,97} Experiments showed that Li is not necessary for C-H activation, the reaction can be also performed on MgO without Li.\cite{99} Addition of Li, however, enhances the OCM activity most likely by restructuring the material accompanied by creating more defects such as edges, corners and kinks.\cite{98} The presence of low coordinated O\(^2⁻\) ions were confirmed by diffuse reflectance UV/Vis spectroscopy.\cite{97} The calculations presented here together with experimental results show that the current hypothesis about Li\(^+\)O⁻ sites being responsible for OCM activity of Li doped MgO needs to be revised.

Since addition of Li to the MgO creates more low-coordinated O\(^2⁻\) sites, a closer look on morphological defects have been taken. Therefore, in addition to models of O⁻ radical sites, also different types of defect sites in MgO were considered and their reactivity towards methane was studied. In this work corner sites were investigated in detail, in particular O\(^2⁻\) site, different F centers and impurity defects.

Contrary to O⁻ sites, \textbf{methane activation on MgO defect sites} is endoenergetic. The second striking difference between these two types of sites is the desorption energy of CH₃. This is closely related to the different splitting of the methane C-H bond caused by different types of sites. In general, three types of H-C(H₃) bond splitting are observed here. The O\(^2⁻\) site and F\(^0\) center in a singlet spin state split the methane C-H bond heterolytically and form a Grignard type Mg-alkyl complex. This is the reason why the CH₃ desorption energies for O\(^2⁻\) site and F\(^0\) singlet are so high (around 200 kJ/mol). All the sites with a doublet spin state (all
F⁺ centers) cause homolytic splitting of the C-H bond, similarly to O•− radicals (which also have one unpaired electron). Therefore the CH₃ desorption energies are also similar for these two types of sites. The last class of defects, F²⁺ centers (charged and neutral ones), are responsible for another type of heterolytic H-C(H₃) splitting into CH₃⁺ and H⁻ species and formation of a methoxy group. As a result the CH₃ desorption energies for F²⁺ centers are almost twice as large as for O²⁻ site and F⁰ singlet.

The calculated barrier height for defective MgO is correlated with the type of the H-C(H₃) bond splitting caused by different types of sites. For the heterolytic splitting on O²⁻ site the barrier is rather low (86 kJ/mol). For F⁺ and Li-F⁰ centers, which cause homolytic splitting of the C-H bond, the barrier is around 130 kJ/mol (which is close to the experimental value, 147kJ/mol). The F⁰ triplet also splits the H-C(H₃) bond homolytically with a lower barrier, but it is not the ground state for the F⁰ center. The F⁰ singlet site is interesting due to its intermediate character, since it splits the C-H bond heterolytically (like O²⁻ site) but at the end it forms H⁻ (like F⁺ centers). The F²⁺ centers have the highest barriers among all the considered sites and split H-C(H₃) bond heterolytically but this time a hydride (H⁻) and a CH₃⁺ group are formed. Thus, the MgO surface though usually alkaline, can locally have other type of environment (caused by defects and doping) and react in different ways with the same molecule.

The H attachment energy has been proposed as a reactivity descriptor for hydrogen abstraction from hydrocarbons. The calculations presented here show that there is a correlation between the energy barriers and the hydrogenation energies for the sites that split the H-C(H₃) bond homolytically (O⁻ radicals, F⁰ triplet and all F⁺ centers). Other sites considered here (O²⁻ site, F⁰ singlet and all F²⁺ centers) are responsible for heterolytic splitting of the methane C-H bond and therefore their calculated barriers do not follow the correlation trend. This indicates that the simple H attachment reaction can be used not only to estimate barrier height but also to distinguish between different types of interaction of CH₄ molecule with defective MgO surface.

