The Structure and Reactivity of Microporous and Oxide Catalysts

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Abstract

Microporous and metal oxide heterogeneous catalysts have been investigated using a range of computational techniques. The results of studies of the factors influencing the synthesis, structure and activity of these materials are presented here.

A study of the interactions between zeolitic frameworks and organic templates has demonstrated how the efficacy of a template can be determined and an energetic rationalisation of templating ability is demonstrated. The location of templates within frameworks are found to be accurately determined and subtle differences in framework structure are rationalised in terms of the template used. We have been able to determine the templating action of bis-quaternary ammonium cations in the aluminophosphate DAF-1, results which have allowed the synthesis of new compositions of this material. We have further used these results to design a new template which will not form DAF-1 and which we propose as a template which may favour a new material. We demonstrate that such computer-aided design of templates can be used to assist the search for new materials.

We have successfully modelled the local geometry of the iron and Brønsted acid site in Fe-ZSM5 using atomistic simulation techniques. A broad range of cation T sites are predicted to be occupied by iron, with T19 and T18 being the most energetically favourable. The accuracy of the calculations is demonstrated by the reproduction of the experimental EXAFS. We further propose improved models which better describe the local environment and which improve on the fit to experimental data. The effect of the inclusion of iron on the physical properties and catalytic activity is determined and compared to similar results for Al-ZSM5. The subtle differences between these two materials is reproduced. Iron incorporation modifies the pore dimensions, reducing the maximum pore dimension by 0.4Å, an effect which can be correlated to experimental data on the selectivity of the material. Calculations on the interaction of the iron and the template, the first of their kind, have provided a model for understanding the experimental data on this material.

The defect chemistry of the bulk and surface of the partial oxidation catalyst Li/MgO is investigated. The proposed active site, a lithium trapped oxygen hole, is found to be bound and segregated to the surface. Low coordinate surface sites are found to be more favourable than the (1 0 0) surface; in...
particular they stabilise untrapped oxygen holes. A mechanism for the improved catalytic performance of the material on doping with Cl\textsuperscript{-} is presented. Cl\textsuperscript{-} is found to be strongly surface segregated and to compete for the lithium with the oxygen holes, forming \([\text{LiCl}]\) defect centres. These calculations also allow us to comment on the relative activity of the different sites and to draw further conclusions on the reaction mechanism.

Quantum mechanical studies of the abstraction of hydrogen from methane by an oxygen hole in MgO demonstrate the importance of accurate treatments of lattice relaxation. We show that there is a critical influence on the results arising from the degree to which surface relaxation and the relaxation of the lattice in response to defect formation are included in the point charge arrays used to simulate the infinite lattice in the embedded cluster calculations. Reaction enthalpies and activation barriers are shown to be over-estimated and under-estimated respectively if these effects are not considered.
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Chapter 1

Introduction and Aims
Solid heterogeneous catalysts pose many challenges to the investigation of their structure, activity and the mechanism by which they catalyse reactions. The complex and ill-defined nature of many such catalysts prohibits a detailed investigation of their structure. Furthermore, techniques for determining the structure and mechanistic parameters are often incompatible with the conditions under which the catalysts are active. Computational techniques therefore have extensive applications in the study of heterogeneous catalysis. The past 20 years have seen not only a dramatic increase in the range and availability of such techniques, as a result of the rapid development in computational power, but also the development and acceptance of such techniques as viable techniques in their own right for the investigation of heterogeneous catalysis.

The aim of this thesis is to apply a range of computational techniques to investigate two classes of heterogeneous catalysts: zeolites and related microporous materials, and metal oxides. Computational methods will be applied to study aspects of the synthesis, structure, defect chemistry, reactivity and physical properties of these materials.

There is increasing interest in the ‘design’ of new catalysts and this has been most evident in the field of microporous materials. To date the ‘art’ of zeolite synthesis has been based on empirical and Edisonian principles. The development of techniques which would allow the almost routine design and synthesis of materials with pre-determined properties is obviously attractive. One particular feature of zeolite synthesis is the use of organic molecules as structure directing agents or templates, which lead to the formation of specific materials or structural motifs. Although there is much debate as to the extent of this effect, attempts to design novel zeolite structures have, to date, concentrated on designing templates with specific features which were expected to manifest themselves in any microporous material synthesised. In chapter 5 we shall investigate this effect, concentrating on the interactions between the zeolitic framework and the organic species, to determine if it is possible to predict templating ability. These techniques will then be applied to investigate particular subtle templating effects. Furthermore, we shall attempt to design a new material from a detailed understanding of the templating in a known material.

The catalytic activity of a material is inextricably linked to its composition and structure. The solid acid properties of zeolites are no exception and the understanding of the local structure of the Brønsted acid site will provide further insight into their activity. The modification of acid properties is often
achieved by the substitution of the framework aluminium by an isovalent metal ion, producing materials with different physical and catalytic properties, whilst maintaining the same topological structure. Iron substituted ZSM-5 is a case in point and possesses different acid and catalytic properties to the aluminium containing ZSM-5. The structure and properties of Fe-ZSM-5 are investigated in Chapter 6. Of particular interest will be the modifications to the overall pore architecture, the local environment of the iron and the consequent effect on the physical properties of the material. Comparison will be made with Al-ZSM-5. The influence of the iron on the templating ion will also be discussed.

The conversion of methane to more useful chemical feedstocks and more readily transportable hydrocarbons has been the subject of exhaustive research over the past 20 years. Many metal oxide based catalysts for the oxidative coupling of methane, producing ethane, ethene and higher hydrocarbons, have been identified. Of these, one of the most promising for commercial exploitation is lithium doped magnesium oxide. Consequently, Li/MgO has been the subject of extensive research, which has attempted to characterise the active sites and to elucidate the mechanism of its activity. However, many questions remain unanswered.

In chapter 7, simulation techniques are applied to investigate the defect chemistry of MgO based catalysts. The formation, stability and siting of the proposed active site, a lithium trapped oxygen hole, is investigated. Particular attention is paid to the structure of defects at surface sites. Additional doping of these catalysts has proved fruitful in improving their catalytic performance. The addition of chloride to Li/MgO has proved to be particularly effective and simulation techniques are applied to determine a mechanism for this effect.

Finally, in chapter 8, embedded cluster quantum mechanical techniques are used to study the reaction pathway of the abstraction of hydrogen from methane by an oxygen hole. Experimentally this has been determined to be the initial and rate determining step in the oxidative coupling reaction. Particular attention will be paid to the description of the MgO lattice used in the embedding technique. Previous studies have treated the surface as a simple termination of the bulk. However, this work will show how an accurate description of the surface has a significant effect on the resulting reaction profile.

The work described in this thesis breaks new ground in three main areas: firstly, it takes computational methods closer to genuine “materials design” - one of the overall aims of computational materials chemistry; secondly, it shows
how these methods may now yield highly accurate models for localised states in microporous solids - models which, moreover, allow detailed interpretation of experimental data. Thirdly, we have been able to construct models of surface defects and reaction processes with a level of detail which has not previously been achieved.
CHAPTER 2

Catalysis
2.1. Heterogeneous Catalysis

"Many bodies... have the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action they produce decomposition in bodies, and form new compounds into the composition of which they do not enter. This new power, hitherto unknown, is common both in organic and inorganic nature... I shall... call it catalytic power. I shall also call catalysis the decomposition of bodies by this force"


Thus wrote Berzelius to define catalysis. Our knowledge now allows us to begin to understand the processes alluded to here. Thermodynamics, kinetics, structure determination and mechanistic studies enable us to determine the effect, action and composition of the catalysts involved.

Since this early definition, catalysts and more importantly the processes which they catalyse have been as important industrially as they have been in the laboratory of the academic scientist. Indeed, the catalytic use of platinum was patented 5 years before the work of Berzelius quoted above. The industrial application of catalysts has produced the strongest impetus for their study. The use of catalysts in such processes results in the production of billions of pounds worth of fuel and chemicals each year. Furthermore, the production of catalysts is estimated to be a business worth more than £2500m per annum worldwide.

Many of the discoveries and advances in catalysis have been as a result of Edisonian (try it and see) research and serendipity. This manner of research is partly a consequence of the nature of the catalysts themselves, many being multicomponent and poorly characterised. Furthermore, in industrial processes, additional factors such as the scale-up of the process, catalyst lifetime and regeneration, disposal concerns and the overall economics of the system are also part of the development cycle of a catalyst. Thus to this day the study of
catalysis, of both fundamental and applied aspects, is an important and ever expanding field.

Catalytic processes can be classified as either homogeneous, heterogeneous or enzymatic. This thesis shall be concerned with the study of solid heterogeneous catalysts. This class of catalysts poses numerous problems for the investigator which are not present with liquid phase heterogeneous catalysts or those used in homogeneous processes. Heterogeneous solid state catalysis is effected by the surface of the material. It is at this surface that the active sites, which we wish to study, are located. However, this surface is often, under the conditions used, ill-defined. Furthermore, experimental techniques useful for probing such surfaces are also ill-suited to the environment of the reaction. Many surface science techniques not only require clean surfaces but also operate under ultra-high vacuum. Thus the study of catalysts and catalysis has led to many innovative and exciting developments in such techniques. The techniques are varied; bulk structure determination by X-ray and neutron diffraction, local structure and geometry by EXAFS and solid state NMR and surface structure and activity by infrared, Auger spectroscopy and surface EXAFS. Furthermore, techniques are available for the in-situ analysis of catalyst (and reactant) structure under reaction conditions.\textsuperscript{3-5} Computational methodologies are also becoming increasingly important in the study of catalysts and catalytic processes.\textsuperscript{6-9}

The structure of catalysts and the reactions which they catalyse are as varied as the fields of chemistry in which they are applied (as illustrated in Table 2-1). Two important types of catalysts are the basic metal oxides and microporous materials. Both classes will be investigated in this thesis and this work will attempt to show that computational methodologies can be applied to gain an insight into the synthesis, structure, activity and the mechanism of the catalytic reactions. Aspects of microporous and metal oxide catalysts will now be reviewed.
### Table 2-1. Examples of catalysts and reaction types.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Reaction Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>hydrogenation</td>
<td>Fe, Ni, Pd, Pt, Ag</td>
</tr>
<tr>
<td></td>
<td>dehydrogenation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>oxidation</td>
<td></td>
</tr>
<tr>
<td>Semiconducting oxides</td>
<td>oxidation</td>
<td>NiO, ZnO, MnO₂</td>
</tr>
<tr>
<td>and sulphides</td>
<td>dehydrogenation</td>
<td>Cr₂O₃, Bi₂O₃-MoO₃</td>
</tr>
<tr>
<td></td>
<td>desulphurisation</td>
<td>WS₂</td>
</tr>
<tr>
<td></td>
<td>hydrogenation</td>
<td></td>
</tr>
<tr>
<td>Insulator oxides</td>
<td>oxidation</td>
<td>MgO, Al₂O₃, SiO₂</td>
</tr>
<tr>
<td></td>
<td>dehydration</td>
<td></td>
</tr>
<tr>
<td>Acids</td>
<td>isomerisation</td>
<td>H₃PO₄, H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>cracking</td>
<td>SiO₂-Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>alkylation</td>
<td>Zeolites</td>
</tr>
<tr>
<td></td>
<td>polymerisation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hydrogenation</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Zeolites

2.2.1. Zeolite Structure

Zeolites are a class of crystalline aluminosilicate microporous materials, which have three-dimensional structures arising from a framework of [SiO₄]⁴⁻ and [AlO₄]⁵⁻ tetrahedra which are linked by corner sharing. This results in structures which contain voids, cavities and channels. Typical structures arising from this sharing of tetrahedra are illustrated in Figure 2-1. These aluminosilicate structures have the generalised formula of

\[ M^{m_+}_{x/m} \cdot [Si_{1-x}Al_xO_2] \cdot nH_2O \]

Non-framework cations  Framework  Sorbed phase
Non-framework cations are present as charge compensating ions when aluminium or another heteroatom (see below) is present in the framework. A non-neutral framework can also be charge compensated by the formation of Brønsted acid sites at the bridging oxygens, which imparts solid acid characteristics on the material.

Further substitution of the tetrahedral atoms (T atoms) in the framework is also possible with a wide range of cations such as Fe, B, Ti and Ga. Thus the composition of the framework can be modified and this has a direct bearing on the physical properties of the material - both of the framework itself and of the non-framework species within the material.

![Diagram of zeolite structure](image)

**Figure 2-1. Elements of zeolite structure.** (a) Tetrahedra are linked through shared oxygen atoms to form (b) chains and (c) cages and rings. (c) and (d) show the sodalite cage, the latter omitting the oxygen positions for clarity. Also shown in this manner are the structures of (e) Sodalite, (f) Zeolite A and (g) Faujasite.

It is the ability to absorb and desorb water which gives the name to this class of materials. Zeolite literally means boiling stone - from the Greek ζεύμ (boil) and λίθος (stone) - from the observation of Cronstedt in 1756 that the natural mineral stilbite froths and gives off steam when heated. Furthermore, these materials can freely absorb and desorb many species without change in the overall structure of the framework itself. This property is one of the cornerstones of the physical properties of zeolites which is exploited most obviously in the field of gas separation and in catalysis.
Although the term zeolites refers strictly to aluminosilicates, there are numerous related systems of microporous materials. Of particular importance are the aluminophosphates (APOs) which arose from work at Union Carbide in the early 1980's, and which are composed of alternating tetrahedra with Al and P as the T atom resulting in an overall composition of \([\text{AlPO}_4] \cdot n\text{H}_2\text{O}\), a neutral framework which we can consider as consisting of alternating \([\text{AlO}_2]\) and \([\text{PO}_2]^+\) units. This framework neutrality results in organophilic and non-acidic materials. Partial aliovalent substitution of the framework T-atoms thus results in materials which have an ion exchange capacity and acidity - desirable properties for catalysts. The term zeolite will be used throughout this thesis as a general term for all these types of microporous materials.

Zeolites are microcrystalline, with a typical particle size of 0.1 - 5 μm. In contrast to almost all other solid catalysts in which the catalytic activity is restricted to the external surface, the microporous nature of zeolites means that much of the internal surface is also available. This results in effective surface areas of 300 - 700 m²g⁻¹ which implies that, for a typical crystallite size, ca. 98% of the total surface is internal.

2.2.2. Zeolite Chemistry

Zeolites possess four major physical properties which are related to their catalytic activity:

1. cation exchange capacity
2. sorption properties of the pores and channels
3. shape selectivity of the pores and channels
4. the acidity of the materials.

Cation exchange has been the most widespread application of zeolites on an industrial scale. Applications include water softening in detergent systems, nuclear effluent treatment, waste water treatment and soil nutrition. These applications generally exploit natural zeolites such as clinoptilolite and
mordenite which are relatively inexpensive. However, synthetic zeolites are also used. For example, zeolite A is extensively used in the detergency industry as a replacement for water softening agents such as sodium tripolyphosphate. Sorption behaviour and shape selectivity are related properties which have been exploited in the field of liquid\textsuperscript{18} and gas separation.\textsuperscript{19} Important industrial applications of this property are the PAREX process\textsuperscript{20} which separates mixed xylenes and the oxygen enrichment of air by the selective sorption of nitrogen on zeolites. However, catalytically, it is the acidity of zeolites which is most important (although it cannot be considered in isolation from, and is influenced by, the other properties of the material). Exchange of cations with protons produces a strongly acidic framework, resulting in a solid acid catalyst which, due to its open pore architecture, is shape selective. The concentration of these acid sites, both Brønsted and Lewis sites, is directly related to the catalyst's composition (particularly the Al/Si ratio in aluminosilicates). Their acidity is also related to the local environment; being strongest for an isolated Brønsted sited next to a framework aluminium. This acidity has been exploited in a wide range of applications, some of which are summarised in Table 2–2.

\subsection*{2.2.3. Zeolite Synthesis}

Zeolites are formed naturally under hydrothermal conditions and laboratory syntheses generally attempt to reproduce these conditions,\textsuperscript{33} a synthesis usually involving crystallisation from a gel medium. The gel is multicomponent and is commonly based on silica with a suitable solvent and a base component to regulate the pH. For example, a gel for the synthesis of zeolite A consists of a solution of hydrated alumina in concentrated NaOH which is added to a solution of sodium metasilicate to give a gel with a typical composition of 2.1Na\textsubscript{2}O:Al\textsubscript{2}O\textsubscript{3}:2.1SiO\textsubscript{2}:60H\textsubscript{2}O.\textsuperscript{19} Crystallisation takes place after an initial incubation period and the crystallisation time can vary from a few hours to as long as a few months. Crystallisation occurs under autogeneous pressure in a temperature range of 60-200°C. The synthesis is controlled by many factors.
including gel (or solution) composition, pH, temperature, template effects, time, pressure, gel ageing, seeding effects and agitation. As a result the chemistry of synthesis of microporous materials is still the subject of much investigation and speculation.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid catalytic cracking</td>
<td>Y, ZSM-5,</td>
<td>21</td>
</tr>
<tr>
<td>Dewaxing</td>
<td>ZSM-5, Mordenite, Ferrierite, ZSM-23</td>
<td>22,23</td>
</tr>
<tr>
<td>Friedel-Crafts reactions</td>
<td>H-β, H-Y</td>
<td>24</td>
</tr>
<tr>
<td>Butene isomerisation</td>
<td>DAF-1, SAPO-11</td>
<td>25</td>
</tr>
<tr>
<td>Methanol to gasoline conversion</td>
<td>H-ZSM-5</td>
<td>26</td>
</tr>
<tr>
<td>Synthesis of amines</td>
<td>H-ZSM-5, ferrisilicates</td>
<td>27</td>
</tr>
<tr>
<td>Fischer-Tropsch reactions</td>
<td>K-Fe-L</td>
<td>28</td>
</tr>
<tr>
<td>Oxidation with $\text{H}_2\text{O}_2$ of e.g.</td>
<td>Ti-Silicalite (TS-1)</td>
<td>29</td>
</tr>
<tr>
<td>cyclohexane, phenol, propene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_x$ reduction</td>
<td>Cu-ZSM-5, Ni-Y</td>
<td>30</td>
</tr>
<tr>
<td>Oligomerisation of light alkenes</td>
<td>SAPO-11, Ni-ZSM-5, Ni/Zn-ZSM-5, MeAPO-11</td>
<td>31,32</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_2$ - benzene</td>
<td>Ni-Y</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 2-2. Catalytic reactions involving zeolite catalysts. Laboratory, Pilot and Industrial scale processes are included.

Of particular importance in this thesis will be the role of organic molecules as templates in these syntheses. These organic molecules are occluded within the pores of the zeolites and are usually removed after the synthesis by calcination (heat treatment). Although their use is widespread, the complex and varied conditions in zeolite syntheses have given rise to several theories of the role of such organic molecules in the crystallisation process. These species not only
modify the gel composition but also act as spacefilling and structure directing agents which modify the crystallisation process. A computational study of templating is presented in this thesis.

2.2.4. Modification of Zeolite Structure

As mentioned previously, the composition of a zeolite structure can be modified in such a way that the framework topology is unchanged. These modifications result in local changes in the structure and lead to changes in the physical and catalytic properties of the zeolite. These can be brought about in numerous ways:

2.2.4.1. Modification of framework composition during synthesis

The addition of metal oxides (for example Fe₂O₃, TiO₂, GeO₂) to the synthesis gel can result in the formation of frameworks with the metal atoms substituting for Si on a T site - as Al does in aluminosilicates. This has led to numerous materials with a range of heteroatoms being substituted in a number of framework types. For example, Fe can be substituted into the framework of silicalite-I (siliceous ZSM-5),¹⁰ silicalite-II (siliceous ZSM-11),³⁵ ZSM-23,³⁶ zeolite β³⁷ and zeolite L.³⁸ Ti can similarly be inserted into silicalite-I³⁹ and silicalite-II.⁴⁰ This method of framework modification is the most suitable for producing well characterised materials without the formation of framework defects and extra-framework nanoparticles, as can occur with the method described in section 2.2.4.2.

2.2.4.2. Modification of framework composition post-synthesis

The removal of T atoms and the substitution of T atoms post-synthesis is also possible. The de-alumination of zeolites is common³³ resulting in the modification of Al/Si ratio. Similarly, framework heteroatoms can be removed. Although not directly characterised there is evidence for hydrogarnet type hydroxyl nest defects in such materials.⁴¹ Following the removal of framework
T atoms, it is possible to re-insert a different T atom. This can be Si, resulting in higher Si/Al ratios, or other heteroatoms.

2.2.4.3. Cation exchange

The ability to exchange extra-framework cations is one of the fundamental properties of zeolites. In addition to being a useful process in itself (as in water softening using zeolite A) it can also be used to modify the activity and selectivity of the zeolite as a catalyst or as a molecular sieve. An example is the exchange of potassium ions for sodium in zeolite A. Na-A is accessible to small hydrocarbons and alcohols, whilst they are excluded in the presence of the larger K ions which block the pore entries.

The effect of isomorphous substitution of Fe atoms into the framework of ZSM-5 structures will be investigated in this thesis. There has been considerable interest in this material as a result of its catalytic properties which are subtly different to those of purely aluminosilicate ZSM-5. Experimental techniques have determined that the iron substitutes into the framework and elucidated some detail of the local geometry of the iron. However, they cannot give any indication of the siting of the iron and the effect of the local geometry changes on the overall structure. Computational techniques have been applied to investigate this and to model other physical properties of the material.

2.3. Metal Oxide Catalysts

Oxides are commonly used as catalysts for a wide range of reactions some of which are illustrated in Table 2–3. Unlike most metal catalysts they are often used unsupported - although there are exceptions, such as molybdenum oxides. Many metal oxide catalysts are in fact multicomponent or doped systems, for example the reforming catalyst (Cr,Al)₂O₃ and the methane coupling catalyst Li/MgO. Indeed, it is the defects formed on the addition of dopant to pure metal oxides which provide many catalysts with their activity. Furthermore, the
concentration and coordination of such dopants is crucial. This was elegantly demonstrated by the study of Stone where a range of materials was formed based on the doping of varying concentrations of transition metal ions in MgO. It was found that the activity of the materials for N₂O decomposition was highest when the metal ions were highly dispersed and isolated. Likewise, it was found that Ni²⁺ had a higher activity in MgO than ZnO, suggesting that the activity was influenced by a change in the coordination from octahedral to tetrahedral. Defect chemistry, especially the surface defect structure, is of great importance in understanding the catalytic properties of these materials. The use of metal oxides for the oxidative coupling of methane will be investigated in this thesis using computational techniques.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydrogenation</td>
<td>Cr₂O₃, (Cr,Al)₂O₃, Mo/Al/O</td>
</tr>
<tr>
<td>Selective Oxidation</td>
<td>Fe/Mo/O, Bi/Mo/O, Cu/O, Fe/Sb/O</td>
</tr>
<tr>
<td>NO Oxidation</td>
<td>Perovskites</td>
</tr>
<tr>
<td>Methanol Oxidation</td>
<td>Mo/O, Ag/O</td>
</tr>
<tr>
<td>Hydrocarbon Cracking</td>
<td>Al₂O₃, Si/AlO, Si/Mg/O</td>
</tr>
<tr>
<td>Methanol Synthesis</td>
<td>Cu/Zn/O</td>
</tr>
<tr>
<td>Sulphuric Acid Synthesis</td>
<td>K/V/O</td>
</tr>
</tbody>
</table>

Table 2–3. Reaction types and metal oxide materials which catalyse them.
2.3.1. Metal Oxide Catalysts for the Oxidative Coupling of Methane

2.3.1.1. The Need for Gas Conversion

The past 20 years have seen extensive research into the production of chemicals from, and the conversion into transportable liquids of, natural gas sources.\textsuperscript{48} Although an abundant natural resource,\textsuperscript{4} the remote location of reserves and the difficulties of gas transport to the consumer make many of these reserves commercially unexploitable. In addition, much natural gas is simply "flared off", particularly when it is associated with crude oil production and processing. Consequently, the ability to convert natural gas into liquid fuels or into more useful chemical feedstocks would be both economically and environmentally beneficial.

2.3.1.2. Catalytic Conversion of Methane

Methane, the principal component of natural gas is chemically stable and, although valuable as a fuel, is not a particularly useful feedstock. For example, the commercial route to methanol from methane is via oxidation to CO, CO\textsubscript{2} and H\textsubscript{2} followed by conversion of these products to methanol. Thus processes for the direct conversion via partial oxidation and oxidative coupling of methane to more useful products such as methanol and ethane have received considerable attention.\textsuperscript{49} Since the pioneering work of the 1920s on high pressure gas phase conversions\textsuperscript{50} research has concentrated on developing catalytic processes. In particular, this work has concentrated on the development of catalysts for the oxidative coupling of methane to yield ethane, ethene and higher hydrocarbons\textsuperscript{51} (rather than methanol production).

A large range of catalysts has proved to be active for the partial oxidation of methane;\textsuperscript{49} a selection of the more successful materials is given in Table 2–4.

Indeed, at least two of these catalysts have been evaluated for commercial production at pilot plant scale; a supported manganese oxide\textsuperscript{52} and a lithium promoted magnesium oxide\textsuperscript{53,54}. This latter material has received considerable attention, due to its good performance and relative simplicity and has, as a result, been extensively investigated in both fundamental and applied studies.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group IIA Metal Oxide</td>
<td>MgO, Li/MgO, Bi/MgO, CaO, Na/CaO, SrO, BaO</td>
</tr>
<tr>
<td>Lanthanide Oxides</td>
<td>La\textsubscript{2}O\textsubscript{3}, Li/La\textsubscript{2}O\textsubscript{3}, Sn\textsubscript{2}O\textsubscript{3}, Li/Sm\textsubscript{2}O\textsubscript{3}, Gd\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2},</td>
</tr>
<tr>
<td>Transition Metal Oxides</td>
<td>MnO\textsubscript{2}/\alpha-\text{Al}<em>{2}O</em>{3}, MnO\textsubscript{2}(MnO\textsubscript{2}/SiO\textsubscript{2}), Li/ZnO</td>
</tr>
<tr>
<td>Group III, IVA and VA Metal Oxides</td>
<td>Tl\textsubscript{2}O\textsubscript{3}/\alpha-\text{Al}<em>{2}O</em>{3}, SnO\textsubscript{2}/SiO\textsubscript{2}, PbO/SiO\textsubscript{2}, Bi\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>Complex Metal Oxides</td>
<td>SrCe\textsubscript{0.9}Yb\textsubscript{0.1}O\textsubscript{2.95}, SrCeO\textsubscript{3}, PbMoO\textsubscript{4}, Bi\textsubscript{2}Sr\textsubscript{2}O\textsubscript{7}, LiFeO\textsubscript{2},</td>
</tr>
</tbody>
</table>

\textit{Table 2-4. Metal Oxides for the oxidative coupling of methane.}\textsuperscript{49}

2.3.2. \textit{MgO based Catalysts}

The research on MgO based catalysts has included a number of detailed studies of the nature of the active sites and the reaction mechanism for methane conversion. The presence of lithium for optimal activity appears crucial. The solution of Li\textsuperscript{+} in MgO leads to a decrease in surface area and a dramatic increase in both activity and selectivity for C\textsubscript{2} hydrocarbons.\textsuperscript{55,56} Even very low concentrations (ca. 0.4\% by mass) result in this behaviour.\textsuperscript{57} Extensive e.p.r. spectroscopy studies by Lunsford and co-workers\textsuperscript{55,58-63} have shown the presence of oxygen holes (O\textsuperscript{−}) as a surface species. These holes are stabilised by the formation of [Li\textsuperscript{+}O\textsuperscript{−}] centres, known as lithium trapped holes; they shall be denoted as [Li\textsuperscript{+}]\textsuperscript{−} for the remainder of this work. Evidence of methyl radicals during conversion and the direct correlation of the concentration of these radicals with the concentration of [Li\textsuperscript{+}]\textsuperscript{−} has led to the conclusion that the reaction proceeds by the abstraction of a hydrogen from methane by the oxygen holes,
followed by radical combination to form ethane. Furthermore, it has been demonstrated that this is the rate limiting step.

Although many of the fundamental processes in the partial oxidation reaction over MgO have been identified, many questions remain unanswered. In particular the location, activity and mobility of the active sites and other defect centres on the catalytic surface are not well understood. The reaction energy pathway of the hydrogen abstraction has previously been investigated using quantum mechanical techniques. However, the effect of surface relaxation and lattice relaxation around defects was not considered. These relaxations may have a considerable effect on the calculated enthalpies, activation barrier and the transition state geometry of the reaction. The addition of chloro species to numerous materials has been effective in increasing catalytic activity and is found to be particularly effective in Li/MgO. However, little is known about the cause of this effect or the effect of chlorination on the structure of the catalyst. These topics will be addressed in this thesis.

2.4. Theoretical Applications in Heterogeneous catalysis

With advances in methodologies and the availability of large-scale computational resources the application of computational modelling to solids and catalysts is becoming more widespread. These techniques have been applied in numerous fields of study. Examples include: assisting in the interpretation of experimental data (for example the refinement of structural data), the investigation of surface structure and of surface impurities, the determination of active sites and the elucidation of reaction pathways and intermediates. This thesis will apply a range of computational techniques to specific problems in both metal oxides and microporous solid catalysts. In particular we will report computational studies of the effect of template
molecules during zeolite synthesis, the structure of active sites in zeolites, the structure of metal oxide surfaces and defect chemistry at these surfaces, and an investigation of reactions at metal oxide surfaces.

2.5. References


(23). S.J. Miller, US Patent 5,135,638


Chapter 3

Atomistic Simulation Theory and Methodologies
3.1. Introduction

Matter at the atomic level can be modelled by constructing a suitable description of the potential energy of the system with respect to its structure parameters. Such models can then be applied to the investigation of the properties of the system. In contrast to quantum mechanical methods (described in Chapter 4), these techniques neglect the explicit treatment of the electrons. Nevertheless, these methods can be applied successfully to a wide range of chemical problems, ranging from the solid state \( ^1 \) to large organic molecular systems. \( ^4 \) Different approaches to the construction of the potential model are used depending on the chemical nature of the system under consideration. Here we will describe the Born model and molecular mechanics approaches. We will then review methods based on these two potential models for investigating bulk and surface structure, defect chemistry and intermolecular interactions.

3.2. Interatomic Potentials as a Description of Interatomic Forces

Interatomic potentials describe, in an analytical or numerical form, the forces between atoms. By evaluating these forces it is possible to calculate the total energy of the system and also to minimise this energy with respect to the nuclear coordinates. The potential model usually consists of two parts, the first describing the long range (Coulombic) interactions and the second describing the short range interactions (such as Pauli repulsion and van der Waals attraction). A variety of potentials forms are available, describing not only two body forces but also higher terms involving three and four atoms. These potentials forms and their derivation will be discussed later in this chapter.

Of the several classes of potentials, two main categories are relevant to this thesis. The first approach considers the constituents of the system as atoms or ions interacting by means of long and short range forces. This model is
particularly useful for extended solids and ionic systems. Models based on the Born model of the solid use this approach and will be further discussed in detail. The second approach is based on a description of the system in terms of a covalently bonded network. Here, the total energy is defined by potentials describing bond lengths, bond angles, torsional angles and higher order cross-terms. This is known as the molecular mechanics forcefield approach. This forcefield definition is most useful for describing molecular systems and has extensive applications in organic chemistry and biochemistry.

Although the parameters for both approaches can be derived in broadly similar ways, there is a distinct difference in the definition of the total energy of the system. The ionic model has a definite unique zero point of the energy of the system, i.e. when the constituent ions are infinitely separated. However, the energy of the equilibrium state of a particular molecule using a molecular mechanics forcefield is unique and bears no relationship to the energy of a different molecule. Thus it is only strictly correct to compare the energies of different conformers of the same structure and not of different systems.

The potential forms and the techniques used to derive them will now be described in detail.

### 3.2.1 Interatomic Potential Functions for Ionic Born Model Systems

The summation of the long range Coulombic and the short range interactions over all atoms in a system gives the total energy of the system:

\[
E = \sum_{i<j} \frac{q_i q_j}{r_{ij}} + V_i \quad (3.1)
\]

The Coulombic term corresponds to the monopole-monopole electrostatic terms of the system as defined by the Born model and neglects higher terms (such as dipole-dipole interactions). This is the simplest charge model and an adequate
description for most ionic systems. More sophisticated charge descriptions (such as those based on distributed multipoles\(^6\)) are available for describing the electrostatic interactions between covalently bonded molecules and also systems where it is apparent that a spherical description of the charge is inadequate (such as in ions which exhibit Jahn Teller distortion). However, for the systems considered in this thesis, the spherical point charge model is considered sufficient to provide an accurate description of the charge interactions. The short range forces consist of two-body, three body and higher order terms. In ionic systems, inclusion of only the two body terms is often an acceptable approximation. These terms combine the repulsive and attractive forces acting between ion pairs. The repulsive interactions arise from the overlap of neighbouring electron clouds, resulting in nuclear repulsion and repulsion as a result of the Pauli exclusion principle. The attractive short range forces result from dispersion in the formation of instantaneous dipoles; the van der Waals interaction, whose magnitude is dependent on the polarisability of the ions concerned and the covalency of the system. These short range forces are commonly described by the following analytical function (often known as the Buckingham potential\(^7\)):

\[
E_{ij}(r) = A_j \exp \left( \frac{-r_j}{\rho j} \right) \frac{C_{ij}}{r_j^6}
\]  

(3.2)

The exponential term can be considered to represent crudely the size and 'hardness' of the ion whilst the \(r^6\) term represents the van der Waals interactions. If the polarisability of the ion is small this term can be omitted reducing the expression to a Born-Meyer\(^8\) potential. For a better description of the interaction between ions bonded by a partly covalent bond a Morse potential can also be used:

\[
E_{ij}(r) = D \left[ 1 - \exp \left[ \alpha (r - r_0) \right] \right]^2,
\]  

(3.3)
where $D$ is the dissociation energy of the bond, $r_0$ the equilibrium bond length and $\alpha$ is a constant determined from spectroscopic data which represents the degree of anharmonicity of the potential. Furthermore, in materials that have a degree of covalent character, it is often necessary to include a three-body term to model the directional character of the bonding. This is usually in the form of a harmonic potential:

$$E_{ii}(\Theta) = \sum_{i,j\neq i} k_{ij}(\Theta_{ij} - \Theta_{ij}^0)^2,$$  \hspace{1cm} (3.4)

where $\Theta$ is the angle between the bond between atom pairs $ij$ and $il$ and $\Theta_{ij}^0$ denotes the equilibrium bond angle. Four body terms are important in the treatment of organic systems and are discussed later in relation to molecular mechanics forcefields.

Thus, we can expand equation 3.1 to give a typical expression for the energy in an ionic solid:

$$E = \sum_{i,j} \frac{q_i q_j}{r_{ij}} + \sum_{i,j} A_{ij} \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C_{ij}}{r_{ij}^6} \sum_{i,j\neq i} k_{ij}(\Theta_{ij} - \Theta_{ij}^0)^2.$$  \hspace{1cm} (3.5)

$q_i, q_j$ charges on atoms $i$ and $j$

$r_{ij}$ separation of atoms $i$ and $j$

$A_{ij}, \rho_{ij}, C_{ij}$ Buckingham parameters for the ion pair $ij$

$\Theta_{ij}$ Angle between the bond between atom pairs $ij$ and $il$, $\Theta_{ij}^0$ denotes the equilibrium bond angle

$k_{ij}$ Three body force constant
3.2.1.1 The Ewald Summation

The electrostatic terms with their \( r^{-1} \) dependency are long-range in nature and the summation converges slowly in real space as \( r \) increases and is furthermore conditionally convergent. Conversely the short range terms converge rapidly, and a cut-off distance can be employed to further minimise computational time. Thus direct summation of the Coulombic energy is both unreliable and computationally expensive. The method of Ewald\(^9,10\) provides a solution to this problem. This technique resolves the electrostatic sum into two parts. The first (at short distance) is summed in real space, whilst the second (at longer distance) is computed in reciprocal space. The basis of the method is that the charge about an ion site is described by a Gaussian charge distribution. These leads to an expression for the electrostatic contribution to the total energy given by:

\[
E_{ES} = \frac{1}{2} \frac{4\pi}{N v_{\text{cell}}} \sum_\sigma \frac{G^2}{\eta^2} \sum_{ij}^n q_i q_j \exp\left(-G \cdot \frac{r_{ij}}{2N v_{\text{cell}}}\right) + \frac{1}{2} \sum_{ik}^{\sigma'} \sum_{jk}^{\sigma'} q_i q_j \frac{\text{erfc}(\eta r_{ij})}{r_{ij}}
\]

where

\[N\] is the number of ions in the unit cell

\[v_{\text{cell}}\] is the unit cell volume

\(G\) are the reciprocal cell vectors

\(l\) are the real space cell vectors

\(\text{erfc}\) is the complementary error function \(\frac{2}{\pi} \int_\gamma^\infty \exp\left(-e^2\right) dt\)
\( \eta \) is a constant which determines the partition and convergence of the two parts of the summation. This has been given by Catlow and Norgett\(^{11} \) as being optimal when

\[
\eta = \sqrt{N} \frac{\sqrt{\pi}}{\sqrt{v_{\text{cell}}}} \tag{3.7}
\]

and the real space and reciprocal space summation cut-offs as \( \frac{\sqrt{\log C}}{\eta} \) and

\( \frac{\eta \sqrt{\log C}}{\pi} \) respectively, where \( C \) is the Madelung summation accuracy; typically \( 10^6 \).

### 3.2.1.2 The Shell Model of Ionic Polarisability

Ionic polarisability is included in these simulations by means of the shell model of Dick and Overhauser.\(^{12} \) This simple mechanical treatment of polarisability is illustrated in the figure 3-1.

---

**Figure 3-1. Illustration of the shell model of ionic polarisability**
The polarisable electron cloud is represented by the massless shell which has a charge of $q_{shell}$ and is connected to the core (which bears the mass of the ion) by a harmonic spring. The self energy of the polarised ion is thus given by

$$E_{pol} = \frac{1}{2} k_{shell} x^2$$  

and the polarisability by

$$\alpha = \frac{(q_{shell})^2}{k_{shell}}$$

where $x$ is the core-shell displacement from the zero point, $k_{shell}$ is the harmonic force constant and $q_{shell}$ the charge on the shell. The sum of the core and shell charge is the total charge on the ion.

The crucial feature of the method is the coupling of the polarisation term to the short range interaction by specifying the short range forces as acting between shells. The shell model is only included on those ions which possess a significant free ion polarisability and whose electron clouds will be susceptible to deformation.

The use of central forces in the Born model does not give a fully satisfactory description of ionic polarisability. Primarily, it cannot account for the Cauchy violation in face centred cubic structures. That is, the model will always yield $C_{11}=C_{44}$ at 0K. To account for this, extensions to the shell model of polarisability have been developed to account for this by allowing distortion of the shell. Examples are the ‘breathing shell model’ of Schroder$^{13}$ which allows spherically symmetric distortion of the shell and the model of Sangster$^{14}$ which allows ellipsoidal distortions.

Chapter 3.
3.2.2 Molecular Mechanics Forcefields - a bond based approach

Molecular Mechanics defines the system by its bonding - the connectivity of the constituent centres. The bonds in the system are the basis of the functions which will be summed to give the total energy. These will include terms related to bond length, bond angle and torsion angles in addition to the long range Coulombic and van der Waals terms. The analytical terms used in such forcefields take many forms but, in all cases they represent energy changes as a function of deviation from equilibrium values.

A typical expression for the total energy of a system is given as:

$$E_{\text{total}} = \sum_i \sum_{j \neq i} q_i q_j \frac{A_{ij}}{r_{ij}} + \sum_i \sum_{j \neq i} \left( \frac{A_{ij}}{r_{ij}^6} - \frac{B_{ij}}{r_{ij}^{12}} \right) + \sum_b k_b (b - b^*)^2 + \sum_{\theta} k_{\theta} (\theta - \theta^*)^2 + \sum_{\phi} k_{\phi} \left(1 + \cos\left\{ n\phi - \phi^* \right\} \right)$$

(3.10)

$q_i, q_j$ effective charges on atoms $i$ and $j$

$A_{ij}, B_{ij}$ van der Waals interaction parameters for ion pair $i$ and $j$ acting at a distance of $r_{ij}$

$b, b^*$ bond length, equilibrium bond length

$k_b$ bond length force constant

$\theta, \theta^*$ angle, equilibrium angle

$k_{\theta}$ bond angle force constant

$\phi, \phi^*$ torsion angle and equilibrium torsion angle

$k_{\phi}$ torsional force constant

Cross terms are included to ensure no interactions are included more than once and that coupled interactions are eliminated. The terms in equation 3.10 are described graphically in figure 3-2.
Figure 3-2. Diagrammatic representations of the interactions between particles in a typical molecular mechanics forcefield.

The parameters can be derived from experimental properties, usually of a set of molecules similar to those to which the forcefield is to be applied. Indeed, no general forcefield exists which is capable of describing all possible interactions. Thus, when using a particular forcefield, care should be taken that it is not being used outside the range of interactions for which it is parameterised. There are a large number of forcefields available, each suitable for a particular field of study. For example, the AMBER\(^1\) forcefield has been parameterised using structures which are present in proteins. A more general forcefield, MM2\(^4\) was fitted to much larger range of systems. However, the transferability of such fitted molecular mechanics parameters can be questioned. With the increasing
availability of quantum mechanical methods for routine calculation of structure and physical properties, there is an increase in the number of forcefields based on \textit{ab-initio} calculations.\textsuperscript{16} It is now possible to derive parameters which are based not only on equilibrium data (such as that from empirical fitting) but also on data from excited states. The potential parameters are fitted to \textit{ab-initio} energy hypersurfaces\textsuperscript{16} of relevant molecular systems. Thus, using suitable basis sets and the applicable correction factors\textsuperscript{+} a more rigorous forcefield can be constructed. Examples are the cff91\textsuperscript{16,17} and cff91_czeo\textsuperscript{18} forcefields which will be used in this thesis.

### 3.3. Energy Minimisation Techniques

From the models presented in the previous sections we can calculate the potential energy of the system. To determine equilibrium geometries this energy must be minimised with respect to all the nuclear coordinates, which involves locating a point on the potential energy surface where the forces on all the atoms are zero;

\[
\frac{\partial V}{\partial r} = 0, \quad (3.11)
\]

where \( V \) is the potential energy and \( r \) is the coordinate system. To achieve this we employ iterative numerical procedures which use the derivatives of the energy (both first and second derivatives in some cases) to locate the energy minimum. Numerous algorithms are available which differ primarily in the derivative information which they require. These include Newton-Raphson,\textsuperscript{19}

\textsuperscript{+} For example at the Hartree-Fock level, the frequencies of vibrational modes are overestimated by approximately 10% which will be reflected in the bond stretching force constants derived for inclusion in the forcefield. However, the systematic nature of the error allows correction terms to be applied.
Steepest Descent\textsuperscript{20} and Conjugate Gradient methods,\textsuperscript{20} the relative merits of which will be discussed below. One important factor which must be considered in the selection of a minimisation technique and in the interpretation of results from such a calculation is the ability of the method to avoid local minima and transition states. The potential energy surface can contain multiple local minima (see Figure 3-3) which satisfy the minimisation criteria. Similarly at a transition state, the first derivative of the energy is again zero. The relative expense of the various techniques is also an issue; for example Steepest Descents is faster than Newton-Raphson since it requires only the first and not the second derivative. Furthermore, the ability of the algorithms to converge quickly is also important. Certain algorithms are poor at rapidly minimising a system from a starting point far from the minimum (Conjugate Gradients for example) and should only be used when the system is close to the minimum. Similarly, techniques which can quickly optimise poor starting points (e.g. Steepest Descents) are usually poor at accurately locating the global minimum. Therefore careful selection of the minimisation technique (with switching between techniques being a good compromise) is important.

\begin{center}
\textbf{Figure 3-3. Representation of an Energy Hypersurface showing possible minima and transition states.}
\end{center}
The minimisation techniques are now outlined in order of complexity and computational expense.

3.3.1 Steepest Descent

The value of the vector of variables $x$ at the $(i+1)$th iteration is related to its value at the $i$th iteration by

$$
\bar{x}_{(i+1)} = \bar{x}_{(i)} - \alpha \left( \frac{\partial E}{\partial x} \right)_{(i)},
$$

where the constant $\alpha$ is chosen at each iteration to improve the efficiency of the procedure. This evaluation of the function is fast, requiring only the first derivative, but is slow to converge. However, the low computational overheads make it ideal for large systems and systems which are a long way from their minimum.

3.3.2 Conjugate Gradient

Here, the gradient at the previous iteration is used to increase the speed of convergence:

$$
\bar{x}_{(i+1)} = \bar{x}_{(i)} + \alpha \bar{S}_{(i)},
$$

where $\alpha$ is a constant as in Steepest Descents and

$$
\bar{S}_{(i)} = -\bar{g}_{(i-1)} + \beta_i \bar{S}_{(i-1)},
$$

and $\beta_i = \frac{\bar{g}_{(i-1)}^T \cdot \bar{S}_{(i-1)}}{\bar{g}_{(i-2)}^T \cdot \bar{g}_{(i-2)}}$.

where $\bar{g}_{(i)}$ are the individual derivative vectors with respect to coordinates and the T notation indicates the transpose of the vector. As with the Steepest
Descent only the first derivative is required to be calculated although previous values must now be stored. This results in improved convergence.

3.3.3 Newton-Raphson

By using the second derivative of the energy we can achieve improved convergence:

$$\mathbf{x}_{(i+1)} = \mathbf{x}_{(i)} - \mathbf{H}_{(i)} \cdot \mathbf{g}_{(i)} \tag{3.16}$$

where $\mathbf{g}_{(i)}$ is as previously defined and $\mathbf{H}_{(i)}$ is the inverse of the second derivative matrix $\frac{\partial^2 E}{\partial x_r \partial x_h}$, also known as the Hessian matrix. This is usually not recalculated at each interaction but updated according to set rules such as those of the Davidson-Fletcher-Powell algorithm. To avoid degradation of the accuracy of the Hessian this is usually recalculated every 10-20 iterations, depending on the course of the minimisation. Although requiring significantly more calculations per iteration (for the Hessian matrix) than the previous methods, the rapid convergence makes this an attractive method. However, the additional memory overhead is significant for large systems.

3.4. Derivation of Potential Parameters

The availability and accuracy of suitable interatomic potentials is crucial to the simulation of atomistic properties of materials. There are numerous approaches to the derivation of such parameters which shall be outlined here. Derivation of molecular mechanics parameters is usually achieved by empirical fitting to the properties of a set of representative molecules and functional groups, or by
fitting to an \textit{ab-initio} energy hypersurface. Only potentials pertaining to Born model simulations were derived for use in the work presented in this thesis and the following discussion on parameter derivation will be restricted to procedures related to such models. However, the methods for deriving parameters for molecular mechanics forcefields are very similar - the reader is referred elsewhere for details, for example Burkett and Allinger\textsuperscript{4} and Maple \textit{et al.}\textsuperscript{16}

3.4.1 Empirical Fitting

The potential parameters are fitted to known structural properties of systems. Other physical properties such as lattice energy, dielectric constants and elastic constants can also be used. The parameters are adjusted in an iterative procedure to achieve the best fit to the experimental properties. The resulting potentials often model very accurately the systems to which they were fitted (naturally) and also point defects in this lattice and closely related systems. However, care must be taken when transferring potentials to other systems, particularly if the equilibrium interionic distances differ significantly between the system in which the potential is fitted and that in which it is being used. This is a consequence of the fitting procedure only sampling a small portion of the interaction energy surface. Simultaneous fitting of potentials to a range of systems is often used to reduce this problem and to obtain self consistent parameters\textsuperscript{22}. 

3.4.2 Ab-initio Energy Surface Fitting

Energy hypersurfaces generated from *ab-initio* calculations are increasingly being used to generate potential parameters for simulation techniques.\(^{23,24}\) For solids, these calculations can be based on infinite solids (utilising periodic ab-initio codes such as CRYSTAL\(^ {25}\)) or on finite clusters.\(^ {26}\) These potentials have the advantage that not only are they derived from first principles but can also investigate non-equilibrium geometries to improve the performance of the potentials when investigating systems in which there is significant deviation from perfect lattice equilibrium spacings as in *e.g.* defects.

3.4.3 Electron Gas Interactions

This method was used extensively in this thesis and will be discussed in more detail. As in the above method, the interactions of two atomic species are calculated at a range of interionic distances, to which a potential is fitted. The methodology used is based on the work of Wedepohl\(^ {27}\) which was developed by Gordon and Kim\(^ {28}\) and for which an useful implementation is available from Harding and Harker.\(^ {29}\) The electron density is treated as a degenerate fermi-gas and the electron density is assumed to be the sum of the individual spherical atomic densities. It is also considered to change slowly with distance and can therefore be treated as a homogeneous electron gas. Although this is clearly not valid for regions close to the nuclei of the ions, these regions contribute little to the interaction energy. However, this approximation does hold for the valence electrons which are the major contributors to the interaction energy. In application to solids the electron densities of the isolated species are calculated in the presence of a suitable Madelung well to simulate the lattice. Whilst this has little effect on the electron density of small cations, it is important when
considering highly polarisable anions. For example, the O\textsuperscript{2-} ion is unstable as a free ion; the second electron is unbound with respect to the O\textsuperscript{-} ion. However, this ion is stabilised in the presence of a suitable crystal field.

The energy of two interacting ions can be expressed as

$$E_{ij} = E[\rho_i(r) + \rho_j(r)] - E(\rho_i(r)) - E(\rho_j(r)),$$

(3.17)

where the first term is the energy of the interacting ions and the second and third terms the energy of the isolated ions; \(\rho\) is the electron density. The energy of the interacting ions can be expanded as;

$$E[\rho_i(r) + \rho_j(r)] = E_{\text{elec}} + E_{\text{kin}} + E_{\text{exch}} + E_{\text{corr}} + E_{\text{disp}}$$

(3.18)

\(E_{\text{elec}}\) is the electrostatic interaction. \(E_{\text{kin}}\) is the kinetic energy and is proportional to \(\frac{5}{3}\rho\) where \(\rho\) is the electron density. The exchange energy \(E_{\text{exch}}\) is proportional to \(\frac{4}{3}\rho\). The correlation energy \((E_{\text{corr}})\) and the dispersive terms \((E_{\text{disp}})\) are similarly approximated (see Harding and Harker\textsuperscript{29} for further details).

Although the method is relatively crude and tends to overestimate lattice parameters and interatomic distances, several studies using this method have obtained good results when applied to both perfect and defective systems.\textsuperscript{30,31} It has the advantage that potentials for impurities and lattice ions with different oxidation states can be calculated in the host lattice Madelung field. Thus, the parameters are all self-consistent, in contrast to empirically derived potentials which may be unreliable when transferred to other systems.
3.5. Simulation Techniques based on the Born Model

The work presented in Chapters 6 and 7 of this thesis will use atomistic simulation techniques based on the Born model. These methods allow the calculation of the properties of both perfect lattices and of defect systems. The techniques are applied to both the bulk and to surfaces. Properties which can be determined include: (i) perfect lattice energies and geometries, (ii) perfect lattice physical properties such as elastic constants and dielectric properties, (iii) vibrational frequencies, (iv) surface structure and (energetic) stability, (v) energetics and lattice relaxation about point defects and (vi) studies of defect siting at surfaces and defect migration.

The techniques as applied to both bulk and surface simulation will be outlined in the next section.

3.5.1 Perfect Lattice Simulations

3.5.1.1 Bulk Systems

The lattice energy of a crystal can be calculated using the periodic boundary conditions scheme using the Ewald summation and direct summation of the short range terms. This energy can be minimised with respect to the internal coordinates within a fixed unit cell (constant volume minimisation) or with respect to coordinates and the unit cell parameters (often referred to as constant pressure minimisation). Calculation of the first and second derivatives of the energy with respect to atomic positions can yield the elastic constants and the dielectric properties of the material. Further details are supplied elsewhere.\textsuperscript{3,32}
3.5.1.2 Surfaces

The creation of a crystal surface essentially removes one of the crystal dimensions. The lattice simulations must therefore be modified to allow the calculation of surface energies and structure. The crystal is defined as a parallelepiped which is split into two regions (Figure 3-4). This is repeated to infinity in the plane of the surface. The ions in region A are relaxed to zero force, whilst those in region B are kept rigid. Care must be taken to ensure that the depth of region A is sufficient so that the ions at the bottom of region A do not move. Furthermore, the unit cell dimensions of the structure cannot change and therefore the unit cell must be that which has minimum energy in the bulk with the potential parameters used.

The Ewald method requires 3 dimensional periodicity. The creation of the surface breaks this condition. Thus, modifications have been made by Parry to account for this.\textsuperscript{33,34} These methods have been implemented in the MIDAS code\textsuperscript{35} and more recently in the MARVIN code.\textsuperscript{36}

3.5.2 Defective Lattice Simulations

Defects in solid materials play a crucial role in the chemistry and structure of catalysts.\textsuperscript{37} They include both point defects and extended defects such as dislocations and shear planes. We shall be primarily concerned with the former class of defect, which consists of vacancies, substitutionals, interstitial species and ‘electronic defects’. Electrons and hole species (positive charges) on lattice or interstitial sites are typical electronic defects. To model such species we must be able to treat the relaxation of the surrounding lattice. The models constructed thus far have been based on perfect periodic systems - for both bulk (3-dimensional periodicity) and surfaces (2-dimensional periodicity). Although
techniques based on super-cells can be used, these require large simulations and are therefore computationally expensive (although this is a decreasing concern), as a consequence of the long range Coulombic forces which dominate the relaxation process. Thus a scheme must be used which allows us to treat an isolated defect centre (at infinite dilution) within an infinite lattice. This scheme will now be described.

Figure 3-4. Representation of surfaces as implemented in the MARVIN and MIDAS surface simulation codes.
3.5.2.1 Bulk Systems

The methodology\textsuperscript{11,39,40} considers the defective lattice as consisting of two regions (illustrated in Figure 3-5). The two regions are considered at different levels of approximation.

![Diagram showing two regions: Region I, Region IIa, and Region IIb](image)

**Figure 3-5. The two-region approach to defect calculations in bulk solids.**

The inner region (region I) is defined as a sphere centred on the defect(s) in question and is treated atomistically; that is the coordinates of all the ions within this region are relaxed explicitly to zero force. The outer region (region II) extending to infinity, will respond to the electric field of the defect and is treated by the continuum approach of Mott and Littleton.\textsuperscript{39} The total energy is written as the sum of three terms:

\[
E_{\text{def}} = E_1(x) + E_2(x, y) + E_3(y) \tag{3.19}
\]

Here, \(E_1\) is dependent on the displacements of the coordinates \(x\) in region I. \(E_2\) is the interaction energy between regions I and II. \(E_3\) is dependent on the...
displacements \( y \) of the ions in region II and is the energy of the remainder of the crystal (to infinity). This component cannot therefore be evaluated directly. However, if it is assumed that \( E_3 \) is a harmonic function of the displacements in region II

\[
E_3(y) = \frac{1}{2} y \cdot A \cdot y, \tag{3.20}
\]

where \( A \) is a force constant matrix, and that at equilibrium \( (\partial E_2(y)/\partial y)_x = 0 \) then

\[
\left( \frac{\partial E_2}{\partial y} \right)_x = -A \cdot y. \tag{3.21}
\]

Therefore substitution into the expression for \( E_3 \) allows us to express the total defect energy as consisting only of interactions within region I and those between region I and II.

Charged defects are modelled by splitting region II into two further regions. The ions in inner region (IIA) are fixed at their perfect lattice sites and are used only in calculating the interaction energies with the ions of region I. The outer region (IIB) is treated as a continuum which responds to the total charge of the defect. This approach (the Mott-Littleton approach\textsuperscript{39}) relates the polarisation of the crystal to the distance \( r \) from the defect:

\[
P = \frac{V}{4\pi} \frac{qr}{r^3} \left( 1 - \frac{1}{\varepsilon_0} \right) \tag{3.22}
\]

where \( V \) is the unit cell volume and \( q \) the effective defect charge. This leads to a \( r^{-4} \) term which diminishes with increasing region I size.

This now gives a calculation scheme as follows:

1. The energy of region I is minimised to give the equilibrium positions \( x \).

2. The Mott-Littleton calculation is performed, to evaluate the response of the ions in region IIA.
3. E1(x) is calculated by explicit summation.

4. E2(x,y) and its derivatives are evaluated for the region IIA ions.

5. The Mott-Littleton displacements of the remainder of the system (region IIB) are calculated assuming a continuum response to the net defect charge.

Minimisation techniques are applied to this scheme to produce the final displacements and defect energy. The Newton-Raphson algorithm is favoured for its rapid convergence. These techniques are embodied in the CASCADE code and this code has been used for all the bulk defect calculations presented in this thesis.

3.5.2.2 Surfaces

The methodology outlined above for bulk defects is modified for surface calculations. The spherical regions of the bulk method are replaced with hemispherical regions (illustrated in figure 3-6). The Mott-Littleton expressions are modified to treat the regions as combinations of planes and volume integrals. The CHAOS code based on this approach was used for the surface defect calculations presented here.

![Figure 3-6](image)

Figure 3-6. The two-region approach to defect calculations modified for the treatment of the surfaces of solids.
3.6. Simulation techniques based on Molecular Mechanics

The type of methods used in calculations using molecular mechanics forcefields descriptions of matter are very similar to those for the Born model methods. Chapter 5 will investigate the interaction of molecules with microporous materials and we will utilise molecular mechanics to describe the molecular interactions. Energy minimisation techniques will be applied to both molecular (or finite lattice) systems and to periodic systems. Further methodological details will be discussed in section 5.3 of Chapter 5.

3.7. References


Chapter 4

Quantum Mechanical Theory and Methodologies
4.1. Introduction

The rapid increase in computational power† and the availability of this power to the theoretical chemist has led to an increase in the use and the further development of ab initio techniques based on solving the Schrödinger equation to obtain the wavefunction of the system studied. This increase in computational power has meant that these techniques, which incorporate a full treatment of the electronic structure (at varying levels of approximation) can now be applied, even to large molecular systems and solid state problems.

The techniques of computational ab initio quantum chemistry are complex and extensive. A brief treatment of the fundamental principles is given here together with specific techniques for the treatment of solid state systems. The reader is directed to specialist texts for a more detailed account.1-3

4.2. The Schrödinger Equation

The energy and properties of a stationary state of a molecule can be obtained by the solution of the Schrödinger equation,

\[ H\Psi = i\hbar \left( \frac{\partial \Psi}{\partial t} \right). \]  

(4.1)

If we consider that the wavefunction is not evolving with time we can consider the time-independent Schrödinger equation:

\[ \hat{H}\Psi = E\Psi, \]  

(4.2)

‡ It is estimated that processor power has doubled every year for the past 20 years.
where $\hat{H}$ is the Hamiltonian, a differential operator representing the total energy. $E$ is the numerical value of the energy of the state and $\Psi$ is the wavefunction which is dependent on the position of all the particles and their spin coefficients. The square of the wavefunction $|\Psi|^2$ (since $\Psi$ can be complex) is interpreted as the probability distribution of the particles within the system.

The Hamiltonian is the sum of the kinetic and potential energies of the system:

$$\hat{H} = \hat{T} + \hat{V},$$  \hspace{1cm} (4.3)

where the kinetic energy is the Laplacian

$$\hat{T} = -\frac{\hbar^2}{8\pi^2} \sum_i \frac{1}{m_i} \left( \frac{\delta^2}{\delta x_i^2} + \frac{\delta^2}{\delta y_i^2} + \frac{\delta^2}{\delta z_i^2} \right),$$  \hspace{1cm} (4.4)

with the sum over all particles (nuclei and electrons), $m_i$ is the mass of particle $i$ and $\hbar$ is Plank's constant. The potential energy is simply the Coulombic interactions:

$$\hat{V} = \sum_i \sum_{j<i} \left( \frac{e_i e_j}{r_{ij}} \right),$$  \hspace{1cm} (4.5)

where the sum is over all distinct pairs of particles.

The exact solution of the Schrödinger equation is not possible for all but the simplest systems. Thus the following approximations are made:

4.2.1 The Born-Oppenheimer Approximation

Atomic nuclei move much slower than electrons, due to their mass. Consequently, it is reasonable to suppose that electronic distributions are dependent on the instantaneous position of the nuclei and not on their motion. This is known as the Born-Oppenheimer approximation. Thus the Schrödinger equation is reduced to that of the electrons in a field of fixed nuclei:
where $\Psi^{\text{elec}}$ is the electronic wavefunctions dependent on the electronic positions $r$, and the nuclear coordinates $R$. The electronic Hamiltonian,

$$\hat{H}^{\text{elec}} = \hat{T}^{\text{elec}} + \hat{V}$$

is now the sum of the electronic kinetic energy,

$$\hat{T}^{\text{elec}} = -\frac{\hbar^2}{8\pi^2 m} \sum_i^{\text{electrons}} \left( \frac{\delta^2}{\delta x_i^2} + \frac{\delta^2}{\delta y_i^2} + \frac{\delta^2}{\delta z_i^2} \right)$$

and the Coulombic potential energy,

$$\hat{V} = \sum_i^{\text{electrons}} \sum_j^{\text{nuclei}} \frac{Z_i e^2}{r_{ij}} + \sum_{i,j<i}^{\text{electrons}} \sum_i^{\text{electrons}} \sum_{i,i<j}^{\text{nuclei}} \sum_j^{\text{nuclei}} \frac{Z_i Z_j e^2}{r_{ij}}.$$  

### 4.2.2 Molecular Orbital Theory

Orbitals, $\phi(x, y, z, \xi)$, functions of the position and spin of a single electron, are used to describe the full wavefunction. However, the product of all these one electron orbitals,

$$\Psi = \phi_1(1)\phi_2(2)\ldots\phi_n(n),$$

is not acceptable to describe the many electron wavefunctions since, according to the Pauli principle, the wavefunction must be antisymmetric with respect to the exchange of any pair of electrons. This is achieved by the use of a Slater determinant;

$$\Psi = \begin{vmatrix} 
\phi_1(1)\phi_2(1)\ldots\phi_n(1) \\
\phi_1(2)\phi_2(2)\ldots\phi_n(1) \\
\vdots \\
\phi_1(n)\phi_2(n)\ldots\phi_n(n)
\end{vmatrix}.$$
Thus the wavefunction can now be described as a function of one electron molecular orbitals.

4.2.3 Basis Set Expansion

In performing calculations on molecular systems, a further approximation is usually made. Each molecular orbital is considered to be a linear combination of the atomic orbitals (LCAO);

\[ \phi_i = \sum_{m=1}^{n} c_{im} \chi_m . \] (4.12)

The set of atomic orbitals \( \chi \) is the basis set, which comprises a finite number of one-electron functions known as basis functions. The molecular orbital expansion coefficients \( c_{im} \) are determined by the variational principle which will be discussed below.

A basis set is defined for a given atom in such a way as to have the symmetry properties of its atomic orbitals and be described similarly (such as s, p, d etc. types). The most common expansion function is a combination of Gaussian orbitals;

\[ \chi = x^i y^m z^s e^{-\alpha z} , \] (4.13)

with \( \alpha \) determining the extent of the radial part of the function. The larger the number of Gaussians used to describe the orbital, the more accurate the calculation as the energy tends towards the limits of the Hartree-Fock energy. Gaussian functions do not represent the orbitals as well as other functions such as Slater functions, particularly in that they do not have a cusp at the origin. However, they have an important advantage in that all the integrals can be evaluated explicitly without recourse to numerical integration.
4.3. Hartree-Fock Theory

Hartree-Fock theory, based on the variational principle in quantum mechanics, allows the coefficients of the molecular orbitals to be determined.\(^5,^6\) If \(\Phi\) is an antisymmetric function of the electronic coordinates, then the energy of the system can be expressed as

\[
E' = \int \Phi^* \hat{H} \Phi d\tau .
\]  

(4.14)

The asterisks denotes complex conjugation and the integration is over all electrons. If the function \(\Phi\) is equal to the exact wavefunction, then the Schrödinger equation is satisfied and the energy is the exact energy of the system. If however, \(\Phi\) is any other normalised antisymmetric function, then it can be shown that the energy \(E'\) will be greater than the exact energy \(E\). The variational principle is applied to optimise the coefficients \(c_{im}\) to minimise the value of \(E'\) to be as close as possible to the exact energy \(E\);

\[
\frac{\partial E'}{\partial c_{im}} = 0 \quad \text{for all } m \text{ and } i .
\]  

(4.15)

Roothan\(^5\) and Hall\(^6\) both derived the algebraic expressions for this variational condition. These are known as the Roothan-Hall equations;

\[
\sum_{\nu=1}^{N} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{vi} = 0 \quad \mu = 1, 2, ..., N
\]  

(4.16),

where \(\varepsilon_i\) is the one-electron energy of the molecular orbital \(\psi_i\), \(S_{\mu\nu}\) are the elements of the overlap integral and \(F_{\mu\nu}\) are the elements of the Fock matrix.

The Roothan-Hall equations are modified for different modes of Hartree-Fock calculations primarily in order to treat open shell systems. Three modes are used:
1. Restricted Hartree-Fock (RHF)

This is the normal mode for closed shell system, where it is assumed that the \( \alpha \) and \( \beta \) spin electrons have the same spatial distribution. If an odd number of electrons is considered then the odd electron is partitioned equally between the \( \alpha \) and \( \beta \) HOMOs with a correction being applied to account for this unphysical representation. Consequently no spin density information is available using this method.

2. Unrestricted Hartree-Fock (UHF)

Here two independent Roothan-Hall equations are solved; one for each spin resulting in two distinct sets of molecular orbitals;

\[
\phi_i^\alpha = \sum_{m=1}^{n} c_{im}^{\alpha} \chi_m \quad \text{and} \quad \phi_i^\beta = \sum_{m=1}^{n} c_{im}^{\beta} \chi_m. \tag{4.17}
\]

Thus spin densities can now be determined. UHF suffers from the disadvantage that during the energy calculation, computational resource requirements are twice those for RHF.

3. Restricted Open-shell Hartree-Fock (ROHF)

This mode resembles UHF but the eigenvectors are constrained to be equal for both spins. This method is not used as commonly as RHF and UHF.
4.4. Self-Consistent Fields

The Roothan-Hall equations are solved iteratively, as the Fock matrix is dependent on the eigenfunctions which are being determined. A general scheme for achieving a self-consistent field is given in Figure 4-1. Convergence is achieved when both the change in the energy and the largest change in the density matrix are less than given criteria on consecutive iterations. Convergence difficulties can arise and direct iteration cannot guarantee convergence. Numerous convergence techniques are available, with the most commonly used being level shifting and DIIS.

Poor convergence is often caused by reordering of the HOMO and LUMO. Level shifting counters this by adding large positive constants to the diagonal elements of the Fock matrix. This restricts the reordering of the orbitals and increases the energy of the virtual orbitals. Increasing the shift parameters improves the convergence rate but also slows the calculation. Thus, level shifting is reduced as the SCF procedure progresses.

Direct Inversion in the Iterative Subspace (DIIS) is useful for rapid final convergence once the SCF is sufficiently close to convergence. The current coefficients are optimised using the previous values of the coefficients as constraints. This method leads to rapid convergence, particularly if high accuracy is required. However, the storage requirements of the method can be restrictive.
4.5. Correlation Corrections

The primary deficiency of Hartree-Fock theory is the inadequate treatment of correlation between the motion of electrons. This is as a result of the Hartree-Fock Hamiltonian only containing the average, rather than the instantaneous, inter-electron potential. At the Hartree-Fock limit, the calculated energies are above the exact energy and, by convention, this is termed the correlation energy;
This can result in qualitative deficiencies in the description of electronic structure, particularly when bond dissociation is concerned. For example, at the Hartree-Fock level, dissociation of a hydrogen molecule to infinite separation results in a wavefunction which requires the electrons to spend half their time on one nucleus and the remainder on the other nucleus. There are two general methods for correcting for these errors - configurational interaction (CI)\textsuperscript{10} and Møller-Plesset theory.\textsuperscript{11} Both these methods include contributions from excited states. CI is an alternative method to the HF SCF for determining the wavefunction of the system, and is therefore a much more general method than Møller-Plesset theory which corrects the HF energy. Although in principle CI is applicable to any system, the computational expense of the method makes it less useful. Thus, further discussion will be limited to Møller-Plesset theory.

4.5.1 Møller-Plesset theory\textsuperscript{11}

Møller-Plesset (MP) theory is based on many body perturbation theory.\textsuperscript{12} A perturbation, $\lambda V$, is defined as

$$\lambda V = \lambda (H - H_0),$$

(4.19)

where $H$ is the corrected Hamiltonian, $\lambda$ is a dimensionless parameter and according to Møller-Plesset theory, the zero order Hamiltonian, $H_0$, is the sum of the one electron Fock operators. The groundstate wavefunction and energy of the system described by the Hamiltonian $H$ can now be expanded according to perturbation theory;

$$\Psi_\lambda = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)} + \ldots$$

(4.20)

$$E_\lambda = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \ldots$$

(4.21)

With $\lambda=1$, the series can be truncated to give different orders of MP correlation. The first order MP energy is therefore the Hartree-Fock energy. Typically the
series is terminated after the second term (giving MP2) but treatments up to the fourth term are possible (MP4). Calculation of the correlation energy according to the MP2 treatment will require the same time as was required to calculate the HF energy.

4.6. Geometry Optimisation and Saddle Point Location

On achieving an SCF, the gradient of the energy with respect to the atomic coordinates can be calculated. This allows the geometry to be optimised with respect to the energy. If the gradient is below a pre-set limit then the geometry, within that limit, is a stationary point on the energy surface; the geometry is optimised. If not, then the geometric parameters to be optimised are varied and the procedure repeated. Note that an initial guess of the energy is now not required as the energy at the last point is available. Strict analytical evaluation of the gradients is a formidable task and thus more approximate methods such as the Fletcher-Powell method and approximate gradients obtained numerically by finite-difference methods are frequently used.

Similar techniques are applied for locating transition states (or saddlepoints) in the energy surface. Again, the gradients are minimised - a saddlepoint is also a stationary point on the energy surface. However, in this case the final force constant matrix has a single imaginary eigenvector at the stationary point.