The transition structures for methane activation by O²⁻ and F⁰ singlet sites represent a chemisorbed complex instead of H abstraction (a redox step). The H-C(H₃) bond splits heterolytically on the Mg²⁺O²⁻ pair forming OH⁻ and a Grignard type Mg-alkyl complex. To complete the redox reaction the CH₃ group has to desorb from the MgO cluster. However, as has already been mentioned this desorption costs about 200 kJ/mol. Three other ways to take out the CH₃⁻ species from the catalyst surface were proposed in this work. All of them are based on an interaction with O₂ molecule. The first one involves substitution of CH₃⁻ species
by a superoxo species, the second inserts oxygen into the surface and in the last one \( \text{O}_2 \) abstracts hydrogen from the O surface site. Based on the reaction energy calculations only the last mechanism is the most likely for the \( F^0 \) center. However, additional calculations of energy barriers are needed. For \( \text{O}^2- \) site the reaction energies are usually too high to make any of the proposed mechanisms possible. The cluster studies of methane activation by defective MgO were confirmed by periodic calculations.

Comparison of the calculated apparent energy barriers with the experimental value (147 kJ/mol)\(^{92}\) shows that \( F^0 \) and \( F^+ \) centers (137 and around 130 kJ/mol for \( F^0 \) and \( F^+ \) centers, respectively) could be the sites responsible for H abstraction from methane in OCM reaction. The two sites cause different types of H-C(H\(_3\)) bond splitting, heterolytic for \( F^0 \) and homolytic for \( F^+ \) center. As a result for \( F^0 \) center \( (\text{CH}_3)^- \) species is formed which binds so strongly to the Mg site that its desorption costs about 200 kJ/mol. Such a problem does not appear for \( F^+ \) centers where the \( \cdot \text{CH}_3 \) desorption energy is 10 times lower. Therefore \( F^+ \) centers as the active sites would be a better choice because they would fit to the Lunsford mechanism,\(^7\) while for \( F^0 \) center a new mechanism would need to be proposed. However the formation energy of a charged \( F^+ \) center is twice as large as that of a neutral \( F^0 \) center. Nevertheless neutral defects with one unpaired electron in oxygen vacancy can be created by addition of Li which was found to migrate close to the \( F^0 \) centers (which are present in MgO) and form Li-\( F^0 \) centers.\(^{98}\) For this type of neutral Li-\( F^0 \) centers the defect formation energy is even smaller than for the \( F^0 \) center (2.3-2.4 and 4.9 eV for Li-\( F^0 \) and \( F^0 \) centers, respectively). The hypothesis that \( F^0 \) centers are responsible for H abstraction in MgO whereas Li-\( F^0 \) together with \( F^0 \) centers in Li doped MgO would be in agreement with experimental findings according to which addition of Li to MgO enhances OCM activity.\(^{64,75}\) The higher activity would be caused by formation of additional Li-\( F^0 \) centers after Li doping. The only missing part is the complete catalytic cycle for \( F^0 \) center.
Zusammenfassung


Die hier vorgestellten Ergebnisse zeigen, dass sich die Strukturen von kleinen \((\text{MgO})_n\) - Gasphasencluster \((n = 2-16)\) stark von der Struktur kristallinen MgO unterscheiden. In der Regel weisen die thermodynamisch stabilsten Konfigurationen der neutralen Cluster eine
käfigartige Struktur auf und stellen keine Ausschnitte des MgO-Kristalls dar (außer für \( n = 4 \)).

Bausteine dieser Cluster sind sechseckige und rhombische Ringe. Zusätzlich kann es zur Bildung von sechseckigen Röhren kommen, bei der Betrachtung von Clustern der Zusammensetzung (MgO)\(_3k\) mit \( k = 1-5 \), während bei mittleren Clustergrößen käfigartige Strukturen bevorzugt werden. Viele der Strukturen die hier vorgestellt werden (aber nicht alle von ihnen) wurden bereits mit anderen Rechnungen Methoden gefunden. Diese Arbeit zeigt aber außerdem die globalen Minima unter allen möglichen Konfigurationen. Der Vergleich mit experimentellen Gasphasen IR-Spektren bestätigt (in den meisten Fällen), die durch die Berechnungen vorhergesagten Strukturen.