4.7. Treatment of Extended Solids

The treatment of solids can be considered by one of two approaches. Firstly, the systems can be considered in its entirety, that is as an infinite lattice. Suitable modifications are made to the Hartree-Fock equations to take into account the periodic boundary conditions required. This approach can be modified to
accommodate surfaces by treating the system as a series of slabs, suitably separated. This technique has been applied to both surface structure\textsuperscript{16} and absorption processes at surfaces.\textsuperscript{17,18} Alternatively the entire crystal can be represented by a finite cluster of atoms (suitably terminated). Here, it is assumed that this cluster will yield electronic states representative of those of the whole crystal. This technique requires considerably less computational expense than the previous method. It has a further advantage when considering reactions; the reaction does not need to be calculated periodically. However, the treatment of an extended solid by a single cluster ignores the most important force which dominates the energetics of the system - the long range Madelung field. Thus, the cluster method is modified to include this as a potential operator in the Hamiltonian of the cluster. This potential is formed by placing the explicit (quantum mechanical) cluster in a finite array of point charges. This array consists of formally charged points at the lattice sites of the crystal. As the size of this array is increased, the Madelung field is better represented. However, a correct description of the Madelung field would require significantly more points that which can be realistically modelled. The array is therefore terminated at a suitable distance, with the charges at the surfaces of the array being modified to maintain neutrality and an uniform and optimal description of the field. The method for construction of such arrays will now be discussed together with a discussion of the problems associated with describing defective surfaces.

4.7.1 Construction of Point Charge Arrays for MgO surfaces

The general approach to constructing a point charge array for a bulk solid is straightforward. The quantum mechanical cluster is placed in a cubic or spherical array representing the remainder of the lattice. For example, consider the case of a cubic material. A cube of lattice point would be constructed. The charges of the points at the outermost surfaces would be reduced to maintain neutrality so that the charges of a point on the surfaces, edges and corners of the
cube would be a half, quarter and an eighth of the formal charge of the ion at that lattice point respectively. This is illustrated for MgO in Figure 4-2.

![Diagram of a bulk point charge array for MgO](image)

*Figure 4-2. Construction of a bulk point charge array for MgO*

The cubic structure of MgO and the planar nature of the surfaces to be considered (the dominant [1 0 0] surface) thus makes the construction of arrays for surface calculations straightforward. Consider the bulk array previously described (Figure 4-2). If the top layer of the array is removed, it exposes a surface of formally charged lattice points. (Figure 4-3) This is the (1 0 0) surface of the material. The resulting surface block has a zero nett charge and for the unrelaxed array, a zero nett dipole moment. The positions of the outermost points are adjusted to optimise the Madelung energy and field of the atoms in the quantum mechanical cluster to best reproduce the field of the infinite system. This is achieved using a least squares procedure, which is constrained to the crystal symmetry.
The lattice points used are usually those of the perfect crystal with the surface being treated as a simple termination of the bulk. However, it shall be demonstrated in this work that relaxed coordinates from atomistic simulations provide a more realistic representation of the Madelung field. Thus, the lattice points can be extracted from surface calculations performed using the MIDAS, MARVIN and CHAOS codes used in this work.

4.8. Semi-Empirical Quantum Mechanical Methods

Due to the expense of \textit{ab initio} quantum mechanical methods, numerous methods have been developed to reduce the computational effort required. The original semi-empirical method is the CNDO (Complete Neglect of Differential Overlap) method developed by Pople \textit{et al.} which was designed to reproduce the full LCAO-SCF using only a minimal valence basis set. By using the Zero Differential Overlap (ZDO) approximation, the method greatly reduces
the number of integrals required during the construction of the Fock matrix. Empirical parameters are used in the specification of the basis and to correct for approximations made in the overlap integral. The later parameters are optimised to reproduce LCAO-SCF calculations.

Owing to the many shortcomings of the ZDO approximation, Dewar\textsuperscript{22} and Dewar and Thiel\textsuperscript{23} developed a semi-empirical method based on the Neglect of Diatomic Differential Overlap\textsuperscript{24} (NDDO). This approach leads to the MNDO (Minimal Neglect of Differential Overlap) method, which in addition to improving the treatment of the one-centre integrals, is also different to CNDO in that its aim is to reproduce experimental results and not other theoretical results which may in themselves be flawed. This requires a number of parameters for each element which are fitted to heats of formation, ionisation potentials, dipole moments and the gradients of geometric variables for a standard set of molecules, which results in a dramatic improvement in the reliability of results as compared to CNDO. This is particularly the case for molecular ions and systems involving lone pairs. The method is implemented in many codes, such as MOPAC\textsuperscript{25} and AMPAC.\textsuperscript{26}
4.9. References


Chapter 5

Predicting The Templating Ability Of Organic Molecules For The Synthesis Of Microporous Materials
5.1. Summary

In this chapter a combination of several computer modelling techniques have been applied to investigate the ability of organic molecules to template microporous materials. From the results of a study of the interaction between templates and framework structures it is shown that the efficacy of a template can be rationalised in terms of the energetics of the host-template interactions. Comparison between the calculated and experimental geometries of the template / framework combinations are in excellent agreement, demonstrating the ability of the techniques used to locate templates within microporous materials. Furthermore, it is shown that it is possible to select templates for a given framework on the basis of these calculations. The procedures used can therefore successfully identify optimum templates for a given host. Finally, the techniques will be applied to investigate a number of specific systems. First, the effect of the template on the unit cell dimensions will be considered by studying the synthesis of NU-3 with two templates. The study of templates in aluminophosphate microporous materials will then be considered and we attempt to design a template to favour the synthesis of a new structure.

5.2. Introduction

The synthesis of microporous materials usually involves crystallisation from a gel medium under hydrothermal conditions. These gels are multicomponent systems containing typically aluminosilicate (or aluminophosphate) species together with solvent (usually water) and a base to regulate the pH. The use of organic bases during the synthesis of clathrasils, zeolites, and other molecular sieves such as aluminophosphates, is widespread. A particular motivation is their apparent templating effect.\(^1\) However, the complex and varied conditions in such syntheses has given rise to several theories of the role of such organic molecules in the crystallisation process.\(^2\) The early work of Barrer and Denny\(^3\) demonstrated that the addition of an organic hydroxide (in this case
tetramethylammonium hydroxide) as the base component of the synthesis gel produced new materials. Furthermore, there are materials which can only be synthesised in the presence of very specific templates. The use of such additives also modifies the rate of crystallisation during synthesis and the morphology of the final product. The crystallisation rate can also be optimised by modification of the base component. These additives shall be known as templates for the remainder of this chapter.

Microporous materials are metastable, and as a consequence the relative importance of the thermodynamics and kinetics of formation is crucial. Ostwald’s law of successive transformation suggests that (thermodynamically more stable) dense phases will result with increasing crystallisation time. Although this appears straightforward for reaction mixtures involving only silica, alumina and inorganic cations the additional stabilisation of structures by template molecules can have a significant effect. For example an aluminosilicate gel of a particular composition shows the following transformation sequence;

$$\text{amorphous} \Rightarrow \text{faujasite} \Rightarrow \text{ZSM-4},$$

whilst the addition of tetramethylammonium to the same gel results in

$$\text{amorphous} \Rightarrow \text{faujasite} \Rightarrow \text{gismondine} \Rightarrow \text{Na-P}.$$  

In many systems the absence of a template in the crystallising gel will lead to the formation of amorphous or dense materials under the same conditions, again highlighting the importance of the template.

Templates are not only occluded within the cages and pores of the microporous materials, but they are also crucial for the formation of many framework types. However, the extent to which the template affects the process is dependent on the structure of the template and other aspects of the gel composition. Certain templates (such as methanol and ethylenediamine) can be considered purely as space-filling species or co-solvents (in addition to the water usually present) and do not significantly contribute to the structure formation. It may also be the
case that a particular framework is formed by several different template molecules. For example ZSM-5 is formed in the presence of over 30 different template molecules. This effect might be more appropriately described as structure directing rather than true templating. That is, the template is directing the formation of particular structural features and not unique framework structures. However, in general, all the templates suitable for a particular framework will possess similar properties - size, shape, basicity, charge distribution - which direct the gel chemistry toward the formation of particular structural motifs, as demonstrated by the work of Gies and Marler, for both clathrasils and zeolites. In certain (albeit rare) cases a particular framework can only be synthesised with a specific template molecule and in these cases the organic base is behaving as a true template. A prime example is the zeolite ZSM-18 which to date has only been synthesised in the presence of the triquaternary ammonium cation $\text{C}_{18}\text{H}_{36}\text{N}_{3}^{+}$. However, it must also be noted that gel chemistry is crucial, and that the templating action will not be effective unless the correct gel environment is achieved. The effect of hydration of both the framework fragments and of the templates is of particular importance.

Structural details of the location of templates within microporous materials is limited, largely as a consequence of the microcrystalline nature of the materials which makes high quality structure determination, particularly of the location of light atoms (such as carbon and nitrogen), difficult. However, the availability of certain materials as large crystallites and the developments in the possibility of obtaining increasingly good quality structural data from powder X-ray diffraction studies is leading to a steady increase in the availability of suitable structural studies of templates (and other sorbed phases). Details are available from the single crystal X-ray studies of tetrapropylammonium in ZSM-5, of cyclic templates in NU-3 and also of crown ethers in EMC-2. There are, however, several experimental studies of other organic molecules within these materials; primarily, of course, of those of catalytic interest (e.g. the siting of benzene in faujasite and the siting of chloroform and dibromobutane in zeolite Y). Powder X-ray and neutron diffraction and
NMR have all been applied in locating absorbed molecules in microporous materials. Recent advances have also included the study of gels during synthesis.

Although in its infancy, the synthesis of new framework structures by rational design and selection of template molecules is becoming increasingly possible. For example, both SSZ-24 and to an extent DAF-1 were synthesised by careful pre-selection of a template which would result in channels of the desired size. However, we are still some way from understanding the mechanism of framework formation under the influence of structure-directing templates. Indeed the mechanism of framework crystallisation is not fully understood. This chapter will highlight the role which computer modelling techniques can play in advancing our understanding in this field and in guiding the synthesis of novel microporous materials.

Computer modelling has been shown to be a valuable tool for investigating the interaction of zeolite structures and sorbed phases. As with experimental studies, work has concentrated on the location and diffusion of molecules within the pores. These studies demonstrate the accuracy that simulations can achieve in reproducing experimental data. Recent studies have highlighted the role of "inverse shape selectivity", i.e. the attractive interaction between sorbate and sorbant, in hydrocarbon sorption and production. The geometry and interactions of template molecules within the ZSM-5 framework have also been investigated. This work has demonstrated that differences in crystal growth are a consequence of differences in the interaction between different geometries of templates within the framework and that modelling techniques can correctly calculate template geometries.
5.3. Methodology

Our approach is based on a combined molecular dynamics, Monte Carlo and energy minimisation technique\textsuperscript{30} to probe the non-bonded interactions between guest molecules and zeolite frameworks. The technique was initially devised to overcome the difficulties in locating favourable sorption sites of small organic molecules in zeolites. The results from energy minimisation techniques can depend on the starting geometry. Furthermore, in zeolites, with the availability of such large a void space for the sorbed species, it is difficult to select (manually) probable sites and to ensure that all possible sites are screened. Although in theory, molecular dynamics techniques will allow the investigation of all the (energetically) possible structures, this is difficult in practice, due to the long calculation times required. The technique will be described in detail below and is illustrated in Figure 5-1.

In outline, the procedure is as follows;

1. The conformational space of the sorbate is searched using molecular dynamics producing a library of sorbate conformations.

2. These conformations are then ‘docked’ at suitable positions within the framework using a Monte Carlo sampling technique.

3. The framework / sorbate geometries are energy minimised

The procedure, which will be referred to as the ‘docking procedure’ will now be discussed in more detail.
5.3.1 Molecular Dynamics - Sorbate Conformation Searching

A molecular dynamics (MD) trajectory for the template molecule in the gas phase is used to generate a library of sorbate (or guest) conformations. This MD trajectory is carried out at relatively high temperatures *ca.* 1000K for a run time of typically 1000fs in steps of 1fs. This is to ensure that a significant portion of the conformational space of the molecule is searched. Snapshots are taken of the
molecule at pre-defined intervals to produce a library of conformations. The sampling of the conformational space is most important when studying the adsorption of small flexible molecules within a host. However, it is apparent from noting the dimensions of templates and of the pores which they form, that the templates cannot be significantly perturbed from their low energy conformers. So, for example, when considering linear molecules which result in linear channels, it is clearly a disadvantage to include the higher energy bent conformers since they will not fit within the dimensions of the frameworks considered. Thus in the such cases, the MD is carried out at a much lower temperature (ca. 500K) than for sorbate molecules.

5.3.2 Monte Carlo Docking

The library of conformations are now inserted into the zeolite framework (or host) using a Monte Carlo docking procedure. The sorbate is inserted at a random position and orientation in the framework. The conformation is accepted if the host-guest interactions meet two criteria:

1. No host - guest contacts are less than 1Å. If this criterion is not met then no energy calculation is required.

2. The non-bonding energy of the system - the components of the total energy which are a consequence of the interactions of the host with the guest - are less than a pre-defined threshold level. The choice of this threshold is a compromise between the strict rejection of sterically strained conformations, the computational expense and the acceptance of unrealistic candidate structures. Indeed, the high repulsion forces, even with only moderate steric overlap, as a consequence of the shape of the Lennard-Jones potentials used, means that this threshold is usually quite large (ca. 500 kJ mol\(^{-1}\)) compared to the final values. However, when considering systems which have a very close match between the template and the framework (such as those systems which exhibit true templating behaviour) this threshold may need to be increased further so that structures which, although more strained than those mentioned previously, are accepted.
If the acceptance criteria are not met then another random position and orientation are selected and the docking procedure repeated. The procedure is thus iterative with the process terminating when a conformer is accepted or a pre-determined maximum number of trials is reached. This Monte Carlo procedure is repeated for all the sorbate structures generated by the MD trajectory. In certain cases, such as those mentioned above where there is a very close match between the framework and the template, the probability of docking the template using a Monte Carlo sampling method is small. Thus, the sampling procedure must be allowed to be extensive with a large number of trials being permitted. This can be computationally expensive. Alternatively, the threshold for acceptance is increased as discussed above. However, in certain instances the probability of locating a satisfactory trial structure is so low that an alternative method of generating structures suitable for minimisation is required. Thus in such cases, the template is manually crudely docked in the framework prior to energy minimisation. To achieve this we use molecular graphics with the assistance of monitors to reduce short non-bonded distances and with interactive monitoring of the non-bonded interactions. The InsightII package from Biosym Technologies\(^\text{37}\) was used when this approach was necessary. However, the problem occurs only in a small number of instances and these are such that the likely location of the template within the framework is readily apparent.

The present Monte Carlo procedure differs from the traditional Metropolis importance sampling technique\(^\text{38}\) as each structure is independent of the previously accepted conformation. Here each accepted conformation is generated at random and has no dependence on any previous or subsequent structure.
5.3.3 Energy Minimisation

Energy minimisation techniques are then applied to these crudely docked structures to yield low energy binding sites for the molecule within the host structure. Thus the final optimised structures are obtained without any direct assumptions being made regarding the location or conformation of the template within the host zeolite structure.

Three important constraints are placed upon these calculations.

1. The calculation is carried out on a finite, fixed geometry portion of framework (generally 60 Å x 60 Å x 60 Å). Thus the docking procedure must be confined to the central portions of the framework cluster which would be expected to be sufficiently “bulk-like”.

2. The framework structure is held rigid. After synthesis, the templates molecules are removed by calcination (high temperature degradation of the template molecules), resulting in only minimal change in the crystal structure of the framework. Therefore this assumption would appear reasonable. Furthermore, the templating action will be more effective if the inclusion of the organic molecules does not perturb the framework structure to any significant degree. This simplification has been previously used in the study of sorption sites and small sorbate dynamics in zeolites.

3. For the majority of the calculations the electrostatic interactions are ignored. Clearly this is a simplifying assumption, particularly when organic ions are considered. However, this work is restricted to neutral end-members of the zeolitic structures (siliceous zeolites and non-acidic aluminophosphates) and therefore, the electrostatic field that the template molecule experiences is largely uniform. Thus, the neglect of Coulombic interactions can be expected to have a comparatively small effect on the calculated structures, as will be further demonstrated in later discussions. The increasing availability of accurate interatomic potentials will make more detailed simulations possible in the future. However, such simulations would demand much more
computational effort as inclusion of charges would necessarily require not only a complete treatment of the long-range Coulombic interactions, but also (in the case of the cationic templates) a large sampling of counter ions and defect models about each potential binding site. This is particularly problematic if the template charge is compensated by the framework, since the location of any heteroatoms (if any) in the framework would have to be determined. Finally we note that recent work has demonstrated that there is little electrostatic similarity between different templates which form the same framework, and that size and shape are the dominant factors.\textsuperscript{42}

The methodology is implemented in the Catalysis\textsuperscript{43} module of the Insight\textsuperscript{II} software available from Biosym Technologies Inc. The Discover program\textsuperscript{44} was used for the energy minimisations of the trial structures.

5.3.4 Simulated Annealing

When templates are docked into a microporous structure with only restricted voids it is possible that local minima are located; that is, although we obtain an energy minimum, the structure achieved is not the global minimum for that particular sorbed molecule. This is particularly true when considering larger template molecules with a large number of degrees of freedom. Such molecules will possess many local minima which the minimisation techniques cannot traverse in order to locate the global minimum - as illustrated in Figure 3-3 in Chapter 3). Further complications arise from the restrictions placed upon the minimisation by the presence of the framework. Therefore the technique of simulated annealing\textsuperscript{45} is used with certain structures as an additional step before energy minimisation. The annealing procedure allows the system to search dynamically the energy hypersurface to find the global minimum. The procedure uses molecular dynamics first to heat the system and then to cool it slowly. Conventional energy minimisation is then used to determine the final optimised structure. A typical simulated annealing procedure is shown in Figure 5-2.
Starting Conformation

Begin Dynamics
1 fs timestep

Heating Cycle
@500K, 1000fs
@1000K, 1000fs

Cooling Cycle
@700K, 1000fs
@500K, 1000fs
@300K, 500fs
@200K, 500fs

Energy Minimisation
to Global Minimum

Figure 5-2. Schematic of a typical simulated annealing cycle

5.3.5 Framework / Template Interaction Energy

The above procedures allow the determination of low energy binding sites for a particular framework-template combination. The energies obtained are a measure of the “match” between the sorbate geometry and the topology of the host framework. The non-bonding interactions between the framework and the template can be measured for each structure, with the interaction energy \( E_{\text{inter}} \) being defined as:

\[
E_{\text{inter}} = E_{\text{host-guest}} - E_{\text{free}}, \tag{5.1}
\]

where \( E_{\text{host-guest}} \) is the energy as a result of placing the template in the framework and \( E_{\text{free}} \) is the minimum energy of the template in the gas phase. The energy of the framework is effectively zero since it is held rigid. \( E_{\text{inter}} \) therefore includes
any effect of conformational change when the template molecule is placed within the framework.

5.3.6 Forcefields

To describe the forces between the atoms we use a molecular mechanics forcefield (as described in Chapter 3). The Born model is not readily suited to the routine description of organic molecules and the interaction of such covalent materials with inorganic materials, as discussed in the calculations on the template molecules in Fe-ZSM-5 in Chapter 6. The development of accurate forcefields for the description of organic molecules within microporous materials is crucial to the development of such techniques in the field. Much work has been done in this field, notably by Hill and Sauer in their development of an ab-initio derived molecular mechanics forcefield for zeolites, which has been incorporated into the cff91 forcefield, with the further inclusion of parameters for the non-bonding terms between framework atoms and atom types of organic molecules. This forcefield, cff91_czeo was used throughout this present work. It is important to note that other workers have found that the non-bonding terms of this forcefield underestimate the binding energy of organic molecules within zeolites. However, only trends and relative energies between similar molecules will be considered in this study. Furthermore, a limited number of calculations have been carried out with other forcefields which indicate that the conclusions drawn from the use of the cff91_czeo forcefield are valid, as will be discussed later. In this context it is also important to note that it is difficult to relate the absolute values to experiment as only a limited amount of thermodynamic data on zeolite synthesis using templates is available. However, with careful parameterisation it is possible to obtain accurate heats of sorption in agreement with experiment.
5.4. Results and Discussion

In the presentation and discussion of our results we consider first the question of the forcefield selection. Secondly and most significantly, results will be presented on the interactions of a large number of framework / template combinations in an attempt to understand if there is an energetic rationalisation of templating behaviour. Comparison of the calculated geometries and experimental structures will then be presented to confirm that the techniques used can replicate such data. The question of template packing within the host framework will be discussed, in particular reference to the ability of these calculations to predict the templating ability of a given template for a range of frameworks.

5.4.1 Comparison of Forcefields

The parameterisation of the non-bonded interactions between the framework atom types and the organic atoms types in the cff91_czeo forcefield were derived from ab-initio calculations. As noted above, the forcefield has been found to underestimate sorption energies of organic molecules in zeolites, specifically benzene in faujasite. However, this forcefield has advantages over empirically derived forcefields in that it is self-consistent. Furthermore, it contains parameters which allow accurate modelling of the framework of aluminosilicates, this will be of importance in any future work which includes the effect of framework relaxation. Thus, the use of this forcefield is preferred from this viewpoint. However, we must ensure that the forcefield yields the same trends as other forcefield which may have been fitted to sorption data.

To validate the choice of the forcefield a number of calculations were performed using the cff91_czeo and the cvff forcefield. The latter was noted by other workers to give results in good agreement with experimental heats of adsorption. The interaction energies of a series of \( \alpha,\omega \)-diamines, with the general formula of \( \text{H}_2\text{N}-(\text{CH}_2)_n-\text{NH}_2 \), \( n=2...6 \), in the zeolite ZSM-5 are presented in Figure 5-3. The geometries of the calculated lowest energy site
using both forcefields is almost identical as illustrated in Figure 5-4. Furthermore the difference between the energies calculated are almost constant and consistent. If the difference in the energy calculated by the two forcefields were entirely a consequence of the non-bonding terms, then the increase would be constant and the energy increase per atom would also be constant. However, this is not quite true indicating differences in bonded (or intramolecular) forces as well. However, the change is only small: the difference between the forcefields varies from 30 kJ mol\(^{-1}\) for 1,2-diaminoethane and 40 kJ mol\(^{-1}\) for 1,6-diaminohexane. This is equivalent to a change from 1.5 to 2.1 kJ mol\(^{-1}\) in the contribution of each CH\(_2\) group to the total energy. It is therefore apparent that any trends in results would be the same regardless of which forcefield was used. Thus, the choice of the *cff91_czeo* in preference to *cvff* is justifiable and also provides the advantages of the *ab-initio* forcefield as mentioned above. This forcefield was therefore used for all subsequent calculations on template/framework interactions.

![Comparison of Forcefields](image)

*Figure 5-3. Comparison of Forcefields. Results for n-diamines in ZSM-5. Difference per non-H atom is on the right hand scale.*
5.4.2 The Energetics of Host-Template Interactions

5.4.2.1 Non-bonding Interactions between Templates and Host.

Can the templating ability of an organic molecule or ion be rationalised in terms of energetics? In attempting to answer this question the non-bonded interactions between the template molecule and the zeolite host will be examined first. The docking technique has been used to obtain minimum energy sites for a large number of experimentally noted template / zeolite combinations listed in Table 5-1, which encompasses not only a large range of different zeolite structures but also a large range of different organic species,
including neutral, cationic, amino, oxy and aromatic systems. A number of these structures are illustrated in Figure 5-5.

| Framework Types | Templates 
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 (MFI)</td>
<td>primary diamines (H₂N-(CH₂)ₓ-NH₂, x=2-6)</td>
</tr>
<tr>
<td>ZSM-11 (MEL)</td>
<td>bis-quaternary amines ((CH₃)₃N⁺-(CH₂)ₓ⁺N(CH₃)₃, x=3-10)</td>
</tr>
<tr>
<td>ZSM-12 (MTW)</td>
<td>tetraalkyl ammonium ions ([CH₃(CH₂)ₓ]₄N⁺, x=0-3)</td>
</tr>
<tr>
<td>ZSM-18 (MEI)</td>
<td>tri-quaternary ammonium ion C₁₈H₃₆N₃³⁺.</td>
</tr>
<tr>
<td>ZSM-23 (MTT)</td>
<td>cyclic amines and other heterocycles; saturated and unsaturated (5,6 and 7 membered rings)</td>
</tr>
<tr>
<td>zeolite-β (BEA)</td>
<td>dialkylamines (e.g. CH₃CH₂CH₂-NH-CH₂CH₂CH₃)</td>
</tr>
<tr>
<td>Faujasite (FAU)</td>
<td>trialkylamines (e.g. tripropylamine)</td>
</tr>
<tr>
<td>Mordenite (MOR)</td>
<td>1,3-diaminopropane</td>
</tr>
<tr>
<td>Dodecasil 1H (DOH)</td>
<td>1, 4, 8, 11-Tetraazaundecane</td>
</tr>
<tr>
<td>Dodecasil 3C (MTN)</td>
<td>1, 5, 8, 12-Tetraazadodecane</td>
</tr>
<tr>
<td>ZSM-22 (TON)</td>
<td>1, 5, 9, 11-Tetraazatridecane</td>
</tr>
<tr>
<td>EU-1 (EEO)</td>
<td>1-Adamanylamine</td>
</tr>
<tr>
<td>Chabacite (CHA)</td>
<td>Piperazines</td>
</tr>
<tr>
<td>Zeolite Sigma (DDR)</td>
<td></td>
</tr>
<tr>
<td>NU-3 (LEV)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-1. Framework types and Templates investigated (IZA structure codes are given for framework types in parentheses).
The non-bonding energy will be correlated with a function of the size of the template. There is a reasonably good correlation between the non-bonding energy and the number of non-hydrogen atoms in the template (Figure 5-6) which implies that non-hydrogen atom environments are at least approximately equivalent for known template-framework pairs. That is, all the atoms in the template contribute approximately equally to the interaction energy and hence occupy similar positions in relation to the framework. This is reasonable considering the tight fit of the template within the framework. Furthermore, it is noted that there is better correlation if we consider trends amongst the different template types. It can see from closer examination of Figure 5-6 that the correlation amongst the α,ω-diamines and tetraalkylammonium ion homologous series is excellent, which also applies to the bis-quaternary ammonium cations. Thus, it is observed that the maximisation of favourable host/guest interactions is a characteristic of successful templates when considering chemically and structurally similar systems.
Figure 5-6. Interaction Energy of experimental framework / template combinations as a function of non hydrogen atoms. Straight line is the best fit through all datapoints. The results for the tetraalkylammonium salts are also highlighted with a line joining the datapoints.
The definition of the molecular mechanics forcefield means that it is not strictly correct to compare the energies of molecules comprising different atoms and atom types. The zero point energy of each molecule is unique and does not have a direct relationship to the energy of the isolated constituent atoms, as is clear from the results. For a homologous series, the comparison of the energy of different members is valid since there is only an increase in the number of particular atoms types and not a change in the atoms types present. However, as noted above, the trend in energies when all the template types are considered, in which there are different atom types, is not as good. Given the evidence for the good correlation within homologous series, it is quite likely that the deviation from this behaviour, noted when considering different types of template, is as a direct consequence of the definition of the molecular mechanics forcefield.

The use of the number of non hydrogen atoms as a measure of template ‘size’ is not particularly correct. For example cyclopentane is significantly different in size and shape to \emph{n}-pentane, but have the same number of non-hydrogen atoms. Therefore the energetics have been analysed with respect to molecular volume (Figure 5-7). The volume is defined as the volume of the overlapping van der Waals radii of the atoms. Molecular volumes have been used successfully in determining the packing of complex inorganic salts. The same trends identified above are again evident. However, there is now improved correlation for certain templates, particularly for the cyclic molecules. Therefore, molecular volume is shown to provide a better measure of template ‘size’ with respect to their efficacy as templates. Correlation with the surface area of the template also shows similar trends (Figure 5-8). The surface area is determined as the solvent accessible area using the Connolly algorithm. This measures the surface area by calculating the area accessible to a probe of a given size; a probe size of zero was used to give the effective van der Waals surface area.
Figure 5-7. Interaction Energy of experimental framework/template combinations as a function of molecular volume. Straight line is the best fit through all datapoints. The results for the tetraalkylammonium salts are also highlighted with a line joining the datapoints.
The apparent correlation between both size and shape of the template molecule and its templating ability is a good indication that it is these factors which control the templating effect. We shall demonstrate later that the effect of charge distribution may be of secondary importance. Correlations of this type are of course simply a quantitative expression of the closeness of the fit between the host and the template which is evident from experimental data.

Figure 5-8. Interaction Energy of experimental framework / template combinations as a function of template surface area. Straight line is the best fit through all datapoints. The results for the tetraalkylammonium salts are also highlighted with a line joining the datapoints.
5.4.2.1.1 The Effect of the Functionality of the Template

Gies and Marler concluded in their work that the chemical character of templates with similar shapes had little influence on templating ability. They showed that the product formed from a series of substituted cyclic templates was dependent on the size and shape of the template and not on the substituent. These included oxy-, amino- and hydrocarbon substituents. To investigate this effect we have calculated the interaction energy of a set of cyclic templates (Figure 5-9) in the clathrasil Dodecasil 3C (Figure 5-10). All the organic molecules used are successful experimental templates for this zeolite. The results of these calculations support the conclusions of Gies and Marler (Table 5-2). The interaction energies are broadly split into three groups which correlate with the size and shape of the templates. The interaction energies of tetrahydrofuran, tetrahydrothiophene, cyclopentane and pyrrolidine with the host are very similar whilst those of furan and thiopene and that of cyclopentyl amine are significantly different: a consequence of the similar non-bonding characteristics of the atom in these molecules. However, it may be that the methods used to derive the non-bonding parameters are not sensitive enough to distinguish between similar atom species. Nonetheless, it is an important confirmation of our general conclusion, and one which can be utilised in future template selection and design. This effect may be particularly important when considering the solubility of templates, as these similarly shaped molecules can have very different physical properties as illustrated in Table 5-3. The hydration of framework building units and the interaction of these hydrated species with hydrated template species is another question which should be considered, especially as this difficult field of study is becoming accessible to modelling techniques.
Figure 5-9. Molecular structures of the cyclic templates used in calculations with the zeolite Dodecasil 3C.

Figure 5-10. Framework structure of Dodecasil 3C.
<table>
<thead>
<tr>
<th>Template</th>
<th>Non-H atoms</th>
<th>Volume (Å³)</th>
<th>$E_{\text{inter}}$ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>furan</td>
<td>5</td>
<td>54.1</td>
<td>-60.2</td>
</tr>
<tr>
<td>thiophene</td>
<td>5</td>
<td>66.0</td>
<td>-57.9</td>
</tr>
<tr>
<td>tetrahydrofuran (C₄H₈O)</td>
<td>5</td>
<td>65.1</td>
<td>-94.4</td>
</tr>
<tr>
<td>cyclopentane (C₅H₁₀)</td>
<td>5</td>
<td>73.0</td>
<td>-105.3</td>
</tr>
<tr>
<td>tetrahydrothiophene (C₄H₈S)</td>
<td>5</td>
<td>78.0</td>
<td>-95.6</td>
</tr>
<tr>
<td>pyrrolidine (C₄H₈NH)</td>
<td>5</td>
<td>82.8</td>
<td>-94.0</td>
</tr>
<tr>
<td>cyclopentyl amine (C₅H₉-NH₂)</td>
<td>6</td>
<td>82.5</td>
<td>-57.9</td>
</tr>
<tr>
<td>quinucilidine (C₇H₁₃N)</td>
<td>10</td>
<td>103.5</td>
<td>-84.3</td>
</tr>
</tbody>
</table>

Table 5-2. Interaction energies of templates and Dodecasil 3C

<table>
<thead>
<tr>
<th>Relative solubility</th>
<th>water</th>
<th>ethanol</th>
<th>acetone</th>
<th>benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Template</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclopentane</td>
<td>1</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>furan</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>thiopene</td>
<td>1</td>
<td>4</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>tetrahydrothiopene</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>pyrrolidine</td>
<td>5</td>
<td>3</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 5-3. Relative solubilities of templates used for Dodecasil 3C synthesis. Solubility given on a scale of 1 = insoluble, 2 = slightly soluble, 3 = soluble, 4 = very soluble, 5 = miscible. Data from the Handbook of Data on Organic Compounds.56
5.4.3 Calculated Structural Properties of the Template-Host Interactions

In order to determine if our methodology is correctly locating template positions, the calculated minimum energy template locations have been compared to the available experimental structural data. As previously noted, this is limited by the availability of suitable samples - the microcrystalline nature of most zeolites being unfavourable for such determinations. Comparisons will be made with the structure of NU-3 with 1-aminoadamantane and N-methylquinuclidinium, ZSM-5 in the presence of tetrapropylammonium (TPA+), and finally with the proposed location of the triquaternary ammonium cation C_{18}H_{36}N_{3}^{3+} in ZSM-18.

5.4.3.1 NU-3 / N-methylquinuclidinium

The calculated location of the template is in excellent agreement with the experimental structure\textsuperscript{13} - see Figures 5-11 and 5-12. Allowing for the difference in the unit cell dimensions (which will be discussed later in section 5.5.1), the agreement is as good as any which may result from experimental errors; the deviation of the calculated structure from the experimental structure is $< 0.02\text{	extdegree}$. Furthermore, all the equivalent rotational conformers are not only calculated to be energetically equivalent but also agree with the experimental structure, as will be discussed in a section 5.5.1.1.

5.4.3.2 NU-3 / 1-aminoadamantane

As for the above structure, the agreement of the calculated and the experimental geometry is excellent (see Figures 5-12 and 5-13). Again, the rotational conformers are represented in the docking results.
Figure 5-11. Comparison of the calculated and experimental location of both N-methylquinuclidinium (left) and 1-aminoadamantane (right) in NU-3. Both the experimental (solid line) and calculated (dashed line) are shown overlaid. Only the silicon atoms of the framework are shown.

Figure 5-12. Comparison of the calculated (left) and experimental (right) location of the N-methylquinuclidinium template in NU-3.
Figure 5-13. Comparison of the calculated (left) and experimental (right) location of the 1-aminoadamantane template in NU-3.

5.4.3.3 ZSM-5 / tetrapropylammonium (TPA)

The calculated geometry of TPA in silicalite (the siliceous analogue of ZSM-5) was compared to the single crystal X-ray structure of ZSM-5/TPA of van Koningsveld et al.\textsuperscript{15} - shown in Figure 5-14a. The calculated position for the N atom is offset from the experimental position by approximately 0.4Å. However, the intramolecular geometry of the template is correct. The magnitude of the error, although not excessive, is greater than expected especially in the context of the excellent agreement found above. Therefore, reasons other than the performance of the method and forcefield may be responsible for this apparent discrepancy. The experimental structure was determined for a material with a composition of Na\textsubscript{0.35}Si\textsubscript{95.7}Al\textsubscript{0.3}4TPA·OH\textsuperscript{+} + nH\textsubscript{2}O.\textsuperscript{15} Thus the exclusion of the framework aluminium and the extraframework sodium cations and hydroxide anions - the positions of which are not determined experimentally - may have an
effect on the results. However, this effect is likely to be very small given the relatively low concentrations of these species. Experimentally, the temperature factors for many of the atoms of the template atoms are significant - for example $U_	ext{iso}(N) = 0.069\,\text{Å}^2$. This may lead to uncertainties in the position of the template ion similar to the differences observed between the calculated and experimental structures. However, it is probably the omission of the neighbouring template molecules which has the greatest effect. A detailed study of templating requires us to consider not just single molecules within the framework as considered so far; the formation of a sub-lattice of template molecules will also be crucial. Thus, the calculations were repeated with the next nearest TPA$^+$ ion included - this will be discussed in detail below (section 5.4.6). The calculated structure is now in excellent agreement with the experimental structure (Figure 5-14b) with errors comparable to those previously discussed. The packing of templates will be shown later to be an important factor in template selection for synthesis.

5.4.3.4 ZSM-18 / C$_{18}$H$_{36}$N$_3$$^+$

The templating effect of this triquaternary ammonium cation is self evident in ZSM-18. The shape of the template results in a tight fit of the template within the framework. Indeed, the fit is so good that even with extensive Monte Carlo sampling the docking procedure did not locate a suitable candidate structure for minimisation. However, such is the match between the shapes of the template and framework, it is easy to dock manually the template within the framework, and this was done repeatedly with a number of orientations to investigate any bias introduced by this procedure. Regardless of starting position, the same final position is obtained. Although not determined experimentally this is in agreement with the proposed siting and geometry. This final geometry is illustrated in Figure 5-15.
Figure 5-14. Comparison of calculated (dark) and experimental\textsuperscript{15} (light) positions of TPA in ZSM-5. A) Isolated TPA ion, B) Position when two TPA ions are used in the calculation. Hydrogen atoms are excluded from the template cations for clarity.

Figure 5-15. Calculated position of the triquaternary amine template in ZSM-18.
The above examples have shown that the procedure is successful at locating the correct siting for the template molecules within zeolite frameworks. The comparison to the available experimental data is on the whole excellent. Where the differences are considered to be significant, they can be corrected by considering the effect of template packing. Therefore, it can be confidently stated that the energies calculated for the binding of the template within the framework refer to the correct geometry.

5.4.4 Effect of Neglecting Coulombic Interactions

A major approximation made in this work has been the neglect of Coulombic interactions. How significant are the contribution of Coulombic interactions in determining templating action? Can this simplification be justified? The calculations on the tetraalkylammonium salts in the ZSM-5 framework were repeated with the inclusion of charge interactions during the final minimisation stage. (Charges were still ignored in the Monte Carlo docking stage of the procedure). Whilst using a finite framework cluster, we must ensure that the cluster size and more importantly the location of the template within that cluster do not affect the results. It is clear, that a template which is not centrally located within a finite cluster will not experience the same Madelung field as in the infinite crystal. This then adds considerably to the amount of work required in constraining the docking procedure to the central portion of the framework clusters which now have to be large enough to ensure satisfactory convergence of the long range Coulombic interactions. We note again that one of the aims of this work was to allow the rapid evaluation of a range of templates and this procedure requires not only considerably longer calculations but also does not lend itself to an automated procedure. For the calculations including electrostatics it was necessary to employ 80Å cubic clusters, terminated with hydroxyl groups with the docking of the template restricted to the central unit cell.

The interaction energies obtained with and without charges are given in Table 5-4 and illustrated in Figures 5-16a and 5-16b. From Figure 5-16a it is evident
that the inclusion of charges does not alter the overall trend. Furthermore, the final geometries obtained are very similar regardless of the neglect or inclusion of charges as illustrated in Figure 5-17. Thus we conclude that the neglect of charge interactions affect only the total energy and not the non-bonding component which appears, for this particular set of templates in ZSM-5, to be confirmed as the dominant factor in determining templating ability.

<table>
<thead>
<tr>
<th>Template</th>
<th>$E_{\text{inter}}$ / kJ mol$^{-1}$</th>
<th>Relative $E_{\text{inter}}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Charges</td>
<td>No Charges</td>
</tr>
<tr>
<td>TMA</td>
<td>-8004.0</td>
<td>-51.7</td>
</tr>
<tr>
<td>TEA</td>
<td>-8733.4</td>
<td>-92.1</td>
</tr>
<tr>
<td>TPA</td>
<td>-9007.7</td>
<td>-133.9</td>
</tr>
<tr>
<td>TBA</td>
<td>-9378.3</td>
<td>-165.5</td>
</tr>
</tbody>
</table>

*Table 5-4. Interaction energies of tetraalkylammonium cations in siliceous ZSM5. The relative interaction energy is defined as $E(TxA)-E(TMA)$ where $TxA$ is TMA, TEA, TPA and TBA.*

However, although this result vindicates the approximation used in this work, we must take care especially when considering more polar species especially those which have a dipole moment; here we have considered molecular ions which are symmetrical in their charge distribution. Furthermore, there will be an obvious need to consider charges if frameworks with an overall charge are considered. The inclusion of charges requires much more careful selection of framework cluster in terms both of size and the space into which the templates can be docked. Although many of these problems would be removed if the framework was considered as a periodic system, this would require the framework structure to fully charge compensate for the organic ions. Furthermore, a scheme for determining any preferential siting or ordering of the
heteroatoms would have to be determined. Only siliceous frameworks are considered here, and it is clear that calculations involving aluminosilicate frameworks would require a great deal more effort. We further note that templating effects appear to be more important in the synthesis of siliceous structures. If we consider ZSM-5, the aluminosilicate material is readily synthesised by a wide range of templates and indeed can be prepared without any templating species at all; Silicalite-I (the siliceous ZSM-5) has not to date been prepared without the aid of a template. A similar effect is noted in the synthesis of EU-1 and EU-2; under the same conditions and with gels which are identical with the exception of the presence in the case of EU-1 or absent for EU-2 of alumina a different product is obtained. Thus it is clear that there is considerable effect on the addition of aluminium into the framework. However, the effect on the interactions between the framework and the template are likely to be secondary to the change in the stability of the framework and more importantly the stability of small silicate fragments present in the gel during nucleation and crystallisation.

These results give us confidence that the neglect of charges do not affect our overall conclusions, enabling us to use a method which is considerably quicker and simpler to implement than if charges had to be considered. In addition, these results support the view which has been proposed by many experimental studies and reviews that templating effects are primarily governed by steric and van der Waals interactions. However, it is clear that further studies are required to fully characterise the effect of aluminium (and other heteroatoms) on the templating action and framework stability.
Figure 5-16. Interaction energies of tetraalkylammonium cations in siliceous ZSM5.
A) Interaction energy plotted for both charged (left axis) and un-charged systems.
B) Plot of the relative interaction energy for both charged and un-charged systems plotted against each other. Energy is defined as in Table 5-4.
Figure 5-17. Comparison of the most stable configuration of TPA in ZSM-5 with and without charge interactions. The TPA cation is shown in black for the calculation with charges and in grey for the uncharged calculation.
5.4.5 Predicting Templating Ability

Can templating ability be predicted? And can a template be selected to synthesise a given framework structure? If so, then the procedures described can be utilised in a predictive manner, to assist with synthesis design. These questions have been addressed by studying in more detail two series of templates. The tetraalkyl ammonium cations, from tetramethyl ammonium (TMA) to tetrabutyl ammonium (TBA), have been used extensively in synthesis. Indeed, TMA was the first template molecule to be used. They are of particular interest since they tend to form three dimensional systems with intersecting channels. The bis-quaternary amines, (general formula 
(CH$_3$)$_3$N$^+$(CH$_2$)$_x$N(CH$_3$)$_3$, x=3-8 and referred to as tri-, tetra-, penta-, hexa-, hepta-, and octamethonium ions), on the other hand, tend, being linear molecules, to form one dimensional channels. These compounds are also extensively used and have been the subject of an extensive synthetic study. Here, each member of the two series has been computationally docked within all the frameworks synthesised by that series. The results of the docking calculations on the two series will be consider separately.

5.4.5.1 Tetraalkyl ammonium cations

The results show that the experimental template/framework combinations (Table 5-5) exhibit the most favourable non-bonding interactions. That is, templates which are too small for a given framework are only weakly bound, whilst repulsive forces act upon those which are too large. The method correctly identifies TEA as the best template for zeolite β and TBA for ZSM-11 as found experimentally. However, there is an anomaly for ZSM-5 with TEA being calculated as more stable than the experimental template, TPA. This is, however, to be expected, because in the calculation (which was carried out on a single template molecule) the longer alkyl chains are able to fit the pores of ZSM-5 without hindrance, increasing the non-bonded interactions with the framework and thus increasing the binding energy. However, as mentioned previously the interactions of the template molecule with the other template
molecules must also be considered. We shall demonstrate later how the inclusion of packing effects removes this anomaly. The calculated energy minima for the experimental templates are shown in Figure 5-18.

<table>
<thead>
<tr>
<th>ZSM-5</th>
<th>ZSM-11</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{inter}}$ (kJ mol$^{-1}$)</td>
<td>$E_{\text{inter}}$ (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>TMA</td>
<td>-51.7</td>
<td>TMA</td>
</tr>
<tr>
<td>TEA</td>
<td>-92.1</td>
<td>TEA</td>
</tr>
<tr>
<td>TPA*</td>
<td>-133.9</td>
<td>TPA</td>
</tr>
<tr>
<td>TBA</td>
<td>-165.5</td>
<td>TBA*</td>
</tr>
</tbody>
</table>

Table 5-5. Non-bonded interactions energy of tetraalkyl ammonium cations in various frameworks. Templates predicted as the most effective template are emboldened.

*Experimental templates.$^{52}$

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Chapter 5.
Figure 5-18. Calculated location of the experimental template / zeolite combinations for the tetraalkylammonium templates. Illustrated are (a) Zeolite β / TEA, (b) ZSM-5 / TPA and (c) ZSM-11 / TBA.
5.4.5.2 Bis-quaternary ammonium cations

From Table 5-6 it is again evident that the calculations on single templates are reasonably successful at predicting the correct template for a given host. However, the zeolites formed by this class of templates differ from those considered for the tetraalkyl ammonium ions; the channel structures are not three-dimensional. The differences in the success of the technique will now be further discussed with respect to these differences in channel topology.

<table>
<thead>
<tr>
<th></th>
<th>E_{inter} (kJ mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EU-1</td>
</tr>
<tr>
<td>trimethonium</td>
<td>-18.6</td>
</tr>
<tr>
<td>tetramethonium</td>
<td>-125.8</td>
</tr>
<tr>
<td>pentamethonium</td>
<td>-147.4*</td>
</tr>
<tr>
<td>hexamethonium</td>
<td>-128.5*</td>
</tr>
<tr>
<td>heptamethonium</td>
<td>-94.9</td>
</tr>
<tr>
<td>octamethonium</td>
<td>-126.1</td>
</tr>
</tbody>
</table>

Table 5-6. Non-bonded interactions energy of bis-quaternary amines in various frameworks. Templates predicted as the most effective template are emboldened.

*Experimental templates.

The pore structure of EU-1 consists of a straight channel which has side pockets on alternate sides of the channel (illustrated in Figure 5-19). Thus although not truly three dimensional as is the case for the zeolites formed by the tetraalkylammonium ions, it is evident that there are features which possess shape and form in three dimensions. The minimum energy structures of all the molecules tested involve the templates fitting into these side pockets. Thus as the size of the templates increase, they first fill the side pocket, then the channel and, for the largest molecules, bend into the channel (Figure 5-20). The experimental templates are those which fill the pocket and channel with the least
amount of distortion of the molecule. It will be shown later that, after including packing effects, the two experimental templates have the maximum binding energy.

Figure 5-19. The channel and pore structure of EU-1. The uni-dimensional channel has pocket on alternate sides, perpendicular to the channel. This is illustrated by the calculated packing arrangement of the experimental template hexamethonium.

ZSM-23 also consists of a straight one-dimensional channel system. However, here, unlike EU-1, it is uniform in its cross section. Thus there are little or no features which may influence the location of the template within the channel. It is calculated that larger (linear) templates are generally favoured over the smaller ones, as a consequence of the increase in the number of non-bonding
interactions with the increase in the number of atoms in the template. However, there are exceptions. Most significantly the trimethonium ion has a large interaction energy since the main contributions to the non-bonding energy is from the amino end groups which in trimethonium are in better contact with the framework. The short alkyl chain allows the end-groups to tilt towards the framework. Conversely with the larger molecules this is not possible and the end groups lie more or less parallel to the channel. This is illustrated in Figure 5-20. It is therefore clearly more difficult to use single molecule calculations to predict correctly the templating ability for systems with one-dimensional channels.

Although the presence of trimethonium is found experimentally to lead to Dodecasil 3C⁵² it has proved impossible to dock this cation successfully within the framework. Although energy minima can be found, the geometry of the organic molecule is unfeasibly strained. It is therefore concluded that any organic species occluded within Dodecasil 3C in this synthesis is not trimethonium, but some smaller product of the decomposition of trimethonium; that is, trimethonium is not acting as a templating agent to any degree in this synthesis. It should be noted, that the synthesis was carried out at the relatively high temperature of 180°C and that trimethonium may decompose at this temperature. Therefore, docking calculations have been performed for possible decomposition products of trimethonium in Dodecasil 3C. Table 5-7 shows the results for some of these ions. If any organic species are occluded within the cages of Dodecasil 3C, the presence of these decomposition products is plausible at the synthesis temperatures.
Figure 5-20. Calculated positions of octamethonium (top left), tetramethonium (top right), pentamethonium (bottom left) and hexamethonium (bottom right) in EU-1.
Table 5-7. Possible templates during the synthesis of Dodecasil 3C using trimethoniun

<table>
<thead>
<tr>
<th>Template</th>
<th>$E_{\text{inter}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetramethylammonium</td>
<td>-75.8</td>
</tr>
<tr>
<td>tripropylammonia</td>
<td>-53.9</td>
</tr>
<tr>
<td>ethyl, tripropylammonium</td>
<td>-49.2</td>
</tr>
</tbody>
</table>

5.4.6 Packing Considerations

Until now, we have considered only calculations on isolated template molecules within the framework. However, for templating and structure directing to be effective it is required that the template molecules are able to self organise and pack effectively within the framework; or (as in the real synthesis) for the crystallisation of the zeolite to be facilitated by construction of the framework about a template lattice. Therefore, the calculations were expanded to include two (and in certain cases more) template molecules: one positioned at the lowest energy site for an isolated molecule and another at the next translationally equivalent site. A packing energy can be defined as follows:

$$\Delta E_{\text{pack}} = \frac{E_n}{n} - E_1$$

(5.2)

where $E_1$ and $E_n$ are the non-bonding energy of one and $n$ template molecule in the host lattice respectively. Thus if the template sub-lattice is unstable, that is adjacent template molecules cannot pack effectively, there will be a positive packing energy. Conversely if the template molecules can pack well together the packing energy will be close to zero or indeed, if the templates stabilise each other, negative. Again, the calculations have investigated the templating ability of the tetraalkylammonium and bis-quaternary amine cations. Particular attention will be paid to trying to understand those systems where the technique has thus far failed to correctly predict the correct template for a particular framework.
5.4.6.1 Tetraalkyl ammonium cations

The single template calculations incorrectly predict that TBA is a more favoured template than TPA for the formation of ZSM-5. However, the packing calculations (Table 5-8) show clearly that the formation of ZSM-5 by TBA is not feasible. In the ZSM-5 framework the butyl chains of TBA are too long to allow neighbouring channel intersections to be occupied which results in an unfavourable packing energy. Conversely, two TPA cations pack satisfactorily at adjacent sites and indeed the system is stabilised by favourable non-bonding interactions between the two molecules. Similarly TBA ions within ZSM-11 again stabilise each other. The effect of packing is further demonstrated when TPA is docked within ZSM-11. Since the propyl chains are more distant from each other when at adjacent channel intersections (nearest contact 5.7Å compared to 5.0Å for TBA), the stabilising effect of template packing is reduced giving a less favourable packing energy. Thus the calculation of interactions of two templates now allows the correct tetraalkylammonium cation for each framework to be successfully predicted.

The addition of further template molecules also leads to better agreement with experimental template positions. Figure 5-14b shows the comparison of the calculated position of TPA in ZSM-5 now that a second molecule is considered, resulting in an almost perfect match.

<table>
<thead>
<tr>
<th>Template / framework</th>
<th>$\Delta E_{\text{pack}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA / ZSM-5</td>
<td>-29.7</td>
</tr>
<tr>
<td>TBA / ZSM-5</td>
<td>+14.9</td>
</tr>
<tr>
<td>TBA / ZSM-11</td>
<td>-18.3</td>
</tr>
<tr>
<td>TPA / ZSM-11</td>
<td>-8.5</td>
</tr>
</tbody>
</table>

Table 5-8 Stabilisation energy of tetraalkyl ammonium template / framework combination when two adjacent template molecules are included.

Chapter 5.
5.4.6.2 Bis-quaternary ammonium cations

The minimum energy sites in EU-1 suggest that the templates are located in the side pockets of the channels. It is reasonable therefore to assume that the templates will occupy each pocket, thus forming a close packed array of templates which mirrors the geometry of the framework (as illustrated in Figure 5-20). Although the single molecule calculations have successfully predicted the correct experimental templates, the differences in energies are small. For example there is little difference in the interaction energies of the experimental template pentamethonium and tetramethonium and octamethonium. Do the packing energy of these systems influence their templating ability? The results of packing the more favoured templates in EU-1 are given in Table 5-9.

<table>
<thead>
<tr>
<th>Template</th>
<th>Number of molecules</th>
<th>$\Delta E_{\text{pack}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetramethonium</td>
<td>2</td>
<td>-2.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-2.6</td>
</tr>
<tr>
<td>pentamethonium</td>
<td>2</td>
<td>-5.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-6.0</td>
</tr>
<tr>
<td>hexamethonium</td>
<td>2</td>
<td>-1.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-2.9</td>
</tr>
<tr>
<td>octamethonium</td>
<td>2</td>
<td>-9.7</td>
</tr>
</tbody>
</table>

Table 5-9. Stabilisation energy of bis-quaternary ammonium templates in EU-1 when multiple template molecules are included.

Tetra-, penta- and hexamethonium ions all fit within the length of the pocket and the channel (Figure 5-20). However, tetramethonium is too short effectively to fill this void and the resulting packing energy (as is the single molecule energy) is not as favourable as those for pentamethonium. Although the packing energy of hexamethonium does not appear particularly favourable, it should be remembered that it is considerably more stable with relation to the
framework than the other templates consider when single molecules are considered (see Table 5-6).

Octamethonium is too long to lie perpendicular to the channel and has to bend. Thus although the packing energy appears favourable we note that it is only possible to fit one template molecule per two side pockets. Therefore if we normalise the packing energy to take into account the number of possible sites occupied, this is clearly not as feasible as the other templates which occupy each available pocket. Thus it is unlikely that this arrangement would result in the formation of the EU-1 framework. Furthermore, we would not expect that required conformation of the template could be achieved for an extended array of molecules. We therefore conclude that only pentamethonium and hexamethonium possess the ability to form EU-1.

The question of template packing is thus straightforward for both the case of the tetraalkylammonium ions, where the channels involved are 3-dimensional and the template molecules were sited at the intersections, and for EU-1 where the nature of the channel shape has an important effect. However, when the packing of molecules within one-dimensional channels systems or systems where the template shape does not imply siting at intersections or in pockets and cavities are considered care must be taken when considering packing effects. In these cases, the framework structure does not introduce any constraints on the siting of the template molecules. In particular we should consider how the template molecules may align with the repeat unit of the framework and how this affects the distance between templates and also the role of solvent molecules.

Consider the templating of ZSM-23. Here we find that a single trimethonium ion is favoured over the experimental template hexamethonium (Table 5-6). Attempts at packing trimethonium ions result in unfavourable packing energies in which the ammonium end groups point in the same direction (Table 5-10 and Figure 5-21). Thus, if the molecules are to close pack such that the end groups 'interlock', alternate molecules must be rotated along the axis of the channel,
which reduces the non-bonding interaction of the molecules and results in an unfavourable packing energy (Table 5-10). Heptamethonium ions can pack with interlocking end groups as a result of the odd number of carbon atoms between the end groups and the geometry of the minimum energy binding conformation. Thus it is possible to close pack the molecules in a favourable manner. Although the end groups of octamethonium do not allow close packing in the lowest energy conformer (as is the case for heptamethonium), the rotation of every other molecule does not significantly reduce the interactions with the framework. Furthermore, the calculated packing arrangement results in the template molecules being commensurate with the repeat length of the framework (also found for heptamethonium). However, it should be noted that the interaction energy of octamethonium is significantly lower than heptamethonium and also lower than that for similarly sized templates. The packing energy is also only marginally favourable. Thus in this case the relationship between non-bonding energy and templating ability is not as clear-cut as for the other systems considered.

<table>
<thead>
<tr>
<th>Template</th>
<th>Number of molecules</th>
<th>$\Delta E_{\text{pack}}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trimethonium</td>
<td>2</td>
<td>+5.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>+7.0</td>
</tr>
<tr>
<td>heptamethonium</td>
<td>2</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-2.2</td>
</tr>
<tr>
<td>octamethonium</td>
<td>2</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

*Table 5-10. Stabilisation energy of bis-quaternary ammonium cations in ZSM-23 when multiple template templates are included.*
Figure 5-21. Calculated packing geometries of tri-, hepta- and octamethonium in ZSM-23.

Although the packing calculations described for ZSM-23 adequately explain the relative templating ability of the bis-quaternary ammonium cations, it is important to note that the effect that other solvents and other molecular species on the packing arrangements have been neglected. It has also been assumed that the templates will pack as closely together as possible (as in the three dimensional channel systems considered previously). However, the possibility that the templates may be further spaced, either with or without the presence of other species must also be considered. For example, it is possible to space the bis-quaternary amines in ZSM-23 by a single unit cell length with only a small reduction in the packing energy. Thus, care must be taken when attempting to
simulate the templating ability of linear templates in one dimensional systems. High quality experimental structural evidence of the location of templates in such frameworks would enable the clarification of the packing arrangements in these systems.

5.4.7 Conclusions

The calculations have identified two complementary criteria which must be satisfied for an organic molecule to successfully template a zeolite. First, the favourable non-bonding interactions between the template and the framework must be maximised. Second, the template molecules must be able to pack efficiently within the framework. In particular, it has been shown that the non-bonding interactions between the template and the framework during the synthesis of microporous materials can have a major influence on the product formed. It has been shown that these interactions control the efficacy of the template and that the ability of the template to pack effectively in the host is also of crucial importance. The action of templating has also been quantified, an action previously considered from empirical observation to be simply a 'good fit' between template and framework. Calculations can correctly predict the positions of the template, thus making the technique a powerful aide in the solution of structures in which template molecules are occluded in the structure. It has been further demonstrated that such calculations can 'predict' suitable templates for a given host. Therefore when considering the synthesis of new materials, we should be able to design templates so that they do not favour the formation of previously synthesised structures. Although at present this work has been limited to calculations on frameworks of known structure, these results indicate that calculations on hypothetical structures will prove useful for the design and synthesis of new materials.
5.5. Applications

The above work has demonstrated how the calculation of the interactions between template molecules and zeolite frameworks can provide insights into the process of templating. We now apply these techniques to particular applications, which will further test these conclusions. Firstly, the subtle differences in the frameworks of two samples of zeolite NU-3 prepared using different templates will be investigated. Secondly the techniques will be used in an attempt to synthesise a new aluminophosphate material. This second application is, as far as is known, the first attempt to ally computational studies of templating with the attempted synthesis of a new material.

5.5.1 Templating of NU-3

Zeolite NU-3, is the synthetic isomorph of the rare mineral Levyne. The mineral, discovered by Brewster in 1825\textsuperscript{59} has an ideal composition of Ca(Al\textsubscript{2}Si\textsubscript{4}O\textsubscript{12})\textsubscript{-6}H\textsubscript{2}O\textsuperscript{60} but normally significant amounts of the calcium are replaced by sodium and potassium.\textsuperscript{61} Thus a typical composition is Ca\textsubscript{2.7}Na\textsubscript{0.7}K\textsubscript{0.2}[Al\textsubscript{6.5}Si\textsubscript{11.7}O\textsubscript{32}]\textsubscript{-16.7}H\textsubscript{2}O as that in the sample used for the determination of the crystal structure by Merlino et al.\textsuperscript{62} The material is rhombohedral possessing $R\overline{3}m$ symmetry with (hexagonal) unit cell dimensions of $a=13.538\text{Å}$ and $c=23.014\text{Å}$. The structure consists of single and double six membered rings which stack to form cages as illustrated in Figure 5-22. The structure is closely related to that of two other minerals, Offretite and Erionite, the three materials differing only in the stacking order of the six-ring structural units. In Levyne the cages are occupied by the hydrated cations.
Figure 5-22. Schematic of the structure of the LEV framework. Tetrahedral vertices only are shown. Note the stacking pattern of the single and double six membered rings.

The structures of two synthetic samples have been determined by powder X-ray diffraction techniques by McCusker, the materials differing in the choice of organic templating molecule. Not only are the positions of the templates reported but appreciably different unit cell parameters are also measured. The symmetry of the framework and templates also result in the presence of equivalent rotational conformations of the templates.

Calculations have been performed to investigate the role of the template in determining the dimensions of the unit cell and to determine if such subtle
effects can be distinguished by the methods used. Furthermore, the presence and relative stability of the rotational conformations and interconversion between these conformers is also investigated. The two templates used in the synthesis of the NU-3 samples, 1-aminoadamantane and N-methylquinuclidinium were docked into three siliceous unit cells - that of Levyne\textsuperscript{62} and the two unit cells of the NU-3 samples.\textsuperscript{13}

5.5.1.1 Location of Rotational Conformers and Partially Occupied Conformations

The two templates were docked in the unit cell of Levyne.\textsuperscript{62} The success of the procedure at reproducing the experimental template location and geometry has already been discussed (see section 5.4.3). Here the presence in the docking results of the rotationally equivalent structures will be discussed.

Experimentally,\textsuperscript{13} it has been determined that there are 3 rotational conformers of 1-aminoadamantane in NU-3 related by the $\bar{3}$ symmetry of the framework. This is shown by the 1/3 occupancy of the nitrogen position. The docking procedure successfully locates all three conformations (Figure 5-23). Furthermore, as we would expect the three conformers are equal in energy (the difference in energy is less than 0.1 kJ mol$^{-1}$). Thus it is reasonable to expect all the conformations to be equally populated - giving the same fractional population as experimentally determined. By performing single point calculations as the molecule is rotated about the $\bar{3}$ axis, an upper value for the energy barrier for rotation can be estimated. This is calculated to be 0.1 kJ mol$^{-1}$ suggesting almost free rotation. However, the experimental evidence suggests that the minimum energy conformations are populated for a significant period and therefore other factors, for example the breathing motions of the framework, must play a role in controlling the rotation of the molecules.
Figure 5-23. The rotational conformers of 1-aminoadamantane in NU-3. The $\bar{3}$ symmetry is shown.

For N-methylquinuclidinium there are also two possible conformers identified experimentally, related by a mirror plane through the cage. The docking calculations also finds two minima which correspond with these conformations (Figure 5-24). They differ in energy by <0.1 kJ mol$^{-1}$ and therefore it would be reasonable to expect similar occupancies for both structures; a result which is borne out by the experimental populations of 3:2. Although the two conformers differ by virtue of the framework structure - the methyl group points towards a single and double six ring respectively - this does not appear to affect the relative energies of the two structures. A barrier for rotation about the $\bar{3}$ axis of 1.7 kJ mol$^{-1}$ is calculated which is significantly higher than that for 1-aminoadamantane - a slightly surprising result given the more uniform and cylindrical shape of N-methylquinuclidinium compared to 1-aminoadamantane. However, the nearest neighbour contacts with the 6-rings of the framework are shorter with N-methylquinuclidinium (3.99Å versus 4.16Å) and this tighter fit could partly account for the difference in rotational barriers.

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However, it is important to note that the above calculations were performed using the same framework unit cell dimensions. McCusker found a significant difference in the unit cell dimensions when the different templates were used. The effect of these differences on the calculations will now be examined.

5.5.1.2 The Influence of Template on the Unit Cell Parameters

The unit cell dimensions vary by up to 1.5% depending on the template used (see Table 5-11). It is evident that this is a result of the shape of the template: 1-aminoadamante has a shorter but wider cross section than N-methylquinuclidinium and consequently results in an larger $a$ parameter and shorter $c$ parameter. It would be interesting to determine if the methods used are sensitive to such small changes in framework structure. The two templates
were therefore docked into the two unit cells determined by McCusker in addition to that of Levyne. These results are presented in Table 5-11.

Most importantly, the template which formed the pertinent unit cell is the most stable in that unit cell. Thus the rounder 1-aminoadamante is more stable in the unit cell with the larger a parameter and the longer and thinner N-methylquinuclidinium is more stable in the unit cell with the elongated c parameter. Thus it is apparent that the choice of unit cell can have a crucial effect on such calculations. The unit cell of Levyne is larger than that of the NU-3 samples. Thus the larger template, N-methylquinuclidinium is found to be the most stable in the material. The occluded hydrated cations in the mineral structure have a similar shape and size to this template (Figure 5-25). The effect of the different unit cell dimensions on the initial random insertion of the template into the framework is also borne out in these docking trials. In these trials of 50 docked structures, a higher population of the "correct" structures are located when the unit cell which was formed with the template under consideration is used. It is therefore clear that these calculations are able to distinguish such subtle effects. However, the results also show that small changes in framework structure may have a noticeable effect on the results of such calculations. Thus any conclusions regarding templating efficacy based on small energy differences should be considered with care.

The effect of the correct unit cell on the rotational barriers can now be determined. When the rotational barrier for a template is calculated in the unit cell as formed by that template, it is found to be greater than when calculated in the unit cell of Levyne. The calculated barriers are 1.0 kJ mol⁻¹ and 3.4 kJ mol⁻¹ for 1-aminoadamantane and N-methylquinuclidinium respectively (compared to <0.1 kJ mol⁻¹ and 1.7 kJ mol⁻¹ in Levyne). This demonstrates clearly that subtle changes in unit cell parameters can have a significant effect on calculated properties. Furthermore, it again emphasises the way in which templates affect the formation of particular structures.
<table>
<thead>
<tr>
<th>Framework formed by:</th>
<th>Lattice parameter ($\text{Å}$)</th>
<th>Template</th>
<th>$E_{\text{inter}}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$c$</td>
<td></td>
</tr>
<tr>
<td>N-methylquinuclidinium</td>
<td>13.0595</td>
<td>22.6061</td>
<td>N-methylquinuclidinium -96.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-aminoadamantane -94.4</td>
</tr>
<tr>
<td>1-aminoadamantane</td>
<td>13.2251</td>
<td>22.2916</td>
<td>1-aminoadamantane -95.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N-methylquinuclidinium -90.0</td>
</tr>
<tr>
<td>Levyne</td>
<td>13.338</td>
<td>23.014</td>
<td>1-aminoadamantane -90.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N-methylquinuclidinium -92.1</td>
</tr>
</tbody>
</table>

Table 5-11. Templates in the different LEV structures. Experimental parameters from McCusker$^{13}$ with the exception of those of Levyne.$^{52}$
Figure 5-25. Illustration of the shape and size of the organic templates, N-methylquinuclidinium (left) and 1-aminoadamantane (centre) and the hydrated calcium cation (right) in Levyne. Calcium is shown hydrated with 6 water molecules at the fully occupied site as determined by Merlino et al.62
5.5.2 Selection and Design of a Template Molecule for the Formation of a New Microporous Aluminophosphate Material.

Materials based on aluminophosphate frameworks (APOs) are an important class of microporous catalyst. Since the early work at Union Carbide, there has been much effort in the synthesis of new APO materials. Many are APO analogues of zeolites (such as AlPO₄-20 which has the sodalite structure) but others are unique to APO materials (for example VPI-5 which possesses 18 membered rings). As with zeolites, the synthesis is gel based and the addition of organic templates is common. The synthesis of new materials is similarly important and again is generally done by trial and error.

A prime motivation for this work was to design a new APO structure, in collaboration with synthetic zeolite chemists. The goal was to synthesise a material similar but distinct to the DAF-1 (DFO) structure synthesised at the Davy-Faraday laboratory. DAF-1 possesses a novel structure with two parallel large-pore channel systems bounded by twelve-membered rings (see Figures 5-26 and 5-27). One of these channel systems (B) is one-dimensional and contains periodic supercages, while the other (A) is more uniform in cross section and is linked three-dimensionally via double ten-ring pores. The two channel systems, are linked to one another only by smaller eight-ring pores. DAF-1 is typically prepared with Mg in the framework with a compositional formula of Mg₀.22Al₀.78PO₄.
Figure 5-26. The structure of DAF-1. The two channel systems viewed perpendicular to the channel direction.

Figure 5-27. The structure of DAF-1. The two channel systems viewed parallel to the channel direction.
DAF-1 has been shown to be a good catalyst for a number of reactions, for example showing higher activity than ferrierite and theta-1 for butene isomerisation at low temperature. Thus, it is reasonable to assume that a structure with similar pore dimension but with a modified interconnectivity and supercage may also possess similar catalytic properties. Therefore a study was carried out of the templating of DAF-1 and other APO structures which are templated with similar templates in order to attempt to determine the action of the templating species. From this study a template could be designed and proposed which would favour the production of a similar but distinct structure.

5.5.2.1 Templates in DAF-1

DAF-1 has been successfully synthesised using two different templates, octamethonium and decamethonium, both bis-quaternary ammonium cations. Both possess the same cross-section but differ in effective van der Waals length by 1.58 Å. The docking techniques have been applied to locate the minimum energy sites of these templates within the DAF-1 structure. As in our previous calculations, to avoid any question of the siting of heteroatoms, a neutral framework is used. In addition, since the forcefields available are not well parameterised for APO type structures we use siliceous frameworks. Any effect consequent upon the difference in charge and other non-bonded interaction will partly be compensated by the ordered distribution of Al and P in the frameworks of APOs. These results are presented in Table 5-12 and Figures 5-28 and 5-29. Subsequently the packing of these molecules was considered (Table 5-12 and Figure 5-30).

The minimum energy sites of both templates lie parallel to the uniform 12-ring channel (A) along the c axis of the crystal. In addition there are a number of less stable conformations within the supercage channel (B) - as illustrated in Figures 5-28 and 5-29. However, in addition to being less stable, these appear to be disordered with respect to the framework and are unlikely to form an extended sub-lattice of molecules, which would be expected if these molecules had any structure directing or templating effect. It is therefore concluded that the
templating action of the octa- and decamethonium ions is restricted to the A channel system with the molecules located in the B channel simply acting as space filling species. If this is the case, and the exclusion of additional templates from the supercage system does not prevent the formation of DAF-1, by careful modification of the amount of template used, the (divalent) metal content of the material can be fine tuned. Thus, materials with a metal content ranging from a minimum based on occupying only the A channels with template molecules (2R²⁺ per unit cell) to a maximum figure dependent on the number of molecules which can be accommodated within the supercage channel system can be synthesised. This result has been corroborated by workers at the Royal Institution by performing a synthesis in which ethylene glycol is used as a co-solvent and a much lower than normal proportion of template is used. Local EDX analysis of the resulting DAF-1 crystals shows a phase with a much lower than normal Mg content (Mg/P = 0.06 rather than a typical value of 0.08). Thus it appears that our hypothesis is correct.

<table>
<thead>
<tr>
<th>Template and Site</th>
<th>E&lt;sub&gt;inter&lt;/sub&gt; / kJ mol⁻¹</th>
<th>ΔE&lt;sub&gt;pack&lt;/sub&gt; / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octamethonium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A channel</td>
<td>-34.0</td>
<td>0.8</td>
</tr>
<tr>
<td>B channel</td>
<td>-23.6</td>
<td>—</td>
</tr>
<tr>
<td>Decamethonium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A channel</td>
<td>-37.5</td>
<td>-3.6</td>
</tr>
<tr>
<td>B channel</td>
<td>-27.0</td>
<td>—</td>
</tr>
<tr>
<td>Dodecamethonium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A channel</td>
<td>-41.5</td>
<td>1.5</td>
</tr>
<tr>
<td>B channel</td>
<td>-25.2</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 5-12. The interaction energies of the experimental and modified templates in various sites within the structure of DAF-1.
Figure 5-28. The calculated locations of the octamethonium template in DAF-1. The global most stable configuration, in the A channel, and the most stable conformation in the B channel are shown. Views parallel and perpendicular to the channel are given.
Figure 5-29. The calculated locations of the decamethonium template in DAF-1. The global most stable configuration, in the A channel, and the most stable conformation in the B channel are shown. Views parallel and perpendicular to the channel are given.
5.5.2.2 Designing a Template to Form a New Material

In order to synthesise a structure which has similar properties (pore diameter, channel dimensionality etc.) to DAF-1, a suitable template must be selected. Although it is difficult to predict a framework topology which will be formed from a template structure, the calculations described here can be used to provide information on the likelihood of forming known structures. Consequently, existing templates can be modified so that they no longer favour the formation of these known frameworks. Thus modifications have been considered for octa- and decamethonium ions so that they no longer favour the DAF-1 structure.