Die Strukturen der kleinen \((\text{MgO})^+\)\(_{n} \)-Cluster \((n = 2-10)\) zeigen ähnliche Eigenschaften wie ihre entsprechende neutralen Spezies, das heißt die Bevorzugung von käfigartigen Strukturen gegenüber die kubischen Strukturen. Die Kationen weisen in der Regel eine niedrigere Symmetrie auf verglichen mit den neutralen MgO-Cluster. Die Symmetrieerniedrigung ist auf das Vorhandensein eines ungepaarten Elektrons und die damit verbundene Jahn-Teller-Verzerrung zurückzuführen. Dennoch ähneln viele der kationischen Cluster ihre neutralen Gegenstücken, aber es sich ähnliche Strukturen müssen nicht in beiden Fällen Minima-Strukturen entsprechen, wie im Fall von \((\text{MgO})^+\)\(_n\) und den entsprechenden neutralen Spezies, für \( n = 5, 7 \) und 10. Die Entfernung eines Elektrons aus dem neutralen Cluster führt zur Delokalisierung der Spindichte in der kationischen Form der Cluster. Für Strukturen die Minimas der Energie entsprechen ist die Spindichte in der Regel über zwei gleichwertige Sauerstoff Positionen delokalisiert (für \( n = 9 \) ist die Delokalisation sogar stärker). Nur für \( n = 7 \) und 10 ist die Spindichte im Grundzustand an einem einzelnen O-Atom lokalisiert, diese Strukturen sind von besonderem Interesse für die Reaktivitätsstudien. Ein Vergleich der theoretischen Ergebnisse mit experimentellen IR-Spektren führte zu neuen Strukturbeschreibungen, zum ersten Mal basierend auf direkten experimentellen Daten der internen Cluster-Struktur.

Die stabilsten Isomere von **Li dotierten MgO-Cluster** bilden käfigartige Strukturen, die entweder hexagonalen Prisme (und Ringe) oder Würfel (und Plätzen) entsprechen. Ein Vergleich mit nicht dotierten MgO-Cluster zeigt, dass die Strukturen der LiO(MgO)\(_{n-1}\)-Cluster \((n = 2-10)\) auf den Strukturen der \((\text{MgO})_{n}\) oder \((\text{MgO})^+\) basieren. Nach Dotierung mit Lithium können zwei verschiedene Arten von Strukturen (in Bezug auf reines Magnesiumoxid Cluster) beobachtet werden - die erste Gruppe, in der Mg durch Li ersetzt wird (z. B. für \( n = 6 \)) und die zweite Gruppe, in der ein LiO Fragment an kleinere \((\text{MgO})_{n-1}\)-Cluster angefügt ist (z. B. \( n = 10 \)). Die Li dotierten MgO-Cluster haben in der Regel eine
niedrigere Symmetrie im Vergleich zu den nicht dotierten MgO-Cluster. Ursache ist die durch Zugabe von Lithium verursachte Verzerrung (in der Regel eine Öffnung) der Struktur. Die Lithium enthaltenen Cluster sind durch eine stärkere Spin-Lokalisierung als die kationische MgO Arten gekennzeichnet. Die globalen Minimastrukturen der Li dotierten MgO-Cluster, die mit Hilfe von HAGA in Kombination mit DFT bestimmt wurden, sind meistens in Übereinstimmung mit Strukturen aus MP2- und CCSD(T)-Rechnungen. Für einige Fälle \( n = 4, 6 \) und 7 konnte keine definitive Aussage über die stablste Struktur getroffen werden, aufgrund der sehr kleinen Energiedifferenzen zwischen den Isomeren.