To maintain a similar pore dimension, a template with the same or similar cross section will be required. Thus, no modification of the methyl end groups will be made. This is demonstrated by calculations on the ethyl analogue substituted bis-quaternary amines, octaethonium, \((\text{CH}_3\text{CH}_2)_3\text{N}^+-(\text{CH}_2)_8^+\text{N(\text{CH}_2\text{CH}_3)}_3\) and hexaethonium, \((\text{CH}_3\text{CH}_2)_3\text{N}^+-(\text{CH}_2)_6^+\text{N(\text{CH}_2\text{CH}_3)}_3\) in DAF-1. The results (Table 5-13) clearly show that favourable interactions between the template and the framework are reduced on substitution with ethyl groups. Another important consideration is the availability of prospective templates. Materials requiring specialised synthesis are not as suitable as those available “off the shelf”. Therefore the search for a new template has been restricted to modification by means of the length of the alkyl backbone of the molecules.

Consider the bis-quaternary ammonium cations series. Shorter members tend to form cage based structures - for example hexamethonium forms \(\text{ALPO}_4\)-17. Thus, it is reasonable to confine the search to longer members of this series. Dodecamethonium, \((\text{CH}_3)_3\text{N}^+-(\text{CH}_2)_{12}^+\text{N(\text{CH}_3)}_3\) was considered to be suitable candidate. The minimum energy site is calculated to be in the A channel (Figure 5-30) (as for octa- and decamethonium). Less stable and disordered sites are again accessible in the B channel. Although for a single molecule dodecamethonium is more stable than decamethonium it is predicted that due to packing considerations dodecamethonium will not form DAF-1. The packing calculations (Table 5-12, Figure 5-30) suggest that it will be difficult to pack
dodecamethonium in a commensurate manner within the DFO structure. We also note that dodecamethonium had not previously been reported as a template for the formation of APOs. Thus we predict that dodecamethonium would not form DAF-1 and may lead to a new structure type.

<table>
<thead>
<tr>
<th>Template</th>
<th>$E_{\text{inter}}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>octamethonium</td>
<td>-34.0</td>
</tr>
<tr>
<td>octaethonium</td>
<td>-19.87</td>
</tr>
<tr>
<td>hexamethonium</td>
<td>-30.51</td>
</tr>
<tr>
<td>hexaethonium</td>
<td>-25.88</td>
</tr>
</tbody>
</table>

*Table 5-13: The interaction energies at the calculated lowest energy configuration of methyl- and ethyl-bis-quaternary amines within the structure of DAF-1.*

A synthesis involving dodecamethonium resulted in the formation of the ALPO$_4$-5 structure. Subsequent calculations on this combination confirmed that the dodecamethonium was a more stable template within ALPO$_4$-5 than that calculated within DAF-1 (see Table 5–14 and Figure 5–31 in section 5.5.2.3). Encouragingly, however, no DAF-1 phase was detected.

Thus the calculations have been partly successful in computationally directing synthesis. A template which does not form DAF-1 has been designed. However, it is apparent that in order to select a template to form a new material, extensive calculations involving many possible structures is required. In particular, care should be taken to include the ‘default’ structures -materials which tend to be formed by a variety of different templates, typically ALPO$_4$-5 for this type of synthesis - in these calculations. However, the methodology allows the automated and reasonably rapid scanning of a large number of framework types.
Figure 5–30. Packing of octamethonium, decamethonium and dodecamethonium in DAF-1. Nearest template contacts are 6.34Å, 3.70Å and 2.30Å respectively.
5.5.2.3 Template Interactions in other APO Structures

In order to establish whether this methodology has further applications in APO synthesis, the calculations have expanded to include a number of typical APO frameworks. The interactions of siliceous ALPO₄₅, ALPO₄₁₇, DAF-1 and MAPO₃₆ frameworks with the bis-quaternary amines \((\text{CH}_3)_3N^+-(\text{CH}_2)_x^+\text{N(CH}_3)_3\) with \(x=6-12\) have been investigated. The non-bonding interaction energy, at the minimum energy geometry, between for each possible template / framework combination has been calculated. These are presented in Table 5–14.

<table>
<thead>
<tr>
<th>Template</th>
<th>DAF-1</th>
<th>ALPO₄₅</th>
<th>ALPO₄₁₇</th>
<th>MAPO₃₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexamethonium</td>
<td>—</td>
<td>—</td>
<td>-25.9*</td>
<td>-28.0</td>
</tr>
<tr>
<td>heptamethonium</td>
<td>—</td>
<td>-31.7</td>
<td>-24.4</td>
<td>—</td>
</tr>
<tr>
<td>octamethonium</td>
<td>-34.0*</td>
<td>-33.7</td>
<td>no fit</td>
<td>-31.4</td>
</tr>
<tr>
<td>decamethonium</td>
<td>-37.5*</td>
<td>-37.0</td>
<td>no fit</td>
<td>-36.1</td>
</tr>
<tr>
<td>dodecamethonium</td>
<td>-41.5</td>
<td>-41.5*</td>
<td>no fit</td>
<td>-39.1*</td>
</tr>
</tbody>
</table>

Table 5–14. Non-bonded interactions energy of bis-quaternary amines in various frameworks. Template predicted as effective template are emboldened. *Experimental template.

It can be seen that, again, the interaction energy is a reasonably good measure of template efficacy. That is, the framework / template combinations with the most favourable non-bonding interactions are those which form experimentally. The importance of optimal non-bonding contacts is emphasised by the close fit of the templates and frameworks as illustrated in Figures 5–11—5–15 and 5–30,5–31.
However, difficulties are found (as discussed previously) when considering frameworks with one-dimensional channel systems. Here, the ability to pack the template within the channels is of utmost importance. Thus, contrary to the single molecule calculations we concluded that dodecamethonium is not likely to be a suitable candidate template for DAF-1 (Table 5-12). However, we should also note that certain frameworks, containing one dimensional channels, are readily synthesised by a number of templates. Their channel structures tend to be uniform and have on the whole short repeat units. Thus, any template which fits within these constraints is likely to form the material. ALPO$_4$5 is typical of these types of framework and thus appears as a 'default' structure in many syntheses. In the case of denser frameworks with only cages, it is readily apparent when templating will not occur. Only hexamethonium and heptamethonium will fit within the cage of ALPO$_4$-17, the docking procedure failing to insert the templates which are too large. Hexamethonium is found to be the most stable, the final geometry being illustrated in Figure 5-32.
Figure 5-31. The minimum energy conformation of the experimental template dodecamethonium in AlPO$_4$-5.
Figure 5-32. The minimum energy conformation of the experimental template hexamethonium in AlPO$_4$-17.

5.5.2.4 Polymeric Templates

As part of the ongoing search for new APO structures, cationic polymers have been considered as suitable templates. Previously, polymers based on cyclic quaternary amines have proved successful in zeolite synthesis. The materials used were co-polymers of $\alpha,\omega$-di-bromoalkanes and 1,4-diazabicyclo(2,2,2)octane. The resulting polymer (the structure of which is shown in Figure 5-33) has been found to be an effective template, forming
Gmelenite, ZSM-12 and Mordenite\textsuperscript{69-71} and are particularly effective at preventing stacking faults.\textsuperscript{71}

\[
\begin{array}{c}
\text{N} \quad \text{N} \quad \text{N} \quad \text{(CH}_2\text{x)} \\
\end{array}
\]

\textit{Figure 5-33. DABCO polymer structure. Possible values of x are 3, 4, 5, 6 and 10. Typical polymers chains have a molecular weight of about 10,000 which corresponds to a chain of 55 monomers for the material produced using dibromohexane.}

Workers at the Davy-Faraday laboratory have subsequently investigated the substituted quaternary ammonium polymer, polyhexadimethrine (illustrated in Figure 5-34). When added to an aluminophosphate gel MAPO-36 is formed.\textsuperscript{67} MAPO-36 (framework code ATS) consists of parallel non-intersecting straight channels formed by 12-rings with pore dimensions of 6.5x7.5Å.\textsuperscript{72} The structure of the polymer chains and the manner in which this interacts with the MAPO-36 framework have been investigated in order to understand the templating action of this polymer.

\textit{Figure 5-34 Structure of the hexadimethrine monomer.}

If the polymer chains are to be occluded within the channel system of MAPO-36 the chains themselves must be straight. A series of short polymer chains were constructed both in random configurations and constrained to be linear. The results of energy minimising all these polymer strands are given in Table 5-15 and clearly show that the straight conformation is favoured. Furthermore, the most stable linear configuration is ordered with respect to the methyl...
substituents on the nitrogen - the most stable configuration has two methyl groups of the monomer \textit{trans} to each other, whilst the methyl groups of adjacent monomers are \textit{cis} to one another (as shown in Figure 5–35).

<table>
<thead>
<tr>
<th></th>
<th>Energy / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>Pentamer</td>
<td></td>
</tr>
<tr>
<td>straight conformer</td>
<td>954.9</td>
</tr>
<tr>
<td>50 Random* chains</td>
<td></td>
</tr>
<tr>
<td>Minimum</td>
<td>954.9</td>
</tr>
<tr>
<td>Maximum</td>
<td>1264.6</td>
</tr>
<tr>
<td>Mean</td>
<td>975.1</td>
</tr>
<tr>
<td>Decamer</td>
<td></td>
</tr>
<tr>
<td>straight conformer</td>
<td>3141.5</td>
</tr>
<tr>
<td>50 Random* chains</td>
<td></td>
</tr>
<tr>
<td>Minimum</td>
<td>3283.0</td>
</tr>
<tr>
<td>Maximum</td>
<td>4259.2</td>
</tr>
<tr>
<td>Mean</td>
<td>3435.4</td>
</tr>
</tbody>
</table>

\textit{Table 5–15. Energy minimisation results for the polyhexadimethrine chains in vacuum.}

\textit{*random torsional angle between monomers.}
Figure 5-35. The structure of polyhexadimethrine. The configuration shown is that calculated to be the most stable. The pairs of adjacent methyl groups are trans to each other.

The most stable polymer strands were docked by sight into siliceous fragments of the framework. The simulated annealing procedure previously described (section 5.3.4) was then used to obtain minimum energy configurations. These calculations demonstrate the excellent fit of this polymeric species within the channel system. The side chain methyl groups 'lock' into the indents in the channel walls (Figure 5-36). There is excellent correlation between the framework structure and the distances between adjacent methyl groups and length of the repeat unit of the polymer.

Similar calculations with the polymers occluded in ALPO₄.5 show the interactions to be more favourable in this case (Table 5-16). Thus, it might be expected that polyhexadimethrine should favour the formation of ALPO₄.5 and not MAPO-36. However, there are numerous reasons why this may not be the case. The difference in energy between the two structures when considering the decamer is only 16 kJ mol⁻¹, which considering the uncertainties concerning the contribution to this difference to the “free” ends of the polymer chain and more significantly the use of siliceous frameworks, is negligible. It is interesting to note that the self energy (the energy of the molecule in vacuum) of the polymer configuration in MAPO-36 is lower than that in ALPO₄.5 by 10 kJ mol⁻¹. Thus it can be argued that the during nucleation the polymers can be considered more stable if MAPO-36 is formed. However, more significantly, the crystallisation
process of ALPO$_4$5 is likely to be the dominant process. The ability to synthesise ALPO$_4$5 with a large number of templates and in gels of varying composition suggests that this framework structure is energetically and kinetically favoured. Thus if the presence of the polymer chains modifies the kinetics for nucleation and crystallisation of ALPO$_4$5, the formation of MAPO-36 may be favoured. However, given the complex synthesis conditions this can only be considered as one of many possible explanations of what is, from the evidence obtained here, a subtle templating effect. Future work on the nucleation of zeolite framework fragments by templates may provide insights.

Figure 5–36. The minimum energy configuration of polyhexadimethrine (decamer) in siliceous MAPO-36. View shows the locking of the methyl groups into the indentation of the channel walls.
### Table 5-16. Comparison of the interaction energies of the polymer chains in siliceous MAPO-36 and ALPO$_4$5

<table>
<thead>
<tr>
<th></th>
<th>pentamer</th>
<th>decamer</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPO-36</td>
<td>-109.3</td>
<td>-203.0</td>
</tr>
<tr>
<td>ALPO$_4$5</td>
<td>-116.3</td>
<td>-219.8</td>
</tr>
</tbody>
</table>

The use of such polymeric species has two advantages over smaller molecules. Firstly, the polymeric nature may prevent the formation of stacking and other defects. Secondly, with these species the degree of metal substitution (forming MeAPOs) in the framework can be closely controlled, since the number of cationic species per unit cell can be more precisely known. This may in turn influence the siting of this substitution. The use of cationic polymers as templates for the synthesis of microporous solids is therefore a promising field for further research.
5.6. References


Chapter 5.


(42). P.A. Cox, A.P. Stevens, L. Banting and A.M. Gorman, “Molecular Modelling Studies of Zeolite Synthesis”, *to be published*


(67). P.A. Wright, manuscript in preparation.


Chapter 6

The Structure of Iron substituted

ZSM5
6.1. Summary

In this chapter atomistic simulations techniques (for both perfect and defectives lattice) will be applied to the study of the zeolite Fe-ZSM5. The siting of the Fe within the framework (at a T site) will be investigated along with the effect of the substitution on the pore structure. Furthermore, the calculations will be compared to experimental EXAFS data and used to refine the models proposed from the data. Additional calculations of physical properties, directly related to the catalytic activity, will also be presented. Finally, large scale calculations will be presented which detail the interaction of the substituted zeolite with the organic template used in its synthesis.

6.2. Introduction

Zeolite ZSM-5\(^1\) is used in many industrially important catalytic processes (see Table 2.2 in Chapter 2) and has been the subject of extensive research. Indeed, the Motunui methanol to gasoline (MTG) plant in New Zealand using ZSM-5 has been in commercial operation since 1986 producing over half a billion litres of gasoline a year.\(^2\) The structure is a three dimensional channel system consisting of straight channels which intersects with a sinusoidal system, the topology illustrated in Figure 6-1. The 10 membered rings result in pore dimensions of 5.22-5.75Å (straight channel) and 5.28-5.60Å (sinusoidal channel).\(^3\) The structure is shown in Figure 6-2
Figure 6-1. Illustration of the channel topology of ZSM-5 shown by cylinders identical in cross-section to the channels which are directed along them. (Illustration is based on that of Kokotailo et al.4)

Figure 6-2. The crystallographic structure of ZSM-5, viewed down the straight channel (1 0 0) with the sinusoidal channel running perpendicular to this. Silicon atoms only are shown for clarity; bridging oxygens are located approximately halfway between the tetrahedral vertices.
Since the catalytic activity of the material is inextricably linked to its composition and structure, recent work has attempted to modify the structure by introducing heteroatoms, such as B, Ti, and Ga into the framework - as discussed in Chapter 2. Much work has been carried out on the inclusion of iron in the ZSM-5 framework. This material has been shown to be an effective catalyst and is manufactured for use on an industrial scale. Of particular interest is that the activity of Fe-ZSM5, with respect to both reactivity and selectivity, is subtly different from that of Al-ZSM5, whilst retaining the same topological structure.

(Fe,Si)-ZSM-5 is normally prepared with varying compositions, having typical SiO$_2$/Fe$_2$O$_3$ ratios in the range 20-200. It has been shown that all the iron is incorporated in framework sites - replacing silicon - in materials with a SiO$_2$/Fe$_2$O$_3$ ratio greater than 50 and that the average iron content is 0.7 Fe per unit cell. Higher iron concentration leads to poorly characterised extra-framework particulates as does extreme heat treatment.

As mentioned before, much of the motivation for continued work on Fe-ZSM5 is its improved catalytic activity. This material has been shown to be an active catalyst for the production of methanol by the direct oxidation of methane and also to be effective as a catalyst in the methanol and hydrocarbon transformation reaction (MHTR) with a higher yield and selectivity towards C$_2$-C$_4$ olefins than (Al,Si)-ZSM-5. Furthermore, (Fe,Si)-ZSM-5 has a higher selectivity than (Al,Si)-ZSM-5 during xylene isomerisation. It is therefore apparent that although iron is present in similar concentrations to aluminium in ZSM-5, it has a subtly different activity. These observations provide a strong motivation to investigate the structure of Fe-ZSM5 on an atomistic level, which may lead to explanations for these changes in activity.

Both EPR and $^{57}$Fe Mössbauer spectroscopy of (Fe,Si)-ZSM-5 have indicated that the predominant iron species is iron(III) located at the tetrahedral sites of the zeolite framework. X-ray diffraction studies reveal no significant
differences in the structure when compared to (Al, Si)-ZSM-5, a consequence of the low concentration of iron, which also suggests that any structural changes are local only. Recently the material has been investigated using EXAFS (Extended X-ray Adsorption Fine Structure), a technique which gives further information regarding the local environment of the iron site. This technique uses modulations in the X-ray absorption spectra due to backscattering of photoelectrons from neighbouring atoms to determine the local geometry and coordination of specific atoms. A brief account is given in section 6.3.2. Axon et al. proposed a 4-coordinated single oxygen shell about the iron in a sample which still contained the organic template. For a calcined and rehydrated sample Axon et al. again found a 4-coordinated single oxygen shell, but Patarin et al. produced a better fit with a 3-coordinated oxygen shell and a further single oxygen at a longer distance. Following the work of Lin et al., this more distant oxygen was attributed to water associated with a tri-coordinated framework iron. Recent work by Bordiga et al. has, however, suggested that the environment of the framework iron species is not tetrahedral in the H+ form, but rather a distorted tetrahedron. Furthermore, adsorption of ammonia lead to a tetrahedral environment and not, as in the case of Ti-silicalite, to an increase in the coordination sphere of the heteroatom.

However, none of the experimental methods yields information regarding the distribution of iron sites in the framework or the siting of the protons which compensate the effective negative charge of the Fe3+ substitutional. Knowledge of which tetrahedral framework T sites are occupied will help our understanding of catalytic activity and reaction mechanisms. Furthermore, no experimental technique has revealed details of the way in which structural changes due to Fe substitution may influence the selectivity and reactivity of the catalyst.

The techniques based on perfect lattice and defect static lattice calculations have been successful in modelling not only the structure (and indeed subtle structural features) of siliceous zeolites but also in determining the structure.
and location of heteroatoms in zeolite frameworks (e.g. aluminium in (Al,Si)-ZSM-5 and ZSM-18, Ti in TS-1) and extra-framework cations sites (e.g. Ni in Ni-Y).

Although quantum mechanical studies have also been used in such studies, they are limited by the expense of the calculations. Calculations are thus usually limited to small clusters of T atoms and in many cases these clusters are only partially optimised to relaxed geometries. Similar calculations have been performed using Extended Huckel Molecular Orbital theory on Fe-ZSM5. Here the geometries of the clusters were kept fixed at the experimentally determined structures. These, as with the partially relaxed cluster calculations, suffer from several disadvantages. The calculated energies will only be useful for structures which are at equilibrium, and it has been shown that relaxation effects play a central role in determining the relative energies of different substitution sites for heteroatoms in zeolites. The problem is particularly acute as the experimental crystallographic geometries which are used refer to the T-O bond length corresponding to the average value and not the equilibrium value for a particular T atom. Another consideration is the accuracy of the experimental data which are used to construct the cluster models. Since thermal effects are not included in either the quantum mechanical or atomistic simulations, low temperature structures are preferred. Furthermore, single crystal data have a higher degree of accuracy than powder pattern data.

As previously discussed in Chapter 2 and in more detail in Chapter 5, the preparation of zeolites usually involves the presence of a structure directing (as well as charge compensating) organic template molecule. Tetrapropylammonium (TPA+) salts are used for the preparation of silicalite and its substituted analogues. X-ray diffraction studies have located the template at the channel intersections in ZSM-5 / silicalite. From their

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† Silicalite (or Silicalite-I) is the purely siliceous analogue of ZSM-5.
EXAFS studies, Axon et al.\textsuperscript{21} have proposed a model for TPA\textsuperscript+ /Fe-ZSM5 in which the TPA\textsuperscript+ is significantly displaced from the centre of the channel intersection, which they suggest is caused by the electrostatic attraction between the cation and the negatively charged framework. Large scale calculations on the framework / template system have been carried out in order to investigate this effect and to study the detailed structure of the Fe substituted ZSM-5 material.

6.3. Methodology

The techniques of lattice and defect energy minimisation based on the Born model (as described in Chapter 3) were employed in this study. For the calculation of the energetics and geometry of the iron substitutional sites the defect methodology as implemented in the CASCADE code\textsuperscript{41} was used. For these calculations an inner region of radius of 9.5Å was used. Periodic perfect lattice calculations using the GULP program\textsuperscript{42} were also performed on the most stable configurations. GULP was also used to perform calculation of the vibrational spectra of Fe-ZSM5 and for the periodic calculations on the interaction of Fe-ZSM5 and the TPA\textsuperscript+ template.

6.3.1 Potential Parameters

The interatomic potentials used consisted of the typical two body short-range pair potential discussed in Chapter 3. However, given the partly covalent nature of the bonding in zeolites, these are supplemented by (three body) bond-bending terms. Furthermore, the potentials used for the organic component in the template calculations are based on a molecular mechanics forcefield model (as described in Chapter 3). A shell model\textsuperscript{43} is included to describe ionic polarisability of the framework oxygen. The quality of these potentials is critical to the success of the simulations. However, it is clear that given
parameterisations of suitable quality, accurate results can be achieved.\textsuperscript{26,27} The potential parameters used for the zeolitic framework are given in Tables 6-1—6-5, where we employ the same potentials as described by Jackson and Catlow,\textsuperscript{26} Winkler \textit{et al.}\textsuperscript{44} and Schroder \textit{et al.}\textsuperscript{28,45}

For the Fe-O interactions, the potentials of Lewis and Catlow\textsuperscript{46} for Fe$_2$O$_3$ are employed but using an unpolarisable cation. These parameters were used in preference to other potentials (for example those of Bush \textit{et al.}\textsuperscript{47}) since they are consistent with the O-O parameters employed in the zeolite potentials. However, we note that this potential was fitted to an octahedral environment which is now being transferred into a tetrahedral environment. The validity of this transfer was investigated by calculating Fe-O distances in both octahedral and tetrahedral environments in a number of iron oxides structures. In the octahedral environment of $\alpha$-Fe$_2$O$_3$ the potentials give a slightly short Fe-O distance of 1.94Å (experimental 1.96Å), whilst in the tetrahedral site of Fe$_3$O$_4$ they give a mean Fe-O distance of 1.87-1.92Å (experimental 1.87-1.92Å\textsuperscript{48}). For the latter all possible distributions of Fe$^{3+}$ and Fe$^{2+}$ ions on the octahedral sites in the full unit cell were studied. The bond lengths obtained are also in good agreement with a value of 1.89Å calculated from the ionic radii of Shannon.\textsuperscript{49} This potential is therefore expected to give acceptable Fe-O distances within the tetrahedral environment of the zeolitic structure.

In the work of Schroder \textit{et al.}\textsuperscript{28,45} the 'OH group is modelled as comprising of O$^{1.4+}$ and H$^{0.4+}$ species. This potential was originally derived using \textit{ab initio} techniques by Saul \textit{et al.}\textsuperscript{50} and leads to an accurate reproduction of the dipole moment of the —OH group. Schroder \textit{et al.}\textsuperscript{28,45} found it necessary to rescale the Si-O potential for the Si-OH interaction to achieve compatibility with this reduced oxygen charge. Thus in the present study the Fe$^{3+}$-O(H) potential was derived from that for Fe$^{3+}$-O$^{2-}$ by scaling the A parameter of the Buckingham potential by the same factor, 0.784, as used by Schroder \textit{et al.}\textsuperscript{45} in scaling the Si$^{4+}$-O(H) and Al$^{3+}$-O(H) potentials from the corresponding Si$^{4+}$-O$^{2-}$ and Al$^{3+}$-O$^{2-}$.
values. No alternative empirical procedure is available since there are no suitable structures containing Fe-OH which could be used for parameter fitting.

Table 6-1. Zeolite Framework Potential Parameters - Buckingham Potentials.

<table>
<thead>
<tr>
<th>Species</th>
<th>A (eV)</th>
<th>ρ (Å⁻¹)</th>
<th>C (eV Å⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O²⁻</td>
<td>1283.90</td>
<td>0.3205</td>
<td>10.66</td>
</tr>
<tr>
<td>Si-O¹⁴⁻</td>
<td>983.56</td>
<td>0.3205</td>
<td>10.66</td>
</tr>
<tr>
<td>O²⁻-O²⁻</td>
<td>22764.00</td>
<td>0.1490</td>
<td>27.88</td>
</tr>
<tr>
<td>O²⁻-O¹⁴⁻</td>
<td>22764.00</td>
<td>0.1490</td>
<td>27.88</td>
</tr>
<tr>
<td>Fe-O²⁻</td>
<td>1102.40</td>
<td>0.3299</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe-O¹⁴⁻</td>
<td>862.08</td>
<td>0.3299</td>
<td>0.00</td>
</tr>
<tr>
<td>O²⁻-H</td>
<td>311.97</td>
<td>0.2500</td>
<td>0.00</td>
</tr>
</tbody>
</table>

A cut-off value of 15Å was used for all potentials.

Table 6-2. Zeolite Framework Potential Parameters - Morse potentials.

<table>
<thead>
<tr>
<th></th>
<th>Dₑ (eV)</th>
<th>α (Å⁻¹)</th>
<th>r₀ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H - O¹⁴⁻</td>
<td>7.0525</td>
<td>2.1986</td>
<td>0.9485</td>
</tr>
</tbody>
</table>

where \( V(r) = Dₑ(1 - \exp[-α(r-r₀)])^2 \).

Table 6-3. Zeolite Framework Potential Parameters - Shell Model Parameters.

<table>
<thead>
<tr>
<th>O²⁻</th>
<th>Shell charge (γ)</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.86902</td>
<td>74.92 eV Å</td>
</tr>
</tbody>
</table>

where the free ion polarisability is given by \( α = γ²/k \).
Table 6-4. Zeolite Framework Potential Parameters - Three body terms.

<table>
<thead>
<tr>
<th>O-Si-O</th>
<th>K</th>
<th>Θ₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.09724 eV rad⁻¹</td>
<td>109.47°</td>
</tr>
</tbody>
</table>

where $E_{THB} = \frac{1}{2} K (\Theta - \Theta_0)^2$ and $O$ is both $O^{2-}$ and $O^{1.4-}$.

Table 6-5. Zeolite Framework Potential Parameters - Framework Ion Charges.

<table>
<thead>
<tr>
<th>Species</th>
<th>Charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si⁴⁺</td>
<td>4.0</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>3.0</td>
</tr>
<tr>
<td>O²⁻ core</td>
<td>0.86902</td>
</tr>
<tr>
<td>O²⁻ shell</td>
<td>-2.86902</td>
</tr>
<tr>
<td>O(H)⁺</td>
<td>-1.426</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.426</td>
</tr>
</tbody>
</table>

*Oxygen and Hydrogen components of OH.

The bonding and non-bonding interactions of the TPA⁺ and the interaction of the TPA⁺ with the oxygen of the framework were treated using the potential parameters of Oie et al.⁵¹ These were derived by fitting to a large number of organic crystal structures and were successfully used by Gale et al.⁵² in their study of pillared clays. The parameters are given in Table 6-6. The charges on the atoms of the TPA⁺ were calculated from the gas phase optimised geometry of TPA⁺ (Figure 6-3) using the semi-empirical MNDO method⁵³ and are given in Table 6-7. The interaction of the framework T sites and the TPA⁺ are considered as entirely Coulombic. Intramolecular Coulombic interactions are subtracted from the energy expressions in the calculations as they are implicitly included in the forcefield definition of the bond stretching, bending and higher terms. We note that the non-bonding parameters used to describe the interaction between the lattice oxygen and the organic molecules are those derived by Oie et al.⁵¹ to describe the interaction of organic oxy species. Thus, since the oxygen in the
zeolite is treated ionically and has therefore a much larger charge than used in deriving these parameters\(^1\) the potential is likely to underestimate these interactions. However, since it is not possible to re-derive these parameters readily (and quickly), they have been used as given. It is also noted that the organic species is surrounded by the electric field of the framework, which suggests that any overestimation in Coulombic interaction will cancel out due to the symmetry of the field. Furthermore, the electric field at the centre of channels approaches zero and thus it will be the non-bonding parameters which will dominate the interactions between the template and the framework. The suitability of these parameters to simulate this system has been further verified by the simulation of the structure of the ZSM-5/TPA\(^+\) system determined by single-crystal X-ray crystallography,\(^{35}\) details of which will be given in the results section of this chapter.

![Diagram of TPA+ cation](image)

**Figure 6-3. The gas phase optimised geometry of the TPA\(^+\) cation. Calculation was done using the semi-empirical MNDO method.**

\(^1\) Semi empirical (MNDO) calculations on a number of oxy species including alcohols, ethers, esters and acids suggest a typical oxygen charge of -0.25 (cf. -2.0 in our ionic model)
Table 6-6. Potential parameters for the intramolecular interactions in TPA⁺ and the intermolecular non-bonding parameters for the organic-organic and organic-inorganic interactions.

<table>
<thead>
<tr>
<th>Species</th>
<th>Potential Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding Terms</td>
<td>$k_b$ (eV Å⁻²)</td>
</tr>
<tr>
<td>$C^* - C^*$</td>
<td>1971.389</td>
</tr>
<tr>
<td>$C^* - H^*$</td>
<td>2060.998</td>
</tr>
<tr>
<td>$C^* - N^*$</td>
<td>2060.998</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Bending Terms</th>
<th>$k_\theta$ (eV rad⁻²)</th>
<th>$\theta_\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_\beta-C_\alpha-N$</td>
<td>0.716070</td>
<td>105.200</td>
</tr>
<tr>
<td>$C_\alpha-N-C_\alpha$</td>
<td>1.381890</td>
<td>109.000</td>
</tr>
<tr>
<td>$H_\alpha-C_\alpha-N$</td>
<td>0.502510</td>
<td>109.000</td>
</tr>
<tr>
<td>$H_\beta-C_\beta-C_\gamma$</td>
<td>0.502510</td>
<td>109.000</td>
</tr>
<tr>
<td>$H_\gamma-C_\gamma-C_\beta$</td>
<td>0.502510</td>
<td>109.500</td>
</tr>
<tr>
<td>$H_\alpha-C_\alpha-C_\beta$</td>
<td>0.502510</td>
<td>109.000</td>
</tr>
<tr>
<td>$H^<em>-C^</em>-H^*$</td>
<td>0.414570</td>
<td>109.200</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Torsional Terms</th>
<th>$k_\phi$ (eV)</th>
<th>$(i_sign)n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^<em>-C^</em>-C^<em>-H^</em>$</td>
<td>0.005050</td>
<td>+3</td>
</tr>
<tr>
<td>$H_\beta-C_\beta-C_\alpha-N$</td>
<td>0.005210</td>
<td>+3</td>
</tr>
<tr>
<td>$C_\gamma-C_\beta-C_\alpha-N$</td>
<td>0.003470</td>
<td>+3</td>
</tr>
<tr>
<td>$C_\beta-C_\alpha-N-C_\alpha$</td>
<td>0.003470</td>
<td>+3</td>
</tr>
<tr>
<td>$H_\alpha-C_\alpha-N-C_\alpha$</td>
<td>0.017350</td>
<td>+3</td>
</tr>
</tbody>
</table>

continues...
...continued

<table>
<thead>
<tr>
<th>Non-bonded Interactions</th>
<th>A (eV)</th>
<th>r (Å⁻¹)</th>
<th>C (eV Å⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H*- O</td>
<td>880.5980</td>
<td>0.2740</td>
<td>11.0617</td>
</tr>
<tr>
<td>C*-O</td>
<td>1356.6410</td>
<td>0.2994</td>
<td>29.7364</td>
</tr>
<tr>
<td>N-O</td>
<td>2743.3010</td>
<td>0.2833</td>
<td>32.9682</td>
</tr>
<tr>
<td>H*-H*</td>
<td>282.6330</td>
<td>0.2667</td>
<td>3.7293</td>
</tr>
<tr>
<td>H*-C*</td>
<td>211.4650</td>
<td>0.2792</td>
<td>3.6742</td>
</tr>
<tr>
<td>H*-N*</td>
<td>880.5980</td>
<td>0.2755</td>
<td>11.0617</td>
</tr>
<tr>
<td>C*-C*</td>
<td>670.8980</td>
<td>0.3208</td>
<td>26.7474</td>
</tr>
<tr>
<td>C*-N</td>
<td>1356.6410</td>
<td>0.3021</td>
<td>29.7364</td>
</tr>
<tr>
<td>N-N</td>
<td>2743.3010</td>
<td>0.2857</td>
<td>32.9682</td>
</tr>
</tbody>
</table>

Where:

Bonding Terms \( E(r) = \frac{k_o}{2} (r - r_0)^2 \)

Bond Bending Terms \( E(\theta) = \frac{k_o}{2} (\theta - \theta_0)^2 \)

Torsional Terms \( E(\phi) = k_\phi (1 + isign \ast \cos(n \ast \phi)) \)

Non-bonding Terms \( E(r) = Ae^{-\gamma r} + \frac{C}{r^6} \)

Notation for C and H atoms is as defined in Figure 6-4. C* and H* refer to any C or H species respectively. Oxygen species in the non-bonding terms is the framework O² species.
<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-0.125800</td>
</tr>
<tr>
<td>Cα</td>
<td>0.082530</td>
</tr>
<tr>
<td>Hα</td>
<td>0.052905</td>
</tr>
<tr>
<td>Cβ</td>
<td>-0.043255</td>
</tr>
<tr>
<td>Hβ</td>
<td>0.031025</td>
</tr>
<tr>
<td>Cγ</td>
<td>0.021230</td>
</tr>
<tr>
<td>Hγ</td>
<td>0.017793</td>
</tr>
</tbody>
</table>

Table 6-7. MNDO calculated Mullikan charges on the TPA⁺ cation. Mean charges for each unique site were used.

Figure 6-4. Illustration of labelling scheme for the TPA⁺ ion used throughout.

In the calculations on the framework substituting iron and bridging hydroxyl these are treated as isolated “defects” at infinite dilution. Given the typical ratios SiO₂/Fe₂O₃¹⁷ present in the system we would not expect any interaction between iron sites and therefore this assumption is reasonable. Furthermore, in the periodic calculations one iron per P1 unit cell (96 T sites) was used, corresponding to a SiO₂/Fe₂O₃ ratio of 71; again a typical experimental ratio. In presenting the results we use the site notation of van Koningsveld et al. for the monoclinic P2₁/n.1.1 structure of ZSM-5 with 24 different T sites⁵ which is illustrated in Figure 6-5.
Organic-framework interactions have previously been investigated using these techniques for pillared clays\textsuperscript{52} and in, for example, the absorption of butanol isomers in ZSM5.\textsuperscript{54} However, no calculations of this type have been reported on the interaction of zeolites and templating molecules. The calculations were carried out with the iron at the lowest energy site determined by our calculations and with the TPA\textsuperscript{+} molecule initially at the position determined in silicalite.\textsuperscript{35}
6.3.2 Extended X-ray Absorption Fine Structure (EXAFS)

spectroscopy

In order both to verify the results of our calculations and to further analyse the available experimental data, we have simulated the Extended X-ray Absorption Fine Structure (EXAFS) spectra of Fe-ZSM5. A brief outline of the technique is now given.