Untersuchungen zur Reaktivität kleiner kationischer und Li dotierter MgO-Cluster zeigen, dass die H-Abstraktion von Methan in ähnlicher Weise verläuft, unabhängig von der Art der Cluster und im Einklang mit dem Mechanismus, vorgeschlagen von Schröder und Roithova.\(^{[78]}\) Im ersten Schritt bildet sich ein Begegnungskomplex, durch Wechselwirkungen zwischen dem Methan-C-Atom und dem Mg oder Li Atom des Clusters. Im Übergangszustand interagiert eines der Wasserstoffatome des CH\(_4\) mit einer O\(^{-}\) Spezies des Clusters, welche durch Ionisation oder Substitution eines Mg-Ions durch ein Li-Ion erzeugt wurde. Durch H-Abstraktion von Methan wird ein Methyl radikal gebildet und dieses bindet anschließend an das hydrierte Cluster. Die Endprodukte werden durch die Dissoziation erhalten. Für alle Cluster verläuft die Methanaktivierung exoenergetisch.

Die Energiebarrieren der H-Abstraktion durch \((\text{MgO})_n^+\) und LiO(MgO)\(_{n-1}\)-Cluster (in ihrer globalen Minimumstruktur) sind alle kleiner als 32 kJ/mol. Die Energiebarrieren vergrößern sich um etwa 20 kJ/mol bei der Betrachtung von LiO(MgO)\(_8\) slab-Modellen mit einer O\(^{-}\) Seite an der Ecke. Beim Übergang von der Ecke auf die Terrasse steigt die Energiebarriere auf 61 kJ/mol für die Cluster-Rechnungen. In der Regel führen periodische Berechnungen zu höheren Energiebarrieren. Sie sind aber immer deutlich kleiner als der experimentelle Wert bestimmt für einen festen Li/MgO-Katalysator (147 kJ/mol).\(^{[92]}\) Dies deutet darauf hin, dass die Li\(^{+}\)O\(^{-}\) Zentren zu reaktiv sind und daher nicht verantwortlich für den Geschwindigkeitsbestimmenden Reaktionsschritt in der OCM Reaktion sein können. Zusätzlich konnten neue Studien keine Beweise für Existenz von Li\(^{+}\)O\(^{-}\) Zentren, unter für OCM relevanten Reaktionsbedingungen, erbringen.\(^{[96,97]}\) Experimente zeigten außerdem, dass die Anwesenheit von Li-Ionen nicht notwendig ist, für die Aktivierung der C-H-Bindung, und dass die Reaktion auch mit undotierten MgO durchgeführt werden kann.\(^{[99]}\) Die Zugabe von Li führt allerdings zu einer Erhöhung der Katalysatoraktivität. Erklärbar am ehesten durch eine Umstrukturierung des Katalysators durch die Bildung von mehr Defekten, wie zum Beispiel Kanten, Ecken und Stufen.\(^{[98]}\) Die Anwesenheit von niedriger koordinierten O\(^{2-}\) Ionen
wurde durch diffuse Reflexion UV/Vis spectroscopy bestätigt.\textsuperscript{[97]} Die hier präsentierten theoretischen Untersuchungen zusammen mit den experimentellen Ergebnissen zeigen, dass die aktuelle Hypothese über Li$^+$O$^{•–}$ Zentren, als aktive Zentren für OCM Reaktion, mit Li dotierten MgO überarbeitet werden muss.

Da die Dotierung von MgO mit Li die Fehlstellenkonzentration erhöht und dadurch auch die Konzentration von niedrig koordinierten O$^{2–}$ Seiten, wurde ein genauerer Blick auf die morphologischen Defekte geworfen. Deshalb wurden neben Modellen mit O$^{•–}$ Radikal-Seiten, auch verschiedene Modelle von MgO mit morphologischen Defekten betrachtet und ihre Reaktivität gegenüber Methan untersucht. Im Detail wurden dabei niedrig koordinierte O-Atome auf Ecken untersucht, zusammen mit Sauerstofffehlern verschiedener elektronischer Struktur.