Modulations appear in the x-ray absorption spectrum of bonded atoms above the absorption edge. This is the EXAFS (illustrated in Figure 6-6) and extends typically 1000eV beyond the absorption edge. Its origin lies in the back-scattering of a photoelectron by neighbouring atoms onto the atom which emitted the photoelectron.

The high energy of the photoelectrons means that the mean free path of the photoelectrons are short; thus the EXAFS contains information about the short range structure surrounding the absorbing atom. The modulations depend on the phase of the back-scattering photoelectron wavefunction and the path length to the back-scattering atoms. Thus, the distance to the near neighbours and the coordination number of the absorber to these atoms can be extracted from the EXAFS. Furthermore, the thermal and static disorder can be determined; this is expressed as the Debye-Waller factor. Fourier transformation of the EXAFS (after suitable treatment of the background) yields a radial distribution function which offers an qualitative guide to the local environment of the absorbing atom. Although possible on a laboratory X-ray source, high flux synchrotron sources are best suited for EXAFS studies. The main advantage of EXAFS is that it provides local structural information rather than the average structure provided by diffraction techniques. Furthermore, unlike many other techniques, EXAFS experiments do not require UHV and can be performed on powder and amorphous samples. EXAFS is therefore a very powerful techniques for probing the local environment of materials, particularly catalysts where the
active site is not only often dilute but also consists of specific atoms. The reader is directed elsewhere for more detailed discussions.\textsuperscript{55-57}

Figure 6-6. Schematic representation of the X-ray absorption spectrum at the absorption edge. The pre-edge yields information about the electronic configuration and symmetry of the absorbing atom, whilst the position of the edge itself is sensitive to the oxidation state of the atom. The XANES (X-ray Absorption Near Edge Structure) can yield long range ordering information. The EXAFS contains short range information.
6.4. Results and Discussion

Results are presented for two cases: first, the (Fe,Si)-ZSM-5 structure without template which is referred to as the calcined system; secondly the sample with the TPA+ ion — the templated system. Here the calcined sample refers to the acidic (H+) form of the material after calcination. The structure of each material will be discussed particularly with reference to the comparison with experimental EXAFS data. Other physical properties such as cell volume and acidity will also be discussed for the calcined material.

6.4.1 Calcined System

6.4.1.1 Isolated Fe Substitutional

We will consider first the substitution of an isolated Fe$^{3+}$ ion (without charge compensation) at the tetrahedral sites. The relative calculated substitution energies are presented in Figure 6-7 and the mean distances in Table 6-8. The substitution energy is the energy required to remove the Si atom to infinity and replace it with an iron atom (taken from infinity). The results show a quite narrow energy distribution with a range of ≈26kJ mol$^{-1}$. It can be seen that the calculated geometries do not reproduce well the experimental distances derived from the EXAFS data$^{22,23}$ for the proton form of Fe-ZSM5; the calculated mean Fe-O distance and Fe-Si bond lengths are shorter than those given in the latter analysis. Since these discrepancies are larger than the uncertainties which can be expected from both the simulations and the experiment, it is concluded that isolated Fe$^{3+}$ substitutionals are minority species (in the H+ form of Fe-ZSM5) and that protonation of the neighbouring oxygen to generate a charge compensating bridging hydroxyl group needs to be included to give an accurate model of the iron sites. This conclusion holds for the acid form of Fe-ZSM5; ion
exchange may result in modification of the iron sites. However, it would be expected that these sites would be closely associated with extra-framework cations to provide charge balance, which would lead to further distortion of the local iron environments. No calculations will be presented for such systems as there is no experimental data for comparison and also it is the H⁺ exchanged form which is of catalytic importance.

Figure 6-7. Substitution energy of an isolated iron (III) for a silicon at all possible T sites. Energies are given relative to the lowest substitution energy of 42.91eV. Note, some sites have the same defect energy.
Table 6-8. Mean geometries of isolated Fe$^{3+}$ substitutional at each tetrahedral site.

<table>
<thead>
<tr>
<th></th>
<th>Calculated/Å</th>
<th>Experimental/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean Fe-O distance</td>
<td>1.76</td>
<td>1.83, 1.89*</td>
</tr>
<tr>
<td>mean Si-Fe distance</td>
<td>3.14, 3.21</td>
<td>3.2, 3.38</td>
</tr>
<tr>
<td>mean nn Si-Si distance</td>
<td>3.08</td>
<td>-</td>
</tr>
</tbody>
</table>

*Experimental results from Axon.$^{22,23}$

Fe-Si distances are presented as a mean of two shell, with two Si atoms in each shell. All sites exhibited this distribution of silicon distances. The experimental coordination number for the Fe-Si distances is also two at both distances.$^{22,23}$

### 6.4.1.2 Fe Substitutionals compensated with Bridging Hydroxyls

The calculations for each iron site were repeated with a bridging hydroxyl included at an adjacent oxygen site to give 96 sites. This is a more realistic model of the iron site. The resulting relative substitution energies are presented in Figure 6-8. Again, the substitution energy is given as the energy required to remove the T atom and adjacent oxygen to infinity and replace them with the iron and hydroxyl group. The mean site geometries are given in Table 6-9, and the geometries of the four most and least stable sites are given in Table 6-10.
Figure 6-8. Substitution energy of an iron (III) and a bridging hydroxyl at all possible sites (24 T sites, 4 oxygen sites per T site). Energies are relative to the minimum substitution energy of 49.44eV. Note, some sites have the same defect energy.

The substitution energies now have a broader range of 82kJ mol\(^{-1}\). However, the majority of the sites lie within a narrower distribution of 67kJ mol\(^{-1}\). The most stable sites are T19 and T18. The four most stable sites lie within 10 kJ mol\(^{-1}\) of each other which is of the same order as \(kT\) at synthesis temperatures. These sites - involving T sites 19, 18 and 7 - are therefore predicted to be the preferred substitution sites at such temperatures. Sites T4, T12 and T14 are the least stable for substitution by Fe\(^{3+}\) and are therefore predicted as unlikely to be occupied. The structure of the most stable Fe-OH site is illustrated in Figure 6-9.
Table 6-9. Mean geometries of Fe$^{3+}$ substitutional with adjacent -OH at all 96 unique sites.

<table>
<thead>
<tr>
<th></th>
<th>Calculated /Å</th>
<th>Experimental† /Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean Fe-O(H)</td>
<td>2.02</td>
<td>-</td>
</tr>
<tr>
<td>mean Fe-O (over 4 Fe-O)</td>
<td>1.82</td>
<td>1.83, (1.87, 2.18)*</td>
</tr>
<tr>
<td>mean Si-O(H)</td>
<td>1.68</td>
<td>-</td>
</tr>
<tr>
<td>mean Si-Fe</td>
<td>3.12, 3.40</td>
<td>3.2, 3.38</td>
</tr>
<tr>
<td>mean nn Si-Si</td>
<td>3.07</td>
<td>-</td>
</tr>
<tr>
<td>mean Si-Si</td>
<td>3.10</td>
<td>3.10†</td>
</tr>
<tr>
<td>mean Si-H</td>
<td>2.35</td>
<td>-</td>
</tr>
<tr>
<td>mean Fe-H</td>
<td>2.39</td>
<td>-</td>
</tr>
</tbody>
</table>

†Experimental results from Axon.$^{22,23}$

*Experimental results from Patarin et al.$^{24}$ are given in parenthesis.

† in ZSM-5.$^3$

The Fe-Si distances are presented as the mean of the three shorter distances and the single longer distance. All sites exhibited this distribution of bond lengths. The experimental coordination number for the Fe-Si distances is two at both distances.$^{22,23}$
Table 6-10. Geometries of the most stable and least stable bound Fe-O(H) sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Fe</th>
<th>Si</th>
<th>Erel</th>
<th>mean Fe-O(H)</th>
<th>Fe-O</th>
<th>Si-O(H)</th>
<th>Fe-Si</th>
<th>Fe-H</th>
<th>Si-H</th>
<th>θFeOSi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Least stable</td>
<td></td>
<td></td>
<td></td>
<td>19 4 0.0 2.04 1.82 1.67 3.15,3.36 2.46 2.39 131.5</td>
<td>19 20 5.3 2.02 1.82 1.67 3.12, 3.33 2.43 2.28 137.1</td>
<td>18 9 5.3 2.02 1.82 1.67 3.13,3.33 2.44 2.34 137.1</td>
<td>7 8 9.9 2.01 1.82 1.67 3.12, 3.35 2.41 2.31 142.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Least stable</td>
<td></td>
<td></td>
<td></td>
<td>14 13 71.8 2.03 1.83 1.67 3.13, 3.42 2.29 2.26 155.3</td>
<td>14 15 72.5 2.01 1.83 1.64 3.09,3.38 2.22 2.25 155.8</td>
<td>12 11 80.3 2.01 1.81 1.81 3.13, 3.38 2.20 2.26 153.8</td>
<td>4 3 82.2 2.02 1.81 1.69 3.18,3.49 2.42 2.80 150.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

E_{rel} is given in kJ mol^{-1}, distances in angstroms, angles in degrees. Si-Fe distances are given as described in Table 6-9.

The bond lengths obtained from the calculated geometries now better reproduce the experimental results of Axon et al., particularly for the nearest neighbour oxygens. The experimental Fe-O distance derived from the EXAFS experiments of Axon et al. for the calcined sample is reproduced by the mean of the calculated Fe-O bonds at the various T sites. The calculated Fe-O bond is, as expected from the relative ionic radii (Si 0.40Å, Al 0.53Å, Fe 0.63Å) longer than the Si-O bond (1.59Å in ZSM-5) and the Al-O bond (1.73Å in Zeolite A) and is also in good agreement with the value of 1.85Å calculated from considering the ionic radii and coordination number. As might be expected the most stable sites are those in which the nearest oxygen shell surrounding the iron is closest to a tetrahedral environment, without introducing major distortions in the nearest neighbour silicon geometries. The least stable sites tend to show greater distortion from this ideal geometry with generally longer Si-Fe distances, shorter Fe-O bonds and a larger FeOSi angle than in the more stable sites.
Figure 6-9. Ball and stick illustration of the geometry of most stable Fe-OH site. Distances are given in Å.
The Fe-Si distances are broadly split into two subshells, the first containing three silicon atoms at a mean distance of 3.12 Å and the second containing one silicon atom at the longer mean distance of 3.40 Å. The distances fitted to the experimental\textsuperscript{22,23} show two Si ions at distances of 3.20 Å and 3.38 Å from the Fe respectively with a further Si being present at a distance of 4.30 Å. Thus the calculated Fe-Si distances are reasonably close to those of the experimental model. However, we shall show later that the remaining discrepancies are caused by the omission of oxygen shells from the experimental model and that the calculated Si distances are indeed consistent with the experimental data.

The results are also in reasonable agreement with those of Patarin et al.\textsuperscript{24} for samples which had been calcined and subsequently re-hydrated (Fe-O distances of 1.86-1.89 Å). However, the calculations do not reveal the additional Fe-O distance of 2.18 Å determined in these experiments. Since the present model does not include any non-framework oxygen species, it is concluded that the oxygen at 2.18 Å does not relate to framework oxygen and therefore the calculations support the suggestion that this could be as a result of water coordinating to a 3-coordinated framework iron. It is also noted that for a dehydrated sample, Patarin et al.\textsuperscript{24} have fitted the first shell to give a 3 coordinated iron. However, it is also possible that these data could be consistent with a four coordinated iron, but with a split oxygen shell.

The results are also in agreement with the XANES and IR/Raman studies of Bordiga et al.\textsuperscript{25} which show that the iron environment is a distorted tetrahedron. Furthermore, they showed that exchanging the proton with NH\textsubscript{4}\textsuperscript{+} resulted in a tetrahedral iron environment. This is consistent with the calculations for the protonic form and also suggests that the geometry which we calculated for the isolated iron substitutional (which was tetrahedral) may be a reasonable approximation of the structure of the site in the presence of larger cations. This is illustrated in scheme 6-1.
Scheme 6-1. Modification of the symmetry of the iron site on the exchange of protons for bulkier cations. Iron has an effective charge of -1 since it substitutes for Si\(^{4+}\). Equals signs (=) denote which bonds are equal in length.

6.4.1.3 Comparison to Experimental EXAFS data

In order to investigate further the comparison with experiment, the Fe K-edge EXAFS (see section 6.3.2) curves and their Fourier transforms (referred to hereafter as the FT) have been calculated using the distances obtained from our simulation results. For the purpose of simulating the EXAFS from our calculated geometries we used the EXCURV92 code\(^{59}\) which employs calculated phaseshifts that can be compared with those from model compounds. The non-structural parameters (viz. the constant potential to describe the lifetime of the photoelectron and the energy independent amplitude reduction factor due to multiple excitations) were determined using FePO\(_4\) as a model compound, as in the study of Axon et al.,\(^{21}\) and then fixed for further simulation of the EXAFS data. These parameters are shown in Table 6-11. We examined the K-range of 3.4Å\(^{-1}\)-14Å\(^{-1}\) as in the experimental study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPI</td>
<td>-0.0489</td>
</tr>
<tr>
<td>A(_{FAC})</td>
<td>0.84370</td>
</tr>
</tbody>
</table>

*Table 6-11. EXAFS simulation parameters*
Using the distances obtained from the simulations, the FT of the EXAFS has been calculated for the first coordination shell of oxygen (Figure 6-10 and Table 6-12). With a split oxygen shell, of 3 short and 1 long distance, there is excellent agreement with the experimental data, with a reasonable Debye-Waller factor (given here as 2σ²). Indeed, these results better fit the experimental data than does the model proposed by Axon et al.\textsuperscript{22,23} This is particularly evident for the subtle features which arise from the longer Fe-O(H) distance (shown inset in Figure 6-10). The Debye-Waller factor for the split shell model is also more reasonable than that obtained for the single shell model (the 4-coordinated shell model in Table 6-12). Moreover, to achieve a reasonable Debye-Waller factor in the latter, variation in the coordination number must be allowed. However, this results in a coordination number of less than 3. If both the coordination number and the Debye-Waller factor are allowed to vary, the fit is still not as good as for the calculated shells, and the resulting coordination number and Debye-Waller factor are less satisfactory (given in Table 6-12 as the best single shell fit). The results therefore clearly demonstrate that the calculated values have reproduced the geometry found in the experimental data and that the split oxygen shell is a realistic representation of the experimental structure.

Table 6-12. Parameters for the various first oxygen shell models (see Figure 6-10).

<table>
<thead>
<tr>
<th></th>
<th>Coordination Number</th>
<th>Distance (Å)</th>
<th>Debye-Waller factor (2σ²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>3.0</td>
<td>1.83</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.01</td>
<td>0.011</td>
</tr>
<tr>
<td>4 coordinated shell</td>
<td>4.0</td>
<td>1.82</td>
<td>0.014</td>
</tr>
<tr>
<td>Best single shell fit</td>
<td>4.2</td>
<td>1.82</td>
<td>0.012</td>
</tr>
<tr>
<td>Axon et al.\textsuperscript{22}</td>
<td>4.5</td>
<td>1.83</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Figure 6-10. Comparison of the experimental data and the Fourier Transformed Fe K-edge EXAFS of the calculated geometries. The first oxygen coordination shell is shown for the calcined system. The figure show FT of the EXAFS for the experimental data, the calculated geometry (at the calculated most favoured site), the best fitted single shell with a coordination number of 4, and the best fit to a single shell fitted for optimum Debye-Waller factor.
On addition of the silicon shells, the extent of the agreement with the experimental data is dependent on whether further higher oxygen shells are included. Omission of higher oxygen shells gives a poor fit: on fitting a starting model based on the calculated silicon shells the best fit distances closely resemble those proposed by Axon et al.\textsuperscript{22,23} However, inclusion of the next oxygen shells reproduces the experimental data using the calculated silicon shells. Further fitting of the silicon shells (the oxygen shells are fixed at their calculated positions) produces an excellent fit (see Figure 6-11 and Table 6-13). This is as a direct consequence of overlapping shells and highly correlated variables in the fitting procedure. Construction of such a complex model without the information provided by the calculations would have been extremely difficult and dangerous, thus highlighting the role of calculations in assisting the interpretation of experimental data. The calculations allow the construction of this complex model thereby avoiding all the problems associated with the fitting methodology, multiple scattering and interference effects in the higher shells.

It might be argued that the better fit is simply a consequence of increasing the number of variables but, in this case only the first oxygen and the silicon shells were fitted; the higher oxygen shells were fixed. There is a limit to the number of variables which can be used to analyse a given set of data. Simply increasing the number of variables to this limit may give a better reproduction of the experimental data. However, this may not be an improved model as some parameters may become unphysical, as will be further demonstrated when the templated system is considered below. The comparison to the EXAFS data clearly demonstrates the calculated bond distances are accurate and it is concluded that the model proposed from the calculations improves on that obtained by direct fitting to the experimental data.
Figure 6-11. Fourier Transform of the Fe K-edge EXAFS for the calcined material. The best fit between the model derived from calculated distances and the experimental data for the calcined system is shown. The parameters for the calculated EXAFS are given in Table 6-13.

Table 6-13 Final values for bond lengths around the Fe for the calcined sample after fitting of first oxygen and silicon shells. Note the minimal change in the silicon shell from the calculated values (Table 6-10), compared to the larger discrepancy with the experimental model of Axon et al.22,23 (given in Table 6-9). The initial model was constructed using the calculated shells and then the nearest neighbour oxygens and first silicon shells were optimised.

<table>
<thead>
<tr>
<th>Number</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Debye-Waller factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>O</td>
<td>1.835</td>
<td>0.008</td>
</tr>
<tr>
<td>1.0</td>
<td>O</td>
<td>2.020</td>
<td>0.010</td>
</tr>
<tr>
<td>3.0</td>
<td>Si</td>
<td>3.134</td>
<td>0.031</td>
</tr>
<tr>
<td>1.0</td>
<td>Si</td>
<td>3.311</td>
<td>0.027</td>
</tr>
<tr>
<td>6.0</td>
<td>O</td>
<td>3.561</td>
<td>0.024</td>
</tr>
</tbody>
</table>
6.4.1.4 Effect of Iron Incorporation on the Pore Dimensions of the MFI Structure

The Fe-O-Si angle, at the more stable sites is seen to be smaller than the experimental Si-O-Si angle,\(^3\) and that calculated for Al-O-Si.\(^{28}\) This coupled with the longer Fe-O(H) bond length results in a modification of the pore dimensions. The lengthening of the Si-O(H) bond and the slight contraction in first shell Si-Si distances also contribute to this change. The effects of these distortions are demonstrated in Figure 6-12. The sinusoidal channel diameter is reduced by between 0.4Å and 0.8Å measured from the nearest oxygen neighbours to the iron site, and by 0.5Å measured from the third oxygen neighbours to the iron. The changes in the dimensions of the straight channel is similar, although it is interesting to note that the maximum diameter has now increased by 0.2Å. Thus the general overall effect is to make the channels more elliptical with the iron site being on the short diameter of the resulting ellipse. Indeed, a change of this magnitude is obtained simply by the phase change from the orthorhombic to the monoclinic phase.\(^3\) The active site, however, is located at the origin of this channel distortion. Modifications in the activity of this site can therefore be envisaged with, in particular, the reactant orientation being changed by the alterations in the channel shape and size. Changes of this magnitude would have a significant effect on the shape selectivity and reactivity compared to (Al,Si)-ZSM-5, as has been observed experimentally.\(^{10-13}\)

6.4.1.5 Effect of Iron Substitution on the Unit Cell Volume

A perfect lattice calculation was carried out using the most stable defect site. The calculated unit cell volume is in good agreement with the experimental result of Szostak \textit{et al.}\(^{14}\) for a material of comparable Si/Fe ratio (Table 6-14).
Table 6-14. Calculated and experimental unit cell volumes for silicalite and (Fe, Si)-ZSM-5. The calculated value is for a material substituted at the most favoured site. The Si/Fe ratios were 96 and 102 in the calculated and experimental materials respectively. Experimental results from Szostak et al.\textsuperscript{14}

<table>
<thead>
<tr>
<th></th>
<th>Unit Cell Volume (Å\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td>silicalite</td>
<td>5299</td>
</tr>
<tr>
<td>(Fe, Si)-ZSM-5</td>
<td>5352</td>
</tr>
<tr>
<td>% volume change on iron substitution</td>
<td>+1.000</td>
</tr>
</tbody>
</table>

Figure 6-12. Effect of iron substitution on the pore dimension in Fe-ZSM-5. Upper figures show the sinusoidal and straight channels with the Fe-OH defect at the minimum energy site. The iron site is indicated by an asterisk (*). Lower figures show these pores in ZSM-5.\textsuperscript{3} Distances shown are measured using van der Waal radii of 1.35 Å for the oxygen.

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6.4.1.6 The Acidity of Fe-ZSM5

Experimental infrared and ammonia desorption studies of Fe-ZSM5 have shown that the acidity is lower than in Al-ZSM5.\textsuperscript{8} Also, the relative narrowness of the infrared bands associated with the acid proton\textsuperscript{14} suggests there is very little site variation in the properties of the OH group. A crucial factor influencing the acidity is the binding of the proton to the oxygen adjacent to the iron. This binding energy, $\Delta E$, is defined as the energy difference between the bound Fe-OH defect species and isolated substitutional Fe$^{3+}$ and OH$^-$ defects at the same crystallographic sites:

$$Fe^{3+} + (OH)_{o(r)} \rightarrow Fe - O(H).$$

(6.1)

$\Delta E$ will be the major factor controlling variations in the acidity of the proton. A high binding energy would be expected to reduce acidity, whilst conversely a low binding energy would lead to acidity enhancement. The binding energies of the hydroxyl group to the iron site have been calculated for the four most stable and four least stable sites and are given in Table 6-15.

The binding energy at the more stable sites are calculated to be significantly greater (by \textit{ca.} 50 kJ mol$^{-1}$) than at the least stable sites. Furthermore, the magnitude of the binding energy at all the Fe substitutional sites suggests that protons will be strongly bound to neighbouring oxygens — a result which, as we have seen, is fully consistent with our comparison with the structural data. The large differences in binding also supports the conclusions drawn regarding iron siting if the less stable sites calculated were occupied, the large differences in acidity would lead to substantial broadening of the absorption bands associated with the Brønsted acid site. But as noted, this effect is minimal, with the v(OH) band having a bandwidth of \textit{ca.} 30 cm$^{-1}$\textsuperscript{14} and therefore only sites with similar acid strength are occupied.
In order to determine the effect of the heteroatom on the acidity of the framework proton the binding energies (as defined above) for protons adjacent to Al in (Al,Si)-ZSM5 have also been calculated (Table 6-16), using the energetically favoured Al substitution sites identified by Schroder et al.\textsuperscript{28} The binding energy in (Fe,Si)-ZSM-5 is found to be significantly higher, by ca. 60 kJ mol\(^{-1}\), than that in (Al,Si)-ZSM-5. The result is fully consistent with the reduced acidity of (Fe,Si)-ZSM-5 and shows that the substituting heteroatom has a significant effect on the acidic properties of the proton. This effect is of course noted experimentally with the stretching frequency of the Bronsted hydroxyl in Fe-ZSM-5 being 3630 cm\(^{-1}\) compared to 3610 cm\(^{-1}\) in Al-ZSM5.

<table>
<thead>
<tr>
<th>Site</th>
<th>Site</th>
<th>-E(_{\text{bind}})/kJmol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most stable</td>
<td>Fe 19</td>
<td>Si 4</td>
</tr>
<tr>
<td></td>
<td>Fe 19</td>
<td>Si 20</td>
</tr>
<tr>
<td></td>
<td>Fe 18</td>
<td>Si 9</td>
</tr>
<tr>
<td></td>
<td>Fe 7</td>
<td>Si 8</td>
</tr>
<tr>
<td>Least stable</td>
<td>Fe 14</td>
<td>Si 13</td>
</tr>
<tr>
<td></td>
<td>Fe 14</td>
<td>Si 15</td>
</tr>
<tr>
<td></td>
<td>Fe 12</td>
<td>Si 11</td>
</tr>
<tr>
<td></td>
<td>Fe 4</td>
<td>Si 3</td>
</tr>
</tbody>
</table>

Table 6-1S. Binding Energies of Fe\(^{3+}\) and hydroxyl groups. The binding energy is defined as the energy change on locating a previously isolated -OH group on a site adjacent to an Fe\(^{3+}\) ion.
Table 6-16. The binding energy of Al$^{3+}$ and hydroxyl groups. The aluminium is located at the three most favourable sites as calculated by Schroder et al.$^{28}$ and at the most favoured iron site (Fe19Si4).

<table>
<thead>
<tr>
<th>Site</th>
<th>-E$_{\text{bind}}$/kJmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Si</td>
</tr>
<tr>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>19</td>
<td>14</td>
</tr>
<tr>
<td>20</td>
<td>19</td>
</tr>
<tr>
<td>19</td>
<td>4</td>
</tr>
</tbody>
</table>

We may also calculate vibrational frequencies in periodic structures using the quasi-harmonic approximation, which assumes that the vibrational modes in a solid are comprised of harmonic oscillators. Full details are given elsewhere.$^{60,61}$ This method will yield the harmonic frequency, $\omega$(OH), of the vibration. This gives us a calculated stretching frequencies in Fe-ZSM5 of 3792cm$^{-1}$ compared to 3732cm$^{-1}$ for Al-ZSM5. The calculations were performed with the Fe and Al located at the calculated most stable site. The corresponding anharmonic fundamental is given by

$$u(\text{OH}) = \omega(\text{OH}) - 2\chi_{\text{OH}}$$  \hspace{1cm} (6.2)

where $\chi_{\text{OH}}$ is the anharmonicity constant. This later value is observed to be between 70 and 80cm$^{-1}$ for H-faujasite and mordenite$^{62}$ and is predicted to be 75cm$^{-1}$ by ab-initio calculations.$^{63}$ Using a value of 75cm$^{-1}$ we obtain values for $u$(OH) of 3642cm$^{-1}$ in Fe-ZSM5 and 3582cm$^{-1}$ in Al-ZSM5. These compare well with the experimental values of 3630cm$^{-1}$ and 3610cm$^{-1}$ respectively. Thus the effect of the nature of the heteroatom on the acidity of the hydroxyl group is evident. Furthermore, we have two measures of acidity which are in excellent agreement with the experimental data.
6.4.2 Templated System

There have been numerous attempts to locate template molecules within zeolites, primarily using X-ray diffraction techniques. The location of TPA+ in ZSM-5 has been determined to be at the intersection of the two channel systems. In their study of Fe-ZSM-5, Axon et al. proposed a model for the location of the TPA+ ion from their EXAFS data, which suggests that the location of the TPA+ is significantly different to that in ZSM-5 with the cation being much closer to the iron site than that found in ZSM-5. This apparent effect has been investigated using energy minimisation.

The single crystal X-ray structure of ZSM-5/TPA of van Koningsveld et al. was used as the starting point of the simulation. Iron was substituted at the lowest energy (T) site. The GULP code was then used to minimise the energy of the entire unit cell with respect to all structural variables. The final geometry is illustrated in Figures 6-13—6-15. The interatomic distances between Fe and various neighbours including C and N of the template molecule are listed in Table 6-17.

The Fe-O bond distances match well the results of Axon et al. However, there are significant differences in the higher shell neighbour distances. The calculations give Fe-C and Fe-N distances of 4.5 Å and 5.2 Å respectively, in line with those found in other templated zeolitic systems. Moreover, there is a small displacement of the template from the central position found in silicalite (Table 6-18 and Figure 6-16). However, it is significantly smaller than that suggested by Axon et al. and in fact shows a repulsion of the TPA+ from the iron site. This is mainly a consequence of the calculated charge distribution on the TPA+ molecule which has the positive charge delocalised on the propyl chains and a negative central nitrogen atom.
Figure 6-13. Illustration of the final calculated position of TPA$^+$ in Fe-ZSM-5 in the straight channel. Hydrogen atoms are omitted for clarity.
Figure 6-14. Illustration of the final calculated position of TPA$^+$ in Fe-ZSM-5 in the sinusoidal channel. Hydrogen atoms are omitted for clarity.
Figure 6-15. Illustration of the nearest neighbour contacts between the iron site and the TPA⁺ ion. Hydrogen atoms are omitted for clarity.

Table 6-17. Distances in TPA⁺/(Fe, Si)-ZSM-5: those around the iron site for the calculated system; those proposed in the EXAFS work of Axon et al. and those for the same crystallographic site for TPA⁺/ZSM-5. Cα, Cβ, Cγ refer to the propyl chain carbon atoms as illustrated in Figure 6-4. Axon et al. did not differentiate between carbons.
<table>
<thead>
<tr>
<th>N</th>
<th>$C_a$</th>
<th>$C_\beta$</th>
<th>$C_\gamma$</th>
<th>Channel</th>
</tr>
</thead>
<tbody>
<tr>
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<td>+0.09</td>
<td>-0.33</td>
<td>-0.16</td>
<td>straight</td>
</tr>
<tr>
<td>+0.16</td>
<td>+0.77</td>
<td>+0.21</td>
<td></td>
<td>straight</td>
</tr>
<tr>
<td>-0.10</td>
<td>-0.38</td>
<td>-0.26</td>
<td></td>
<td>sinusoidal</td>
</tr>
<tr>
<td>-0.32</td>
<td>-0.19</td>
<td>-0.58</td>
<td></td>
<td>sinusoidal</td>
</tr>
</tbody>
</table>

Table 6-18. Calculated displacement of TPA$^+$ in (Fe,Si)-ZSM-5 from TPA position in TPA$^+$/ZSM-5 after matching the frameworks of calculated TPA$^+$/Fe,Si-ZSM-5 with that of TPA/ZSM-5$^{35}$ by a least squares fitting procedure. Positive and negative displacements indicate whether the atom is further or closer respectively to the iron site, compared to its starting position in TPA$^+$/ZSM-5.

Figure 6-16. Illustration of the displacement of the TPA$^+$ ion in Fe-ZSM5 (light lines) from the position in ZSM-5 (dark lines). Note the distortion of the TPA$^+$ ion.
6.4.2.1 Verification of the Model and Parameters for the Templated System

The above results may of course be significantly influenced by the model used to obtain them. Two aspects in particular require verification: the charge distribution model of the TPA⁺ ion and the performance of the non-bonding parameters between the framework and the template.

**Charge Distribution**

*Ab-initio* quantum mechanical calculations on NH₄⁺, tetramethyl, tetraethyl and tetrapropylammonium using a range of basis sets (including STO-3G, 6-31G** and TZVP) were carried out to determine if the charge model is accurate. These calculations show that the *ab-initio* charges give the same trends and approximately the same charges as the MNDO calculations and that the distribution of the charge, with a negative nitrogen atom is correct (results are given in Table 6-19). It is concluded that the charges used give an accurate representation of the charge distribution and are not a consequence of the semi-empirical methodology employed in their derivation.

**Non-bonding Parameters**

The differences between the calculated and the experimental structure of Axon *et al.* could be a result of errors introduced by the transfer of the non-bonding parameters from the organic system for which they were derived to the current different application. As discussed in the Methodology section of this chapter (section 6.3), the parameters were derived for organic systems and therefore the charges on the oxygen species would be much less than the full ionic charge of -2.0 used here. In order to determine if this could cause difficulties and to estimate the magnitude of any errors, the structure of ZSM-5/TPA⁺ has also been determined and compared to the experimental data of van Koningsveld *et al.* The ZSM-5 material whose structure was determined by van Koningsveld *et al.* had a composition of Na₀.₃₇Si₉₅.₇Al₀.₃₄TPA⁺OH⁻ + nH₂O. To simulate this
exact composition would be very difficult; no sodium sites have been identified and also the location of the Al would have to be considered. Furthermore, no site has been proposed for the hydroxide anion present to charge balance the system.

Table 6-19. Comparison of MNDO and ab-initio charges. All geometries were optimised using the basis set used for the charge distribution calculation. Mean values are given for each unique C and H atom.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Charges</th>
<th>MNDO</th>
<th>STO-3G</th>
<th>6-31G**</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>N</td>
<td>-0.064</td>
<td>-0.234</td>
<td>-0.234</td>
</tr>
<tr>
<td></td>
<td>H</td>
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<td>0.064</td>
</tr>
<tr>
<td>TMA⁺</td>
<td>N</td>
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<td>-0.097</td>
<td>-0.102</td>
</tr>
<tr>
<td></td>
<td>C</td>
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<tr>
<td></td>
<td>H</td>
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<td>0.051</td>
<td>0.051</td>
</tr>
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<td>TEA⁺</td>
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<td>-0.165</td>
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<tr>
<td></td>
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<td>-0.03, -0.17</td>
</tr>
<tr>
<td></td>
<td>H</td>
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<td>0.05, 0.07, 0.08</td>
<td>0.05, 0.07, 0.07</td>
</tr>
<tr>
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<td>N</td>
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<td>-0.174</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.082, -0.043, 0.020</td>
<td>0.010, -0.003, 0.017</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.059, 0.050, 0.020</td>
<td>-0.11, -0.08, -0.07</td>
<td></td>
</tr>
</tbody>
</table>

Thus two models have been used to approximate this composition and to test the suitability of the potentials. First, a purely siliceous material was considered. Since this would result in a charge imbalance - an excess charge of +4 per unit cell as a consequence of the TPA⁺ cations - this excess charge was distributed evenly over the framework silicon atoms, giving a silicon ion charge of $4 \times \frac{1}{2}$. Given the now uniform electric field of the zeolite, this approximation is likely to have minimal effect on the structure of the templated system, only modifying the total energy of the system. The resulting geometry is compared...
to the experimental structure in Figure 6-17. Secondly, a system with a single aluminium ion per orthorhombic unit cell (1 Al per 24 T site) was considered. The Al was located at T14 which was determined by Schroder et al. to be the most energetically favoured site. Again, the resulting geometry is compared to the experimental structure in Figure 6-18. The displacement of the atoms of the TPA$^+$ ion from their experimental positions are given in Table 6-20.

Figure 6-17. Final geometry of the TPA$^+$ ion (gray lines) in the fully siliceous silicalite structure. Comparison is made with the experimental structure (black lines) of van Koningsveld et al.$^{35}$
Siliceous Model

The calculated intramolecular geometry of the TPA+ ion is the same as that determined experimentally within experimental error (cf. the distortion experienced in the Fe-ZSM5 system - as illustrated in Figure 6-16). However, the location of the TPA+ ion is displaced from the experimental site by 0.35 Å (for the nitrogen atom).

Aluminium substituted Model

The distortion of the TPA+ ion is again minimal compared to that in the experimental structure. However, the difference in nitrogen atom position is 0.59Å, which is greater than that for the purely siliceous and iron substituted models. We can therefore consider this to be the maximum error in the calculations which is significantly smaller than the differences between the calculated distances and those proposed experimentally for Fe-ZSM-5.
The differences between the experimental and calculated geometries in the case of Fe-ZSM-5/TPA+ are over 1.7 Å, much greater than the differences between the experimental and the calculations above. Therefore, we can be confident that any errors arising from the potential model will not alter the overall conclusions regarding the siting of the template molecule in the Fe substituted material.