Die berechnete Energiebarriere für die Methanaktivierung durch defekten MgO, korreliert mit der Art der H-C(H$_3$) Bindungsspaltung an verschiedene Arten von morphologischen Defekten. Für die heterolytische Spaltung an O$^{2–}$ Seiten ist die Barriere eher gering (86 kJ/mol). Für F$^+$ und Li-F$^0$ Zentren, die eine homolytische Spaltung der C-H-Bindung verursachen, ist die Barriere 130 kJ/mol (das ist nahe experimentelle Wert 147 kJ/mol).\textsuperscript{[92]} Das F$^0$ Triplett-Zentrum spaltet die H-C(H$_3$) Bindung auch homolytisch mit einer geringeren Barriere, aber es ist nicht der Grundzustand des F$^0$ Zentrum. Die F$^0$
Singulett-Seite ist interessant wegen ihres intermediären Charakters, da sie die C-H-Bindung heterolytisch (wie O\(^2^-\) Seite) spaltet, aber am Ende zur Bildung von H (wie für F\(^+\) Zentren) führt. Die F\(^{2+}\) Zentren weisen die höchsten Aktivierungskohlenhydrate auf, bei allen betrachteten Systemen und spalten die H-C(H\(_3\)) Bindung heterolytisch. Hier bilden sich jedoch eine Hydrid (H\(^-\)) und CH\(_3\)\(^+\) Gruppe. Obwohl die MgO-Oberfläche meist als alkalisch betrachtet wird, kann ihre chemische Umgebung variieren (verursacht durch Defekte und Dotierung) und MgO kann in unterschiedlicher Weise mit dem gleichen Molekül reagieren.

Die **Hydrierungsenergie** ist als Reaktivitätsdeskriptor für die Wasserstoffabspaltung aus Kohlenhydraten vorgeschlagen worden.\(^{[81]}\) Die hier vorgelegten Berechnungen zeigen, dass es einen Zusammenhang zwischen den Energiebarrieren und den Hydrierungsenergien gibt, zumindest für die homolytische Spaltung der H-C(H\(_3\)) Bindung (O\(^-\) Radikale, F\(^0\) Triplet und alle F\(^+\) Zentren). Die anderen hier betrachteten (O\(^2^-\) Seite, F\(^0\) Singulett und alle F\(^{2+}\) Zentren) Zentren sind gekennzeichnet durch eine heterolytische Spaltung der C-H-Bindung des Methans und daher folgen ihre berechneten Barrieren nicht diesem Trend. Das zeigt, dass einfache Hydrierungsenergien eingesetzt werden können, nicht nur um die Aktivierungskohlenhydrate abzuschätzen, sondern auch um zwischen verschiedenen Arten der Interaktion des CH\(_4\) Molekül mit Defekten der MgO-Oberfläche zu unterscheiden.