<table>
<thead>
<tr>
<th>Model</th>
<th>N</th>
<th>Cα</th>
<th>Cβ</th>
<th>Cγ</th>
<th>Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purely Siliceous</td>
<td>+0.11</td>
<td>+0.09</td>
<td>-0.33</td>
<td>-0.16</td>
<td>straight</td>
</tr>
<tr>
<td></td>
<td>+0.16</td>
<td>+0.77</td>
<td>+0.21</td>
<td></td>
<td>straight</td>
</tr>
<tr>
<td></td>
<td>-0.10</td>
<td>-0.38</td>
<td>-0.26</td>
<td></td>
<td>sinusoidal</td>
</tr>
<tr>
<td></td>
<td>-0.32</td>
<td>-0.19</td>
<td>-0.58</td>
<td></td>
<td>sinusoidal</td>
</tr>
<tr>
<td>Al-ZSM5</td>
<td>+0.59</td>
<td>+0.34</td>
<td>+0.49</td>
<td>+0.34</td>
<td>straight</td>
</tr>
<tr>
<td></td>
<td>+0.64</td>
<td>+0.55</td>
<td>+0.31</td>
<td></td>
<td>straight</td>
</tr>
<tr>
<td></td>
<td>-0.63</td>
<td>-0.61</td>
<td>-0.56</td>
<td></td>
<td>sinusoidal</td>
</tr>
<tr>
<td></td>
<td>+0.52</td>
<td>+0.73</td>
<td>+0.46</td>
<td></td>
<td>sinusoidal</td>
</tr>
</tbody>
</table>

Table 6-20. Displacement of TPA⁺ in two models for ZSM-5 from TPA⁺ position in the experimental system. Distances are calculated after matching the frameworks of calculated structures with that of TPA⁺/ZSM-5 by a least squares fitting procedure. Positive and negative displacements indicate whether the atom is further or closer respectively to T19 site (where the iron is located in the TPA⁺/Fe-ZSM5 calculation), compared to their starting position in TPA⁺/ZSM-5.

6.4.2.2 Modification to the TPA⁺ Structure in Fe-ZSM5

It is of interest to note that the final energy minimised geometry for the templated Fe-ZSM-5 results in the propyl chains being closer to the ideal tetrahedral environment relative to the nitrogen than found in TPA/ZSM5 with bond angles in the range 107.2-112.5°, as opposed to the values of 94-122°.
obtained in the crystallographic study of van Koningsveld et al.\textsuperscript{35} Although this difference in nitrogen geometry could be due to inadequacies in the torsional terms in our potentials, it might also explain why it is relatively easy to substitute the iron into the framework. Addition of iron distorts the framework, such that the TPA\textsuperscript{+} may be accommodated in a less strained configuration than in silicalite. However, this apparent modification to the local nitrogen environment may also be due to the presence of Al and extraframework cations in the experimental materials, whilst in the calculated model, exact charge balance is provided by the framework iron.

### 6.4.2.3 Comparison to Experimental EXAFS data

In order to confirm that the calculated distances fit the EXAFS data, the Fe K-edge EXAFS and the FT were again calculated using a procedure similar to that which we have described for the calcined system. The results of the simulation did not agree completely with the experiment when only oxygen, silicon and the carbon and nitrogen of the template molecule were included as Fe neighbours. Indeed, fitting, starting with a model based on the the calculated distances, results in distances similar to those reported by Axon et al.,\textsuperscript{21} particularly for the Fe-Si shells. However, as discussed for the calcined sample the inclusion of the next oxygen neighbours is critical to correctly model this system. Inclusion of these oxygen shells in the simulated EXAFS resulted in a good match to the experimental data and fitting of the Si shells does not dramatically alter the model. Figures 6-19 and 6-20, and Table 6-21 shows the best fit to the experimental data including the second oxygen shells and the calculated carbon and nitrogen shells. An attempt was made to improve the fit of the carbon and nitrogen shell to the features at 4.5Å and 5.5Å. However, this resulted in these parameters becoming unphysical, although the resulting spectrum was a better (mathematical) reproduction of the experimental data. Nonetheless, it is clear that the features at 4.5Å and 5.5Å are indeed related to the carbon and nitrogen shells. It is therefore concluded that the proposed
model of Axon et al.\textsuperscript{21} is inaccurate. Reliable values for such a complex model with second neighbour shells are not obtainable from the data available. EXAFS studies of such complex systems clearly benefit from an input from the computational methods discussed here.

\textit{Table 6-21. Final parameters from fit of calculated shells to experimental data}

<table>
<thead>
<tr>
<th>Atom</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1.846</td>
</tr>
<tr>
<td>Si</td>
<td>3.074</td>
</tr>
<tr>
<td>Si</td>
<td>3.249</td>
</tr>
<tr>
<td>O</td>
<td>3.553</td>
</tr>
<tr>
<td>C</td>
<td>4.500</td>
</tr>
<tr>
<td>N</td>
<td>5.200</td>
</tr>
</tbody>
</table>
Figure 6-19. Calculated and experimental FT of TPA/(Fe,Si)-ZSM-5. Comparison of calculated and experimental data for the templated system, showing the contribution from carbon and nitrogen shells to the features at 4.5Å and 5.5Å.

Figure 6-20. Calculated and experimental FT of TPA/(Fe,Si)-ZSM-5. Closeup of the carbon and nitrogen shells at 4.5Å and 5.5Å.
6.5. Conclusions

We have shown first that T18 and T19 are the most energetically favoured sites, although we predict that Fe$^{3+}$ substitution will occur over a broad range of tetrahedral sites at elevated temperatures provided the substitution site is controlled by the energetics of substitution. The charge compensating protons are strongly stabilised on nearest neighbour oxygen sites to the Fe$^{3+}$ substitutional. The first oxygen shell around the iron is distorted, with the Fe-O(H) distance being longer than the Fe-O distances. The calculations for the templated system have led to a new model being proposed that is significantly different from that previously proposed from EXAFS results$^{21}$ with the template molecule being only slightly displaced from its position in silicalite. The results have been compared to the experimental EXAFS data and are found to be in very good agreement. The simulation of the FT has demonstrated the importance of including distant oxygen shells in any model. This again reinforces the role of calculations in attempting the determine local structural effects of substitutions in host materials. Furthermore, all the calculated properties, including those which affect the chemical activity of the catalyst, are in good agreement with the experimental data, and again demonstrate the ability of the method to model complex structural properties of microporous materials.

6.6. Acknowledgements

Dr. K.K. Fox of Unilever Research Ltd. is thanked for providing the experimental EXAFS data and for useful discussions. Dr. G. Sankar of the Royal Institution of Great Britain is also thanked for his assistance in the generating and fitting of the EXAFS curves and for his introduction to EXAFS.
6.7. References


Chapter 7

The Defect Chemistry of MgO Catalysts
7.1. Summary

Atomistic simulation techniques have been applied to the study of the bulk and surface defect chemistry of MgO and Li/MgO catalysts. The energetics, stability and mobility of defects, particularly those which are thought to influence the activity of the catalysts, have been investigated. Special attention is paid to the effect of dissolving chloride ions in MgO. We consider models for chloride containing defects and the way in which they influence the activity of the catalysts. We are able to comment generally on the factors controlling the overall activity of these catalysts.

7.2. Introduction

Defect in solids play a crucial role in controlling the activity of heterogeneous solid catalysts. Indeed, it is the defect chemistry which controls the structure of active sites. Since catalysis is a surface process, it is also crucial to understand the differences between the surface defect chemistry and that of the bulk. In this chapter, atomistic simulation techniques are applied to the study of the defects present in MgO and Li/MgO catalysts, with special attention to their role in the use of these materials as partial oxidation catalysts.

7.2.1 Partial Oxidation of Methane

Li/MgO is found to produce reasonable yields of ethane and ethene when methane is passed over the material at \( \text{ca. } 700^\circ\text{C} \).\(^1\)\(^-\)\(^7\) Oxygen is also required in the reaction stream and it is further noted that pure MgO has only a limited activity.\(^8\)\(^,\)\(^9\) The prime active site for this reaction is considered to be an oxygen
hole species\textsuperscript{3-6} which initiates the reaction by abstracting a hydrogen from a methane molecule:

\[ \text{CH}_4 + \text{O}^\circ \rightarrow \text{CH}_3^\circ + \text{OH}^\circ \] \hspace{1cm} (7.1)

This surface hole species can either be an intrinsic defect or, most likely formed as a consequence of the presence of lithium. Moreover, lithium stabilises the hole species by the formation of the neutral [Li+O] defect centre, known as the lithium trapped hole and this species will be denoted by [Li]\textsuperscript{0} throughout this work. The presence of other gases such as N\textsubscript{2}O in the gas stream are also known to promote the formation of hole species.\textsuperscript{10} Ethane is produced by gas phase combination of the methyl radicals:

\[ 2\text{CH}_3^\circ \rightarrow \text{C}_2\text{H}_6^\circ \] \hspace{1cm} (7.2)

Other undesirable products such as CO and CO\textsubscript{2} are formed in the gas phase by recombination of these methyl radicals with gas phase oxygen. However, C\textsubscript{2} products are favoured at high temperatures; kinetic factors are therefore clearly important. It has been determined that ethene formation \textit{via} the formation of methylene carbene (:\text{CH}2) does not occur at these active sites. Thus other active sites must also be present which are active for ethane dehydrogenation.

Numerous species have been suggested including\textsuperscript{11} the superoxide O\textsubscript{2}\textsuperscript{−} and the peroxide O\textsubscript{2}\textsuperscript{2−}. F centres have also been postulated as possible active sites.\textsuperscript{12,13} Indeed, it has been suggested that the [Li]\textsuperscript{0} centre is a precursor to these sites and is not directly involved in the activation process.\textsuperscript{14} However, in the accepted scheme involving oxygen holes, the active site is regenerated by the formation of water and the absorption of gas phase oxygen:

\[ 2\text{OH}^\circ \rightarrow \text{O}_2^\circ + \text{V}_0 + \text{H}_2\text{O}^\circ \] \hspace{1cm} (7.3)

\[ \text{O}_2^\circ + \text{V}_0 + \frac{1}{2}\text{O}_2^\circ \rightarrow 2\text{O}^\circ \] \hspace{1cm} (7.4)
The activity of the catalyst is significantly reduced in the absence of a co-feed of oxygen in the gas stream\textsuperscript{8} which supports this scheme. CO\textsubscript{2} poisons the catalyst, which is considered to be a result of the formation of a Li\textsubscript{2}CO\textsubscript{3} phase.\textsuperscript{15}

7.2.2 The role of chlorine in the partial oxidation of methane by MgO and Li/MgO

Recently there has been much interest in the study of oxide catalysts promoted with chlorine species,\textsuperscript{16-18} which have been introduced by the addition of both gas phase chloroalkanes and chloride salts during the catalyst preparation. It has been shown that when chlorine is added to MgO and Li/MgO, oxidative coupling has a lower activation temperature, improved C\textsubscript{2} yield and, more significantly, a higher ethene selectivity.\textsuperscript{19-21} Li\textsuperscript{+}-MgO-Cl\textsuperscript{-} catalysts prepared by a sol-gel method are found to be particularly effective with a CH\textsubscript{4} conversion of about 30\% and a ethene/ethane ratio of 5.9 at 675\degree C compared to 23\% and 1.0 respectively for Li/MgO.\textsuperscript{19} Addition of dichloromethane into the gas stream has a similar effect.\textsuperscript{20} Surface analysis has shown the presence of chloride ions and gas phase reactions are found not to be significant.\textsuperscript{20} It has also been suggested that the chloride binds to the lithium to form neutral [LiCl] defect centres.\textsuperscript{21} The poisoning of the catalyst by CO\textsubscript{2} via the formation a Li\textsubscript{2}CO\textsubscript{3} phase is also reduced,\textsuperscript{22} which may be an effect of the formation of this defect. Furthermore, the presence of a LiCl phase has been noted by XRD on the surface of as-prepared samples of Li-MgO-Cl catalysts.\textsuperscript{21} The ratio of Li:Cl is also crucial to the enhancement of the activity of these materials. Lunsford and co-workers found no performance improvement if the Li:Cl ratio was less than 0.9.\textsuperscript{21}

However, although the effect of the addition of chlorine, both as gas phase chloro and solid chloride species, is well documented, there is little discussion of the exact manner in which it acts to improve the catalyst's performance.
7.2.3 The Effect of Morphology and the Nature of Active Sites in Pure MgO

As discussed above, there is general consensus regarding the nature of the active site for methane activation in Li/MgO. However, the nature of the active site in pure MgO and active sites for the formation of other products are less well characterised. Recent work has demonstrated the importance of the morphology\(^9\) and has suggested that [Li]\(^0\) are pinned at sites of the emergence of line defects. Furthermore, the bottom of step sites are suggested as active sites for methane activation in the undoped MgO. Such low coordinate sites have previously been considered as possible active sites, particularly in theoretical studies.\(^{23-26}\) However, there is no direct experimental measurement of reactions at such sites.

7.2.4 Atomistic Simulations of Alkali Metal doped Alkaline Earth Oxides

The binary metal oxides have long been investigated using the lattice simulation techniques employed here. The nature of the work has mirrored the experimental interest in the materials. Earlier work concentrated on the modelling of the crystal structure and of intrinsic defects in MgO and related materials.\(^{27}\) Interest in defects caused by radiation damage led to work on electronic defects such as oxygen holes.\(^{28}\) Following the work of Ito and Lunsford\(^1\) demonstrating the catalytic activity of MgO and Li/MgO, theoretical studies were performed on likely active sites. Most significantly this now included the study of surfaces\(^{25}\) and surface defects.\(^{29}\) Extensive work was carried out not only on the (1 0 0) surface\(^{30}\) but also on non-planar surfaces\(^{31}\) and the siting of defects on such surfaces.\(^{24-26,29,32}\) This led to quantum mechanical studies which will be discussed in Chapter 8. Later work by Foot\(^{33}\) and
Gorman\textsuperscript{34} investigated the formation of $[\text{Li}]^0$ centres in the bulk and at the surface of MgO.

7.3. Methodology

The atomistic simulation techniques for both the bulk and surface as described in Chapter 3 were applied to the study of the atomistic structure and defect chemistry of doped MgO. For the bulk defect calculations, the defect code CASCADE\textsuperscript{35} was used. Perfect surface structures were calculated using both the MIDAS\textsuperscript{36} and MARVIN\textsuperscript{37} codes. Although the latter is a more modern, user-friendly and stable code, the MIDAS code was used primarily since it generates the correct files for input into the surface defect code used, CHAOS\textsuperscript{38}.

7.3.1 Potential Parameters

A large number of potentials have been derived for simulating MgO\textsuperscript{27,28,39,40}, most of which have been based on empirical fitting procedures (see section 3.4.1, chapter 3). This method of potential derivation can lead to very accurate reproduction of perfect lattice properties. However, to model defects in these system, potential parameters have to be transferable to the host lattice from the system for which they were derived. For example, to model Ca$^{2+}$ impurities in MgO the potential parameters derived for CaO are used. This requires that the common interactions are internally consistent. However, since in this study, electronic defects (such as oxygen holes) are also considered, the potentials were derived using the electron gas methods\textsuperscript{41-43}. These methods allows the development of a set of potential parameters which have all been derived in the same Madelung field, that of the host lattice. Consequently, the potentials are consistent with each other and problems associated with transferring potentials from one structure to another are avoided. Although this method does not reproduce the perfect lattice properties as well as empirical parameters, it has been demonstrated that potentials derived in this way give good results in such materials\textsuperscript{28,29,32}.
The parameters used are primarily the electron gas potentials originally derived by Colbourn et al.\textsuperscript{39} Derivation of parameters for the study of chloride doping are detailed later. The original parameters were supplied in a numerical form, tabulated as distance versus energy. However, to ensure compatibility with all the simulation codes, not all of which support such numerical potentials, the tabulated values were fitted to Buckingham functions (see section 3.2.1, chapter 3). This was done using the weighted least squares method of Levenburg and Marquardt,\textsuperscript{44} which allows the fit to be weighted towards those regions which are considered the most important: those close to the equilibrium position and those typically found in defects. These parameters are presented in Table 7-1. The shell model parameters for the lattice oxygen were empirically fitted by Colbourn et al.\textsuperscript{39} to best reproduce the dielectric properties of MgO. The shell model spring constant and the core charge of O were assumed to be the same as $O^{2-}$, as used successfully by Colbourn et al.,\textsuperscript{39} parameters are given in Table 7-2.

For our study of Cl$^-$ in MgO and Li/MgO, further potentials were derived for the interactions of the chloride ion with the other species of interest; the parameters are listed in Table 7-3. They were derived using both empirical fitting and the electron gas method.\textsuperscript{42,43} For the Mg-Cl interactions and Cl core-shell parameters, the potentials of Lin and Catlow were used\textsuperscript{45} which where fitted empirically to the structure of MgCl$\textsubscript{2}$. All other potentials were derived using the electron gas method. These include the interactions of Cl$^-$ with O$^{2-}$, O$^-$ and Li$^+$. All these potentials were derived in the Madelung well of MgO as discussed in Chapter 3. The suitability of the Li-Cl parameters has been verified by the successful modelling of the LiCl lattice; pertinent results are presented in Table 7-4. Although it has not been possible to verify independently the interactions of Cl$^-$ with the oxygen species, the past success of the electron gas method at generating reasonable potentials\textsuperscript{28,32} gives confidence in these parameters.
Table 7-1. Electron Gas Potential Parameters. Buckingham potentials fitted from original tabulated data of Colbourn et al.\textsuperscript{39} A cut-off of 12Å was used for the short range interactions in all calculations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Buckingham Potential Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (eV)</td>
</tr>
<tr>
<td>Mg$^{2+}$ O$^2$</td>
<td>2134.3908</td>
</tr>
<tr>
<td>Mg$^{2+}$ O</td>
<td>4135.7700</td>
</tr>
<tr>
<td>O$^2$ O</td>
<td>676.9029</td>
</tr>
<tr>
<td>O$^+$ O$^-$</td>
<td>1396.5099</td>
</tr>
<tr>
<td>O$^-$ O</td>
<td>889.6440</td>
</tr>
<tr>
<td>Li$^+$ O$^2$</td>
<td>812.5675</td>
</tr>
<tr>
<td>Li$^+$ O</td>
<td>1583.4274</td>
</tr>
<tr>
<td>Ca$^{2+}$ O$^2$</td>
<td>2282.5694</td>
</tr>
<tr>
<td>Ca$^{2+}$ O</td>
<td>4768.1070</td>
</tr>
</tbody>
</table>

where $V(r) = Ae^{-\rho r} - \frac{C}{r^6}$.

Table 7-2. Shell model parameters. From Colbourn et al.\textsuperscript{39}

<table>
<thead>
<tr>
<th>Species</th>
<th>Shell</th>
<th>$k$ (eV Å$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Charge $Y$</td>
<td></td>
</tr>
<tr>
<td>O$^2$</td>
<td>-2.42</td>
<td>27.4623</td>
</tr>
<tr>
<td>O$^-$</td>
<td>-1.42</td>
<td>27.4623</td>
</tr>
</tbody>
</table>

where the free ion polarisability is given by $\alpha = \frac{Y^2}{k}$.
Table 7-3. Potential Parameters for the study of chloride in MgO

<table>
<thead>
<tr>
<th>Species</th>
<th>Buckingham Potential Parameters</th>
<th>Shell Model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (eV)</td>
<td>ρ (Å⁻¹)</td>
</tr>
<tr>
<td>Mg²⁺ Cl⁻ (1)</td>
<td>4914.5408</td>
<td>0.2567</td>
</tr>
<tr>
<td>Li⁺ Cl⁻ (2)</td>
<td>336.1000</td>
<td>0.3499</td>
</tr>
<tr>
<td>Cl⁻ O²⁻</td>
<td>2119.6500</td>
<td>0.3120</td>
</tr>
</tbody>
</table>

(1) From the work of Lin and Catlow.⁴⁵
(2) From the work of Colbourn et al.⁴⁹ fitted to Buckingham form.

Table 7-4. Structural parameters of LiCl and MgCl₂ determined using the potentials used in the simulation study of chloride in MgO.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lattice parameter (Å)</td>
<td>5.26</td>
<td>5.13</td>
</tr>
<tr>
<td>lattice energy (eV)</td>
<td>-33.51</td>
<td>-35.36</td>
</tr>
<tr>
<td>β-MgCl₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lattice parameter (Å)</td>
<td>3.641</td>
<td>3.640</td>
</tr>
<tr>
<td>a</td>
<td>3.641</td>
<td>3.640</td>
</tr>
<tr>
<td>b</td>
<td>5.930</td>
<td>5.927</td>
</tr>
<tr>
<td>lattice Energy (eV)</td>
<td>-26.18</td>
<td>-24.19</td>
</tr>
</tbody>
</table>
7.3.2 Polaron States

The nature of the untrapped hole can be considered as either localised or delocalised. The results of the atomistic simulations can be used to determine an approximate value for the relative energy of the two states.

In the small polaron state, the hole is localised on a single anion site so that the surrounding lattice will distort around that centre in response. The formation energy of the small polaron will therefore consist of the energy change due to the relaxation of the lattice about the defect plus the ionisation energy of $O^{2-}$ to $O^-$:

$$E_{\text{small polaron}} = E_{\text{lattice relax}} + \text{IE}(O^{2-} \rightarrow O^-). \quad (7.5)$$

For the latter value we used an effective ionisation potential of 8.8eV, calculated by Mackrodt and Stewart\textsuperscript{28} from \textit{ab initio} Hartree-Fock calculations on the oxygen ion in the Madelung field of MgO. Details of the procedure are given by the original authors.

In the large polaron state, the motion of the hole is rapid, so that the hole does not localise long on any one anion site. This motion is so rapid that the lattice ions surrounding the hole site do not have time to relax around the defect. However, the valence electrons of the surrounding ions will be able to respond to the presence of the hole and this can be approximated in our simulations by allowing only the shells of the ions to relax. Thus, the large polaron formation energy can be formulated as being the sum of three terms: the change in energy on allowing the shells to relax; the ionisation energy as given above and half the bandwidth of the oxide:

$$E_{\text{large polaron}} = E_{\text{shells relax}} + \text{IE}(O^{2-} \rightarrow O^-) + \frac{1}{2} \text{BW}. \quad (7.6)$$

The last term approximates the kinetic energy of the hole. An empirically derived value of 7.0eV is used for the bandwidth from the work of Pantelides.\textsuperscript{46}
It should be stressed that this method is approximate; we are attempting to model an electronic process using forcefield methods. Nevertheless, it will provide an insight into the relative stability of the two polaron states from which inferences can be drawn regarding the position and activity of these defects in the catalytic materials in question.

7.3.3 Solution Energies

We are interested in the ease, or otherwise, of dissolving the dopant under investigation in the host oxide. These solution energies can be calculated from simple thermodynamic cycles. As we are primarily interested in the solution of lithium oxide in the host magnesium oxide, this case will be described in detail.

The solution process can be considered in two stages, firstly non-oxidative solution, followed by oxidation to create hole states. Non-oxidative solution of Li₂O in MgO results in the substitution of Li⁺ on Mg²⁺ sites with charge compensation by oxygen vacancy formation;

\[
\text{Li}_2\text{O}(\text{Li}_2\text{O}) \rightarrow 2\text{Li}^{+}_\text{Mg}^{2+} (\text{MgO}) + V_0 (\text{MgO}). \tag{7.7}
\]

The energy change due to this process is given as

\[
E_{\text{sol,ox}} = E_{\text{lat}} (\text{Li}_2\text{O}) + 2E_{\text{sub}}(\text{Li}^{+}_{\text{Mg}^{2+}}) + E_{\text{vac}}(\text{O}^{2-}) - 2E_{\text{lat}}(\text{MgO}), \tag{7.8}
\]

where:

- \(E_{\text{lat}}\) are the lattice energies,
- \(E_{\text{sub}}(\text{Li}^{+}_{\text{Mg}^{2+}})\) is the formation energy of a Li⁺ substitutional at an Mg²⁺ site, and
- \(E_{\text{vac}}(\text{O}^{2-})\) is the formation energy of an oxygen vacancy.
However, given a sufficient partial pressure of oxygen, oxidation will take place resulting in the absorption of gas phase oxygen into the lattice oxygen vacancy sites and the release of holes:

\[
\frac{1}{2} \text{O}_2(g) + V_0(MgO) \rightarrow \text{O}_0^{2-}(MgO) + 2h^+(MgO), \tag{7.9}
\]
giving an oxidation energy of,

\[
E_{\text{ox}}^\text{aid} = \frac{1}{2} E_D(O_2) + EA^{1,2}(O) + 2E_{\text{polaron}} - E_{\text{vac}}(O^{2-}), \tag{7.10}
\]

where:

- \(E_D\) is the dissociation energy of \(O_2\)\(^{47}\)
- \(E_{A^{1,2}}(O)\) is the sum of the first and second electron affinities of oxygen\(^{47}\) and
- \(E_{\text{polaron}}\) is the non-electronic components of the formation energy of the stable polaron form.

The values used for the dissociation energy and electron affinities are given in Table 7-5 from Vedeneyev\(^{47}\) and Mackrodt and Stewart\(^{28}\).

Therefore, the solution energy of \(\text{Li}_2\text{O}\) in \(\text{MgO}\) under a partial pressure of oxygen:

\[
\text{Li}_2\text{O}(\text{Li}_2\text{O}) \rightarrow 2\text{Li}^+\text{Mg}^{2+}(\text{MgO}) + 2h^+(\text{MgO}), \tag{7.11}
\]
is given by,

\[
E_{\text{sol}} = E_{\text{sol,ox}} + E_{\text{ox}}, \tag{7.12}
\]

Similar cycles can be derived for the solution of other dopant in the host lattice.
Table 7.5. Parameters used in the calculation of the solution energies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ dissociation energy</td>
<td>119.12 kcal / mole @ 298.14K</td>
</tr>
<tr>
<td>First Electron Affinity of O @ 0K</td>
<td>1.46 eV</td>
</tr>
<tr>
<td>Second Electron Affinity of O @ 0K$^{28}$</td>
<td>-8.8 eV</td>
</tr>
</tbody>
</table>

7.4. Results and Discussion

7.4.1 Verification of Potentials

In order to verify that the fitted potentials were satisfactory, perfect crystal properties have been calculated using these potentials, as well as the original tabulated potentials and a number of empirically fitted potentials. These calculations are reported for both MgO and Li$_2$O. The results for the perfect lattice of MgO using the electron gas potentials and a selected empirical potential set are presented in Table 7-6. Comparison of the electron gas and empirical potentials for Li$_2$O are given in Table 7-7.

These results demonstrate that the fitting procedure has successfully reproduced the form of the interionic interaction as originally derived. Comparison of calculated defect energies for the present and other potentials will also be made later.

A further test of the suitability of potential parameters is to calculate the phonon dispersion curves. The calculated dispersion curves for the potentials fitted to Buckingham functions is compared to experimental measurements in Figure 7-1. Again the potentials are in good agreement with the experimental values. In particular it should be noted that the largest error - that in the longitudinal optic...
mode (at L) - is a consequence of the use of a central force model rather than deficiencies in the potential parameters.

Table 7-6. *Perfect Lattice Properties of MgO. Calculations using the potentials to be used in this work are compared to other calculated and experimental values.*

<table>
<thead>
<tr>
<th>Property</th>
<th>Electron Gas Potentials</th>
<th>Empirical Potentials</th>
<th>Expt(4)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tabulated(1)</td>
<td>Buckingham(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice Energy (eV)</td>
<td>-40.60</td>
<td>-40.86</td>
<td>-39.48</td>
<td>-40.79</td>
</tr>
<tr>
<td>Lattice Parameter (Å)</td>
<td>2.171</td>
<td>2.159</td>
<td>2.112</td>
<td>2.106</td>
</tr>
<tr>
<td>Elastic Constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10^{11} dyne cm^{-2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{11}</td>
<td>34.76</td>
<td>35.30</td>
<td>27.89</td>
<td>31.0</td>
</tr>
<tr>
<td>C_{12}</td>
<td>19.75</td>
<td>19.57</td>
<td>10.53</td>
<td>9.6</td>
</tr>
<tr>
<td>C_{44}</td>
<td>19.75</td>
<td>19.57</td>
<td>10.53</td>
<td>16.0</td>
</tr>
<tr>
<td>Dielectric Constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>static $\varepsilon_0$</td>
<td>9.91</td>
<td>9.80</td>
<td>9.42</td>
<td>9.86</td>
</tr>
<tr>
<td>high-frequency $\varepsilon_\infty$</td>
<td>2.96</td>
<td>2.99</td>
<td>2.84</td>
<td>2.96</td>
</tr>
</tbody>
</table>

**Notes:**

(1). From Colbourn *et al.*

(2). As given in Table 7-1 and 7-2.

(3). Using the potentials of Catlow *et al.*

(4). From the work of Peckham.

(5). The percentage error between the Buckingham fitted potentials and the experimental value.
Table 7-7. Perfect Lattice Properties of Li₂O. Calculations using the potentials to be used in this work are compared to other calculated and experimental values.

<table>
<thead>
<tr>
<th>Property</th>
<th>Electron Gas Potentials</th>
<th>Empirical</th>
<th>Experimental</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tabulated(^1)</td>
<td>Buckingham(^2)</td>
<td>Potentials(^3)</td>
<td></td>
</tr>
<tr>
<td>Lattice Energy (eV)</td>
<td>-31.6</td>
<td>-31.8</td>
<td>-30.0</td>
<td>-31.6</td>
</tr>
<tr>
<td>Lattice Parameter (Å)</td>
<td>3.27</td>
<td>3.24</td>
<td>3.32</td>
<td>3.26</td>
</tr>
<tr>
<td>Elastic Constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10^{11}) dyne cm(^2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_{11})</td>
<td>28.72</td>
<td>30.04</td>
<td>22.45</td>
<td>-</td>
</tr>
<tr>
<td>(C_{12})</td>
<td>7.15</td>
<td>7.74</td>
<td>4.76</td>
<td>-</td>
</tr>
<tr>
<td>(C_{44})</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>Dielectric Constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\varepsilon_0)</td>
<td>9.55</td>
<td>8.49</td>
<td>10.23</td>
<td>-</td>
</tr>
<tr>
<td>(\varepsilon_{\infty})</td>
<td>2.61</td>
<td>2.63</td>
<td>2.54</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Notes:

(1). From Colbourn et al.\(^\text{39}\)

(2). As given in Table 7-1 and 7-2

(3). From the work of Chadwick et al.\(^\text{49}\)

(4). The percentage error between the Buckingham fitted potentials and the experimental value.
Figure 7-1. Phonon dispersion curves for MgO. Results are given for the wavevectors
\[ \Gamma(0 0 0) \rightarrow X(\frac{1}{2} 0 \frac{1}{2}) \]
\[ X(\frac{1}{2} 0 \frac{1}{2}) \rightarrow \Gamma(0 0 0) \]
and
\[ \Gamma(0 0 0) \rightarrow L(\frac{1}{2} \frac{1}{2} \frac{1}{2}) \]

Experimental results (empty circles) from Sangster et al.\textsuperscript{50}

7.4.2 Defect and Surface Structure of MgO and Li/MgO

We will present first studies of the defect chemistry related to the catalytic activity of MgO based materials. These defects will be considered at bulk, surface and stepped surface sites. The structure of the various perfect surfaces will also be discussed. We will compare the different sites with reference to the stability of the defects and consequences on the activity of the material will also be discussed.
7.4.2.1 Bulk Defects

Tables 7-8 and 7-9 give results for the formation energies of bulk defects, both for intrinsic defects in pure MgO and those formed by the solution of Li$_2$O in MgO. Other theoretical results are also given for comparison. The good agreement with the other work demonstrates the suitability of the present potentials.

Table 7-8. Bulk Defect Formation Energies in MgO

<table>
<thead>
<tr>
<th>Defect</th>
<th>Calculated Energy / eV</th>
<th>Other Calculated Values$^{(1)}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>cation vacancy</td>
<td>25.30</td>
<td>24.40</td>
</tr>
<tr>
<td>anion vacancy</td>
<td>23.02</td>
<td>22.90</td>
</tr>
<tr>
<td>Schottky energy</td>
<td>7.46</td>
<td>7.55</td>
</tr>
<tr>
<td>cation-anion vacancy</td>
<td>45.66</td>
<td>-</td>
</tr>
<tr>
<td>pair</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vacancy pair Binding</td>
<td>-2.66</td>
<td>-</td>
</tr>
<tr>
<td>energy</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Polaron States$^{(2)}$

<table>
<thead>
<tr>
<th></th>
<th>Energy / eV</th>
<th>other calculated Values$^{(1)}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>large</td>
<td>4.74</td>
<td>4.90</td>
</tr>
<tr>
<td>small</td>
<td>6.60</td>
<td>6.63</td>
</tr>
<tr>
<td>Δ(large-small)</td>
<td>-1.86</td>
<td>1.73</td>
</tr>
</tbody>
</table>

Notes:

(1) Other values from the work of Mackrodt and Stewart$^{28}$

(2) Other values from the work of Foot and co-workers$^{33,51}$
Table 7-9. Bulk defect formation energies in Li/MgO and solution energies of lithium oxide in magnesium oxide. The Li⁺ substitutional energy is the energy required to remove a Mg²⁺ cation from a lattice site to infinity and replace it with a lithium. Similarly, the formation energy of the [Li]° is the energy required to remove adjacent Mg²⁺ and O²⁻ ions and replace them with a Li⁺ and O⁻ ions. The stability of the [Li]° is defined as the energy released by bringing an infinitely separated lithium substitutional and oxygen hole to adjacent sites (to form a [Li]°). The solution energies are as defined in equations 7.7 and 7.9.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Calculated Energy / eV</th>
<th>Other Calculated Values⁽¹⁾ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺ substitutional energy</td>
<td>16.18</td>
<td>16.27</td>
</tr>
<tr>
<td>[Li]° formation</td>
<td>30.83</td>
<td></td>
</tr>
<tr>
<td>[Li]° stability</td>
<td>0.98</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Solution Energies

| E_{sol} (No oxid.) | 5.45 | 5.45 |
| E_{sol} (Oxid.)   | -3.68 | -2.28 |
| E_{sol}           | 1.77 | 3.17 |

Notes:

(1) Other values from the work of Foot and co-workers[^33,51]
7.4.2.2 Untrapped Polaron States

We find the large polaron state to be more stable than the small polaron state by 1.9eV (Table 7-8). This agrees not only with other simulation studies\textsuperscript{33,51} and semi-empirical calculations\textsuperscript{52} but also with the experimental evidence which suggests that the large polaron is the state present in MgO.\textsuperscript{53} However, the calculated large polaron energy (4.74eV) presents a problem in that it is smaller than the optical band gap of 7.7eV, a result which could only be rationalised if the electron state in the conduction band were unbound, which is implausible. Therefore, the calculated value is almost certainly too low by almost 3eV. Consequently the formation energy of the small polaron is also too small, by at least 1.1eV, if it is to be less stable than the large polaron (as found experimentally\textsuperscript{53}). There are also uncertainties in the value of the bandgap used, which was derived empirically.\textsuperscript{46} Therefore, we may expect the difference in formation energy of the two states calculated here to be an upper limit. These apparent errors in the formation energies are a consequence of attempting to approximate a purely electronic effect using a simple model based on interatomic potentials. Nevertheless, the results give the correct trends and give a fairly reasonable estimate of the polaron formation energy, which is to be used in calculating the solution energy.