Der Vergleich der berechneten scheinbaren Energiebarrieren mit dem experimentellen Wert (147 kJ/mol)\textsuperscript{[92]} zeigt, dass F\textsuperscript{0} und F\textsuperscript{+} Zentren (137 und etwa 130 kJ/mol für F\textsuperscript{0} und F\textsuperscript{+} Zentren) aktive Zentren für die Aktivierung von Methan in der OCM-Reaktion sein können. Diese beiden Defekte spalten die H-C(H\textsubscript{3}) Bindung auf verschiedene Weisen, heterolytische im Fall von F\textsuperscript{0} und homolytisch für ein F\textsuperscript{+} Zentrum. Als Produkt entsteht im Fall des F\textsuperscript{0} Zentrums eine (CH\textsubscript{3})\textsuperscript{−} Spezies, die so stark an das Mg\textsuperscript{2+} bindet, dass die Desorption 200 kJ/mol kostet. Die CH\textsubscript{3}-Desorptionsenergie ist bei der Betrachtung eines F\textsuperscript{+} Zentrums den Faktor 10 niedriger. F\textsuperscript{+} Zentren scheinen daher die eher als aktives Zentrum in Frage zu kommen. Sie würden außerdem besser zu dem Mechanismus, vorgeschlagen von Lunsford passen.\textsuperscript{[7]} Für die F\textsuperscript{0} Zentrum müsste ein neuer Mechanismus vorgeschlagen werden. Die Bildungssenergie eines geladenen F\textsuperscript{+} Zentrums ist doppelt so groß wie die eines neutralen F\textsuperscript{0} Zentrums. Durch Dotierung mit Li kann die Fehlstellenbildungsenergie einer Sauerstofffehlstelle mit einem ungepaarten Elektron jedoch deutlich gesenkt werden. Es konnte gezeigt werden, dass Li-Ionen zu Sauerstofffehlstellen diffundieren und ein Li-F\textsuperscript{0} Zentrum bilden.\textsuperscript{[98]} Die Fehlstellenbildungsenergie für diese Art von Defekt ist kleiner im Vergleich zur Fehlstellenbildungsenergie eines F\textsuperscript{0} Zentrums (2.3 bis 2.4 und 4.9 eV für Li-F\textsuperscript{0} und F\textsuperscript{0} Zentren, jeweils). Die Hypothese, dass F\textsuperscript{0} Zentren für die H-Abstraktion durch MgO verantwortlich sind, während Li-F\textsuperscript{0} Zentren in Li dotierten MgO als aktive Zentren fungieren, würde in Übereinstimmung mit den experimentellen Befunden stehen. Die belegen einen Anstieg der Katalysatoraktivität durch Dotierung von MgO mit Li.\textsuperscript{[64,75]} Die höhere Aktivität wäre durch die Bildung von zusätzlichen Li-F\textsuperscript{0} Zentren verursacht werden. Der einzige fehlende Teil ist ein vollständiger Katalysezyklus für die Methanaktivierung in der Nähe von F\textsuperscript{0} Zentren.
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Acknowledgements

First of all I would like to thank to my whole family and all friends at home, in Poland, especially my parents, my sister and my brother for trusting me and supporting me all the time and for all beautiful moments spent together. Special thanks are going to my two beloved nieces, Gabi and Zuzia, who do not stop to amaze me. Dziękuję 😊

Then I thank Prof. Joachim Sauer for giving me the nice opportunity to work in his group. For his constructive criticism and encouragement to always try harder and do better. Many thanks to Marek for his guidance. I also thank you, all (ex)members of the group for nice discussions not only about science. Special thanks to Thomas, for his always enthusiastic help in any critical situation and all the chocolate moments. Thanks to Conny for being always a precious help. Grazie to Giovanni for his playfulness and contagious optimism. And very important thanks to Matthias for correcting (or rather rewriting) the German version of the Summary and for support in the very last writing moment. And Asbjörn for helping me with the whole “Promotionsordnung” procedure.

I would also like to thank the IMPRS for financial support which allow me to take part in many nice conferences. Thanks to all IMPRS members for a nice time during workshops, block courses and soft skills seminars. And also thank you, the IMPRS coordinators, Thomas and Niklas, for making it all work.

Many thanks to the experimentalists, Marko and Andre, for a nice collaboration and great results. And also to Jens, for some MP2 and CCSD(T) calculations.

Special thanks are going to Claudia for setting up a contest “who will first finish writing thesis?” and for motivating me every time when I confronted a blank page. Thanks to Chao for her incredible spontaneity. And to Cristina for her friendship.

Many thanks to my friends in Poland and in some other beautiful places in Europe, who though far away are still close to my heart. Special thanks to Dorota and Piotr for cheering me on during this difficult writing time.
Selbstständigkeitserklärung


Berlin, den 27. Oktober 2011,

Karolina Kwapięń