7.4.2.3 Solution Energies

We can now use the calculated polaron energy to determine the solution energy of Li\textsubscript{2}O in MgO (Table 7-9). Solution in a non-oxidising environment is endothermic (5.45eV). However, the process of oxidation is exothermic (-3.68eV) and thus preparation of Li/MgO in air will result in the solution of Li\textsubscript{2}O forming hole states in the material. Both these results are in agreement with previous simulation studies.\textsuperscript{33,51} We shall see later how the solution energy is affected by the partition of the solute between the bulk and the surface of the material.
7.4.2.4 Lithium Trapped Holes

Experiment shows that holes are trapped by the presence of alkali metal ions in alkaline earth lattices. Thus, the neutral lithium trapped hole defect centre is expected to be stable in Li/MgO. The binding energy of this defect is defined as the energy released when previously isolated lithium substitutionals and oxygen hole defects are bought together at adjacent lattice sites;

$$\text{Li}^{+}_{\text{Mg}^{2+}} + \text{O}^{2-} \rightarrow [\text{Li}^{+}\text{O}^{-}],$$  \hspace{1cm} (7.13)

which gives a hole binding energy of;

$$E_{\text{bind}} = E([\text{Li}^{0}]) - E(\text{Li}^{+}_{\text{sub}}) - E(\text{O}^{2-}).$$  \hspace{1cm} (7.14)

The results in table 7-9 show that, in accordance with experiment, the trapped hole state is bound, the calculated binding energy being 0.98eV.

7.4.3 The Perfect Surface of MgO

Prior to discussing the defect chemistry and the nature of the active sites at the surface, we must first determine the structure of the non-defective surfaces of MgO. The structure of the exposed surface must be energy minimised, to give the relaxed surface structure, prior to placing any defects on this surface. The dominant surface in MgO is the (1 0 0) face. However, morphological studies show that the surface of MgO consists of terraces on the (1 0 0) surface which are of the order of ca. 100Å across. These surface terraces can be considered as surfaces with high Miller indices of the general form (1 0 x). The structure of these surfaces will also be investigated as possible sites for defects.

The stability of the surface will depend on the surface energy, which is defined as the energy lost per unit area on creation of the surface. The lower this energy the more stable the surface, as is illustrated in Figure 7-2.
Figure 7-2. Schematic representation of the definition of Surface Energy.

\[ E(\text{surface}) = \frac{E(\text{surface block}) - \frac{1}{2} E(\text{bulk})}{A}, \text{ where } A \text{ is the surface area.} \]

7.4.3.1 Construction of a Low-Coordinate Step Site

Low coordinate step sites have been suggested as possible sites for dopants\textsuperscript{32} and also as possible active sites.\textsuperscript{9} To model such features on the (1 0 0) surface we shall consider a surface with high Miller index face of the form (1 0 x), in which the variable x is varied until:

i. The distance between steps is large enough to remove any significant interaction between neighbouring steps.\textsuperscript{31} Thus, the modification of a step does not perturb the next step.

ii. The surface energy approaches closely that of the (1 0 0) surface.

Before attempting such simulations it is necessary to ensure that the surface energy is converged with respect to the size of the region sizes (as defined in Chapter 3) for all the surfaces. The region size in MIDAS is defined in terms of repeat units normal to the surface and therefore the surface area of the repeat
unit increases as the Miller index of the surface increases. Conversely the interplanar spacing decreases. Thus the number of ions required to describe a given depth increases with the increasing Miller index. To ensure convergence, the region size was altered for each surface to ensure a region I depth of approximately 10Å. Region II is kept to a minimum, equal to the short range cutoff of 12Å. We note that this procedure is simplified in the newer code MARVIN\textsuperscript{37} where the region sizes may be defined by specifying the depth from the surface. However, the defect code CHAOS\textsuperscript{38} required the use of the MIDAS code.

Results for the surfaces with a Miller index of (1 0 \(x\)) with \(x=0\ldots11\) are given in Table 7-10 and the surface energies are also shown in Figure 7-3. We find that even for the (1 0 0) surface, the relaxation lowers the surface energy by an appreciable amount. Furthermore, the surface energy and surface rumpling (ca. 2\%) is in excellent agreement with experimental measurements\textsuperscript{55} and LEED data\textsuperscript{56} respectively. It is clear from these results that surface relaxation effects must be considered significant even for the simplest surface. We shall see the consequences of this result in the quantum mechanical calculations in Chapter 8.

As we might expect, as the Miller index of the surface increases, and the surface thus resembles more closely the (1 0 0) surface, we find that the surface energy of the surface approaches that of the latter surface. The (1 0 11) surface has an inter-step distance of 23.2Å, which is of the order of four times the extent of any distortions produced in these calculations by defect formation. The energy of the surface is within 0.12eV m\(^{-2}\) of that of the (1 0 0) surface and we therefore consider it to be a suitable model for step sites on the surface. We also note, that in typical crystals of MgO, terraces on the (1 0 0) surface are of the order of 100Å in length\textsuperscript{9,57,58} and thus we can safely treat defects on steps as being independent from similar defects at adjacent terraces. Thus, the (1 0 11) surface will be used throughout this work as a model step surface. The structure of this surface is shown in Figure 7-4 and in more detail in Figure 7-5. Note the rounding of the surface of the step, a feature common to all the surfaces considered and which has been noted in other theoretical studies.\textsuperscript{25}

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Table 7-10. Results for the series of surfaces (1 0 x) with x=0..11.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Surface Area / Å²</th>
<th>Surface Energy / J m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unrelaxed</td>
<td>Relaxed</td>
</tr>
<tr>
<td>1 0 0</td>
<td>18.6</td>
<td>1.103</td>
</tr>
<tr>
<td>1 0 1</td>
<td>26.4</td>
<td>3.316</td>
</tr>
<tr>
<td>1 0 2</td>
<td>42.0</td>
<td>2.525</td>
</tr>
<tr>
<td>1 0 3</td>
<td>59.0</td>
<td>2.137</td>
</tr>
<tr>
<td>1 0 4</td>
<td>76.9</td>
<td>1.906</td>
</tr>
<tr>
<td>1 0 5</td>
<td>95.1</td>
<td>1.758</td>
</tr>
<tr>
<td>1 0 6</td>
<td>113.4</td>
<td>1.655</td>
</tr>
<tr>
<td>1 0 7</td>
<td>131.8</td>
<td>1.554</td>
</tr>
<tr>
<td>1 0 8</td>
<td>150.3</td>
<td>1.522</td>
</tr>
<tr>
<td>1 0 9</td>
<td>168.8</td>
<td>1.484</td>
</tr>
<tr>
<td>1 0 10</td>
<td>187.4</td>
<td>1.441</td>
</tr>
<tr>
<td>1 0 11</td>
<td>205.9</td>
<td>1.409</td>
</tr>
</tbody>
</table>
Figure 7-3. The unrelaxed and relaxed surface energies for the series of surfaces (1 0 x) with x=0..11.

7.4.4 Surface Polaron States

The formation energies of large and small polarons were calculated at the (100) surface, and at the top edge of the (1 0 11) step (Table 7-11). The large polaron is more stable than the small polaron at all the sites (as is also the case in the bulk). However, the difference in their energies decreases as the coordination number of the hole decreases from the bulk to the planar surface, to the step. This is consistent with the results quantum mechanical studies by Shluger and co-workers,\textsuperscript{52,59} who calculated that although untrapped in the bulk, oxygen holes are self-trapped at the (1 0 0) surface. We can therefore expect the probability of small polaron formation to increase at the surface and at low coordinate surface sites. We should again note however that the error associated with the energies calculated by this classical treatment of an electronic defect can be up to 3eV (see section 7.4.2.2). Even so, we can conclude qualitatively that untrapped holes are more likely at low coordinate surface sites than in the bulk.

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or on planar surface sites. The calculations involving untrapped oxygen holes in the remainder of the study will therefore assume that the hole is localised; a small polaron.

Figure 7-4. The structure of the (1 0 11) surface of MgO
Figure 7-5. The step in the (1 0 11) surface of MgO showing the rounding of the step on relaxing the ionic positions.

Table 7-11. Polaron formation energies at various sites in MgO

<table>
<thead>
<tr>
<th>Site</th>
<th>Polaron Energy (eV)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>small</td>
<td>large</td>
</tr>
<tr>
<td>bulk</td>
<td>6.60</td>
<td>4.74</td>
</tr>
<tr>
<td>(100)</td>
<td>6.69</td>
<td>5.08</td>
</tr>
<tr>
<td>step</td>
<td>6.09</td>
<td>4.63</td>
</tr>
</tbody>
</table>
7.4.5 The Lithium Trapped Hole and Related Defects at Surface Sites

7.4.5.1 Surface Stability and Surface Segregation

We shall now consider the segregation of defects by calculating the formation energies of the defects in the bulk and at the surface. We shall also consider the formation energies for the defects at various depths below the surface as the defects migrate from the bulk.

The formation energy of the Li\(^+\) substitutional, the localised oxygen hole and the lithium trapped hole are given in Table 7-12. The Li\(^+\) substitutional has a surface segregation energy (the difference between the energy of the defect at the bulk and at the surface) of 0.2eV. The [Li]\(^0\) centre is much more strongly segregated with a surface segregation energy of 0.5eV and is also more strongly bound than in the bulk, with a binding energy of 1.1eV (cf. 0.9eV in the bulk). Therefore, we would expect these centres not only to be stable surface species also to be present in much higher concentrations than the isolated defects, both in the bulk and at the surface. The O\(^-\) is less stable at the surface although only by 0.1eV. Depth energy profiles, where the defect is placed at successive layers from the surface were calculated for the three defects to investigate further any segregation phenomena and are given in Figure 7-6. Most striking is the migration barrier for the [Li]\(^0\) centre immediately below the surface layer, from which we would expect that migration of this defect from the surface into the bulk would be slow. The isolated defects on the other hand do not exhibit this large barrier and therefore migration into the bulk would be quicker. However, as previously noted, the [Li]\(^0\) centre is likely to be the dominant defect species and we would expect the formation of these centres to dominate any migration of the isolated defects. Nevertheless, dissociation may provide an effective mechanism for penetration of the defects into the bulk. Similar conclusions were obtained by Gorman.\(^3^4\)
Table 7-12. The formation energies and surface segregation energies of defects in MgO and Li/MgO. * surface segregation energy = \( E_{\text{surface}} - E_{\text{bulk}} \). Note, negative values indicate that surface segregation is energetically favourable.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Defect Energy / eV</th>
<th>Surface Segregation Energy / eV*</th>
</tr>
</thead>
<tbody>
<tr>
<td>cation vacancy</td>
<td>24.77</td>
<td>-0.53</td>
</tr>
<tr>
<td>anion vacancy</td>
<td>23.24</td>
<td>0.22</td>
</tr>
<tr>
<td>Schottky energy</td>
<td>7.14</td>
<td>-0.32</td>
</tr>
<tr>
<td>Li/MgO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li+ substitutional</td>
<td>15.94</td>
<td>-0.24</td>
</tr>
<tr>
<td>Oxygen hole (see Table 7-11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>small polaron</td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>large polaron</td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td>([\text{Li}]^0) centre</td>
<td>30.36</td>
<td>-0.47</td>
</tr>
<tr>
<td>([\text{Li}]^0) stabilisation</td>
<td>1.1</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 7-6. Depth profile for the Li⁺ substitutional, the small polaron and the [Li]₀ centre from the (1 0 0) surface. Layer 1 is the surface. The [Li]₀ centre defect energy is given on the right hand axis.

7.4.5.2 Surface Solution Energy

The results above show that there is a strong thermodynamic driving force for surface segregation of [Li]₀ centres. We can calculate a solution energy for Li₂O in MgO where we assume that all the solute is present as surface species (see Table 7-13), which will allow us to compare the thermodynamics of the solution process with that previously calculated purely for bulk solution processes.
<table>
<thead>
<tr>
<th>Solution Process</th>
<th>ΔE (eV)</th>
<th>Surface segregation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{soi}$ (No oxid.) (equation 7.7)</td>
<td>5.52</td>
<td>+0.07</td>
</tr>
<tr>
<td>$E_{soi}$ (Oxid.) (equation 7.9)</td>
<td>-3.23</td>
<td>+0.45</td>
</tr>
<tr>
<td>$E_{soi}$ (equation 7.11)</td>
<td>2.29</td>
<td>+0.52</td>
</tr>
</tbody>
</table>

Table 7-13. Surface solution of lithium oxide in magnesium oxide. Bulk values are given in Table 7-9. *Surface Segregation Energy = $E_{surface} - E_{bulk}$

These results suggest that a surface segregated solution of lithium oxide in magnesium oxide is less stable than a bulk solution. This is primarily the consequence of the oxygen vacancy being less stable at the surface (Table 7-12). However, the solution energy process does not account for the formation of $[\text{Li}]^0$ centres and as we have seen not only is this species quite strongly bound but it is also strongly surface segregated. Thus, we can account for this by including the energy released on forming the lithium trapped hole, giving a corrected solution energy of 1.19eV at the surface compared to a similar value of 0.79eV in the bulk. Furthermore, we would expect oxygen vacancies to migrate into the bulk given the higher surface defect energy. Therefore we can see that the solution of lithium oxide in MgO will result in a high surface concentration of $[\text{Li}]^0$ centres as a result of the surface segregation and higher binding energy of this defect.

7.4.5.3 Defect Clustering

The formation of clusters of $[\text{Li}]^0$ centres has been postulated, where $[\text{Li}]^0$ centres aggregate to form extended structures, termed 'microgalaxies', within the MgO host lattice. We have carried out a number of calculations to determine if the clustering of $[\text{Li}]^0$ centres is energetically favoured. We have considered the formation of clusters of $[\text{Li}]^0$ centres in various configurations both in the bulk and at the (1 0 0) surface. The bulk clusters consisted of: a single $[\text{Li}]^0$...
centre, two [Li]$^0$ centres, a cubic arrangement of four [Li]$^0$ centres and 6 [Li]$^0$ centres arranged as a 2×3 cuboid. The results, given in Table 7-14, clearly show that clustering stabilises the defect centres. Furthermore, we can conclude that the larger the cluster the greater this stabilisation energy. The results for aggregation on the (1 0 0) surface also lead us to similar conclusions (Table 7-15).

Here, we have considered clusters of one to four [Li]$^0$ centres planar on the surface and a cube of 4 [Li]$^0$ centres which lies both in the surface and second layer of the surface. The resulting stabilisation energies at the surface is higher than for the bulk, and we can therefore expect clustering to be more prominent at the surface. However, the effect of surface segregation is also evident in these results. The surface cubic cluster which extends into the second layer is less stable than those clusters which lie in the surface layer only which is consistent with the large segregation barrier immediately below the surface layer which we found for the [Li]$^0$ centre.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$E_{\text{defect}}$ (eV)</th>
<th>$E_{\text{defect}}$ / [Li]$^0$ (eV)</th>
<th>Stabilisation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Li]$^0$</td>
<td>30.83</td>
<td>30.83</td>
<td>-</td>
</tr>
<tr>
<td>2[Li]$^0$</td>
<td>60.90</td>
<td>30.45</td>
<td>-0.38</td>
</tr>
<tr>
<td>4[Li]$^0$</td>
<td>120.88</td>
<td>30.22</td>
<td>-0.61</td>
</tr>
<tr>
<td>6[Li]$^0$</td>
<td>181.08</td>
<td>30.18</td>
<td>-0.65</td>
</tr>
</tbody>
</table>

Table 7-14. Clustering energies for the formation of [Li]$^0$ clusters in the bulk structure.

The stabilisation energy is given as the change in the formation energy per [Li]$^0$ centre on clustering. Negative values indicate that clustering is energetically favoured.
<table>
<thead>
<tr>
<th>Cluster</th>
<th>$E_{\text{defect}}$ (eV)</th>
<th>$E_{\text{defect}} / [\text{Li}]^0$ (eV)</th>
<th>Stabilisation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Li]$^0$</td>
<td>30.36</td>
<td>30.36</td>
<td>-</td>
</tr>
<tr>
<td>2[Li]$^0$</td>
<td>59.74</td>
<td>29.87</td>
<td>-0.51</td>
</tr>
<tr>
<td>3[Li]$^0$</td>
<td>89.58</td>
<td>29.86</td>
<td>-0.52</td>
</tr>
<tr>
<td>4[Li]$^0$ planar</td>
<td>117.96</td>
<td>29.49</td>
<td>-0.89</td>
</tr>
<tr>
<td>4[Li]$^0$ cube</td>
<td>119.88</td>
<td>29.97</td>
<td>-0.41</td>
</tr>
</tbody>
</table>

Table 7-15. Surface Clustering Energies for the formation of [Li]$^0$ clusters. The stabilisation energy is given as the change in the formation energy per [Li]$^0$ centre on clustering. Negative values indicate a lower formation energy on clustering. All the clusters consist of single layers of [Li]$^0$ centres at the (1 0 0) surface with the exception of the 4[Li]$^0$ cube which extends into the second layer.

7.4.5.4 Defects at Step Sites

The formation energy of defects at the step formed by the (1 0 11) surface are given in Table 7-16. Removal of ions from the step will lead to a surface of lower Miller index, which we have already shown to be less stable than the (1 0 11) surface, and therefore we would expect this process to be relatively unfavourable. We calculate that the formation energies of the cation and anion vacancies at the step are similar to those for the (1 0 0) surface; the anion vacancy is in fact calculated to be less favourable at the step. Therefore, it is as likely for vacancies to form on the (1 0 0) surface as it is for stepped surfaces to increase their Miller index. From these results we might expect the formation of the cation, anion vacancy pair to be similarly unfavourable at the step. However,
this was not possible using the present defect code, CHAOS, due to problems in handling the symmetry of the system, a problem which we encountered again with similar low coordinate structures (see section 7.4.5.5). However, these results confirm that the smaller terraces are less stable as previously determined by the perfect surface calculations. Furthermore, this demonstrates that migration of ions at a step, away from a terrace leading to an increase in the surface energy, will be slow.

The results for the O\(^-\) and Li\(^+\) substitutional show a marked preference for the lower coordination step site. We would therefore expect any untrapped holes to migrate to such sites. We would also expect from the results for the isolated defects that the [Li]\(^0\) centre would also prefer step sites. However, this cannot be confirmed due to the limitations of the defect code used. All attempts to simulate this defect caused the code to fail due to problems associated with the determination of the symmetry of the defect. However, the preference of the [Li]\(^0\) centre for other low coordinate sites (protosteps) will be shown below.

*Table 7-16. Formation energies of defects at the (1 0 1 1) step site. The step segregation energy is defined as the difference between the defect energy at the (1 0 0) surface and at the step, with a negative value indicating that the defect at the step is energetically favoured.*

<table>
<thead>
<tr>
<th>Defect</th>
<th>Energy (eV)</th>
<th>Step Segregation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cation vacancy</td>
<td>23.76</td>
<td>-0.01</td>
</tr>
<tr>
<td>anion vacancy</td>
<td>22.34</td>
<td>0.10</td>
</tr>
<tr>
<td>Li(^+) substitutional</td>
<td>15.26</td>
<td>-0.68</td>
</tr>
<tr>
<td>O(^-) (thermal)</td>
<td>14.89</td>
<td>-0.61</td>
</tr>
<tr>
<td>O(^-) (optical)</td>
<td>16.93</td>
<td>-0.45</td>
</tr>
</tbody>
</table>
7.4.5.5 Protosteps

The terraced nature of the surface of MgO suggests that, as discussed above, active sites may be segregate to lower coordination sites. To investigate further the possible siting of active sites at low coordinate sites we shall consider the smallest terrace possible; a square dimer of MgO on the (1 0 0) surface (as shown in Figure 7-7). We can consider this structure as the first step in the construction of a larger terrace by surface migration and rearrangement processes and also to be the lowest coordinated site at the surface. The relative stability of the defects at this protostep will be considered particularly with reference to the (1 0 0) surface and the extended terraces described previously by the (1 0 11) surface.

Several relevant protosteps are shown in Figure 7-7 together with their formation energies. The protostep formation energy is defined as the change in energy when the constituents of the protostep are bought from infinity and placed on the (1 0 0) surface. We shall consider first the formation of the non-defective protostep. It has already been shown how the stability of a terraced surface increases and approaches that of the lowest energy surface, the (1 0 0) surface as the length of the terrace increases. Similarly we find that, as expected, that the formation of the protostep is less favourable than these extended terraces. The lattice energy per MgO dimer in the 2MgO protostep is 38.2eV compared to 40.9eV in the bulk. When we consider the next protostep structure consisting of 3 MgO dimers the lattice energy increases to 38.8eV per MgO dimer. We can see therefore that, given conditions suitable for migration of surface species, small protosteps will aggregate to form the extended surfaces, a process evident for clean MgO surfaces which rearrange on annealing to maximise the (1 0 0) surface.⁵⁷
Figure 7-7. The formation energies of various protostep structures on the (1 0 0) surface of MgO.
We shall now consider the protostep as a site for defects involved in the partial oxidation catalysis. We have calculated energies for the reaction summarised by the schemes 7.15-7.18 below, which show that the protostep is indeed a more favourable site for the [Li]$^0$ centre (7.15) and its individual defect components, the small polaron (7.16) and the lithium substitutional (7.17).

\[
\text{O}^- \text{Li}^+ + \text{MgO} \rightarrow \text{O} \quad \Delta E = -2.27\text{eV (7.15)}
\]

\[
\text{O}^- + \text{MgO} \rightarrow \text{O} \quad \Delta E = -0.30\text{eV (7.16)}
\]

\[
\text{Li}^+ + \text{MgO} \rightarrow \text{Li}^+ \quad \Delta E = -0.74\text{eV (7.17)}
\]

\[
\text{O} + \text{Li}^+ \rightarrow \text{Li}^+ \quad \Delta E = -2.40\text{eV (7.18)}
\]

This is primarily a result of the reduced Madelung field at such sites. These results are consistent with those found for the Li substitutional and oxygen hole defects at the (1 0 11) step. We also note that the binding energy of the [Li]$^0$ centre is increased at the protostep (equation 7.18) compared to the (1 0 0) surface, being respectively 2.4eV and 1.1eV. The result for the [Li]$^0$ centre (equation 7.15) also supports our conclusions that this defect is also likely to segregate to step sites. (As mentioned previously, the [Li]$^0$ centre at the step proved not to be calculable using the current surface defect codes).
Unlike the case of the defects at the top of protosteps, the untrapped hole, and substitutional defects are less stable at the bottom of the protostep with respect to the (1 0 0) surface (equations 7.19-7.20). However, we find that the [Li]$^0$ centre is more stable at this site than at the top of the protostep (equation 7.21).

From the results, we can conclude that, if catalytic activity depends inversely on the stability of the active site, then the [Li]$^0$ centre will become less active at lower coordination sites as illustrated in Figure 7-8. However, the results also suggest that the untrapped hole will become more active at lower coordinate sites. In particular, we note that the site at the bottom of the protostep is less stable and therefore possibly more active. We would also expect the same trends to be evident for more extended terraces.

\[ \text{O}^- + \rightarrow \text{O}^- \quad \Delta E = +0.38\text{eV} \quad (7.19) \]

\[ -\text{Li}^+ + \rightarrow \text{Li}^+ \quad \Delta E = +2.69\text{eV} \quad (7.20) \]

\[ \text{O}^+ \rightarrow \text{O}^- \quad \Delta E = -1.47\text{eV} \quad (7.21) \]
7.4.5.6 Defect Migration

We shall now consider the mobility of the defects involved in catalysis. Experimentally it is noted that the oxygen holes in the bulk of Li/MgO are mobile even at temperatures as low as 4.2K. The hole hops around the lithium substitutional (shown in Figure 7-9) and can also produce hole decay by hopping away from the lithium (Figure 7-10). This process involves electronic motion only, which can only be approximated in atomistic simulations by allowing the hole to be split over the two oxygen sites. Foot calculated the hopping activation energy of the hole around the lithium to be 0.79eV which clearly demonstrates the limitation of the approximation used: the value is clearly an overestimate given the evidence for low temperature hopping. Lithium migration, is however, an atomic transport process, with the most likely mechanism being via vacancy hopping (as shown in Figure 7-11). This migration process can readily be calculated using simulation techniques and we shall discuss the migration of lithium and [Li]O centres at surface sites.
Figure 7-9. Hole hopping around a Lithium substitutional. The hole hops between the axial oxygen site (Oa) to the equatorial oxygen site (Oe).

Figure 7-10. Trapped hole decay by the "hopping away" of the hole from the nearest neighbour oxygen to the next nearest neighbour site. O_nn is the nearest neighbour oxygen, O_3nn the next nearest neighbour oxygen.

Figure 7-11. Lithium ion migration in MgO via a vacancy mechanism.
Figure 7-12. Lithium ion migration on the (1 0 0) surface of MgO via a vacancy mechanism showing the ability of the migrating ion to migrate via a pathway above the plane of the surface.

To calculate the energy of the migration barrier for lithium via a vacancy mechanism in the bulk, the lithium ion is moved along a trajectory from one cation lattice site to a vacant cation site and held fixed at each point whilst the remainder of the lattice is relaxed around it (Figure 7-11). A similar pathway is used at the surface. However, once the migration saddle point was determined with the lithium in the plane of the surface, additional configurations were considered with the lithium ion being moved out of the surface (Figure 7-12). The resulting migration barriers are 0.47eV and 0.01eV for the bulk and surface respectively. The nearly barrierless migration at the surface is a consequence of the ion being able to migrate via a pathway which allows it to leave the plane of the surface, with the Li ion being 0.49Å above the plane of the surface at the saddle point. Thus, we might expect lithium ion migration to be rapid at the surface provided that surface cation vacancies are present. However, migration into the bulk will be considerable slower.

We can also consider the decay of [Li]° centres by calculating the binding energy of the hole and the lithium as they are moved apart. The hop-away energy, defined as the change in energy when the oxygen hole is moved from the nearest neighbour lattice site to the next nearest neighbour site, was calculated for both the bulk and the surface. We find that the binding energy of the lithium ion to a hole at the next nearest neighbour site is the same, 0.69eV for
both the bulk and the surface. However, when we consider the decay of a [Li]$^0$
centre by the hopping of the hole away from the lithium, the higher binding
energy of the [Li]$^0$ centre at the surface means that more energy is required to
accomplish this than in the bulk. We calculate a hop-away energy of $0.41\text{eV}$ at
the surface and $0.26\text{eV}$ in the bulk; thus, the rate of lithium trapped hole decay
should be lower at the surface than in the bulk.

7.4.5.7 Migration to and from low coordinate sites.

We have already shown that the formation of [Li]$^0$ centres and oxygen holes at
low coordinate sites is generally favoured over such defects at the planar (1 0 0)
surface. The results on the migration properties of lithium defects and
experimental evidence for rapid hole migration suggest that migration to these
low coordinate sites will be rapid. However, these defects are strongly trapped
at the low coordinates sites thereby preventing further migration. We would
therefore expect that such sites will be heavily populated with Li and hole
species. The morphology of the catalysts will therefore have a significant effect
on the activity of the material, a point to which we return in later sections.
7.4.6 The role of chlorine in the partial oxidation of methane by MgO and Li/MgO

We now present results of a detailed study of the effect of chlorine doping on Li/MgO and MgO catalysts, the experimental background to which we gave in section 7.2.2. The main focus will be on the elucidation of the defect chemistry of these catalysts, in an attempt to understand the role of chloride. These results will later be used to comment on the active sites and product selectivity of these sites in the non-Cl\textsuperscript{-} containing MgO and Li/MgO.

7.4.6.1 Results and Discussion

In order to investigate the effect of the incorporation of Cl\textsuperscript{-} into the lattice, calculations were carried out at the following sites; (i) bulk lattice sites, (ii) at the (100) surface, (iii) at sites close to the (100) surface, that is at sub-surface sites and (iv) at low coordinate step sites.

In considering the incorporation of chloride it has been assumed that chloride ions substitute for oxygen in the lattice, as chlorine is added to Li/MgO as chloride salts.\textsuperscript{19} However, we note that there is no direct evidence for this model for the gas phase addition \textit{via} chloroalkanes. We consider the formation of isolated chloride defects and chloride containing defect clusters and the distribution of these defects between the bulk and the surface as well as their surface siting.
Chloride ions have been treated as substitutional defects on oxygen lattice sites in MgO based materials (Table 7-16). This is a reasonable assumption when the relative ionic radii of the two ions are considered (Cl\(^-\) = 1.81Å, O\(^2-\) = 1.52Å).

To investigate the segregation of Cl\(^-\) substitutionals we calculated the defect energy in the bulk, at the \((1 0 0)\) surface and at the first 6 layers below the surface. Cl\(^-\) is found to be strongly segregated to the surface (see Figure 7-13). The segregation energy (as previously defined in section 7.4.5.1) for Cl\(^-\) is 1.2eV with the barrier to migration being immediately below the surface. Furthermore, the step site is also preferred over the \((1 0 0)\) site with the former being 1.14eV more stable than the latter. This strong segregation is primarily a size effect: the ionic radii of Cl\(^-\), O\(^-\) and O\(^2-\) are 1.81Å, 1.76Å and 1.52Å respectively. Thus it is expected that isolated chloride defects in MgO will exhibit strong surface segregation with low coordinate sites being the most preferred site. However, the non-zero effective charge of the defect suggests that the formation of neutral defect centres is likely, possible models for which will now be considered.

Table 7-17. Chlorine containing Defects

<table>
<thead>
<tr>
<th></th>
<th>Defect Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
</tr>
<tr>
<td>Cl(^-) substitutional</td>
<td>18.27</td>
</tr>
<tr>
<td>[LiCl]</td>
<td>33.71</td>
</tr>
<tr>
<td>(E_{bind}) [LiCl]</td>
<td>0.74</td>
</tr>
<tr>
<td>[Cl(^-) -V(_{Mg})-Cl(^-)] (linear)</td>
<td>58.71</td>
</tr>
<tr>
<td>(E_{bind}) ([Cl(^-) -V(_{Mg})-Cl(^-)])</td>
<td>0.85</td>
</tr>
</tbody>
</table>
Figure 7-13. Depth profile of Cl⁻ and [LiCl] defects. Layer 1 is the (100) surface. [LiCl] defects are considered both parallel and perpendicular to the surface. In the latter the Cl⁻ is closest to surface.

7.4.6.1.2 The [LiCl] Defect Cluster

Lunsford et al.$^{21}$ suggested that chloride binds to the lithium to form neutral [LiCl] defect centres. This defect is calculated to be bound with a binding energy of 0.74eV in the bulk and 1.02eV at the surface;

Bulk: \( \text{Li}^+_{\text{M}^3} + \text{Cl}^-_{\text{M}^3} \rightarrow [\text{LiCl}] \quad \Delta E = -0.74\text{eV} \quad (7.22) \)

Surface \( \text{Li}^+_{\text{M}^3} + \text{Cl}^-_{\text{M}^3} \rightarrow [\text{LiCl}] \quad \Delta E = -1.02\text{eV} \quad (7.23) \)
These values are comparable to those calculated for the lithium trapped hole, 
$[\text{Li}]^0$; 0.98eV and 1.08eV in the bulk and at the surface respectively. As with the 
isolated Cl$^-$ defect, the [LiCl] defect also segregates strongly to the surface with a 
segregation energy of 1.24eV (see Figure 7-17). Furthermore, comparison with 
the results for the Li substitutional (Figure 7-6), which is not significantly 
segregated and for the [LiCl] defect perpendicular to the surface shows that this 
effect is due almost entirely to the segregation of Cl$^-$. All the calculations on 
defects containing chloride suggest strong surface segregation. Bulk chloride 
species are therefore likely to be relatively unimportant.

Since the binding energies of the [LiCl] and [Li]$^0$ defects are similar we would 
extpect an equilibrium to exist between the two defect centres at the surface:

$$[\text{Li}]^0_{(100)} + \text{Cl}^{-}_{(100)} \rightarrow [\text{LiCl}]_{(100)} + \text{O}^-_{(100)} \quad \Delta E = -0.06\text{eV}$$

(7.24)

Thus, the doping of Li/MgO catalysts with Cl$^-$ will result in a modification of 
the number of active lithium trapped holes. In particular, the addition of Cl$^-$ will 
promote the formation of untrapped holes and a reduction in the number of 
[Li]$^0$ centres, which will modify the activity and selectivity of the catalysts. As 
has been found for [Li]$^0$ defects, the formation of larger [LiCl] clusters appears 
to be favoured:

$$2[\text{LiCl}]_{(\text{bulk})} \rightarrow [\text{Li}^+_{(\text{bulk})} + \text{Cl}^-_{(\text{bulk})}] \quad \Delta E = -1.05\text{eV}$$

(7.25)

$$2[\text{LiCl}]_{(100)} \rightarrow [\text{Li}^-_{(100)} + \text{Cl}^+_{(100)}] \quad \Delta E = -0.77\text{eV}$$

(7.26)

Mixed [Li]$^0$ and [LiCl] are also likely;

$$[\text{LiCl}]_{(\text{bulk})} + [\text{Li}]^0_{(\text{bulk})} \rightarrow [\text{Li}^+_{(\text{bulk})} + \text{Cl}^-_{(\text{bulk})}] \quad \Delta E = -0.88\text{eV}$$

(7.27)
Calculations on mixed defect clusters at the surface proved unsuccessful due to deficiencies in the defect code in handling defects with low symmetry, as noted previously. However, we suggest that the formation of such clusters is likely given the results for the bulk and the fact that calculations suggest similar clustering for the individual [LiCl] and [Li]° centres at the surface. We note that Lunsford and co-workers detected a LiCl phase (rocksalt structure) on the surface of as-prepared Li-MgO-Cl catalysts\textsuperscript{21} by XPS which is consistent with the suggestion from these calculations that extended surface clusters of LiCl are likely. The consequence of this may be reflected in the reduction of CO\textsubscript{2} poisoning which will be discussed further in section 7.5.5.

The increased stability of Cl\textsuperscript{-} at steps will result in competition for these sites with the oxygen holes. Thus it is possible that Cl\textsuperscript{-} will preferentially substitute for oxygen holes at step sites, as represented by the following reactions:

\[
\frac{Cl\textsubscript{c}(100)}{Cl\textsubscript{c}(100)} + O\textsubscript{step} \xrightleftharpoons[\Delta E = -0.55eV]{\Delta E = -0.55eV} O\textsubscript{c}(100) + Cl\textsubscript{step} \tag{7.28}
\]

\[
[LiCl]_{c}(100) + O\textsubscript{step} \xrightarrow[\Delta E = -0.59eV]{\Delta E = -0.59eV} [Li]_{c}(100) + Cl\textsubscript{step} \tag{7.29}
\]

Thus it is likely that synthesis of these materials will result in crystal morphologies which are dominated by chloride ions at the edges of terraces.

It can be seen therefore that the addition of chloride has a considerable effect on the nature, stability and location of hole sites. The segregation of Cl\textsuperscript{-} to steps will result in the displacement of holes from steps on to the (100) surface, where they are likely to be more active since they are less stable than at the steps. It would be expected that these free holes would be trapped by lithium. However, the presence of Cl\textsuperscript{-} on the (100) surface will results in competition for lithium. This may allow oxygen holes to remain untrapped and therefore be more active. The degree to which this will modify the catalytic activity will be dependent on the relative concentrations of Cl\textsuperscript{-} to holes. Lunsford and co-workers found that increased activity was only found in catalysts with a Li:Cl ratio of greater than 0.9.\textsuperscript{21} Our calculations suggest that the Cl\textsuperscript{-} will be strongly segregated to low
coordinate sites, and indeed would compete with any untrapped holes at such sites. Furthermore, the [Li]⁰ centre is likely to prefer the (1 0 0) surface. Thus, low doping of Cl⁻ will result in the ‘coating’ of the step sites and will therefore not affect the primary methane activation site and thus have little effect on the activity. However, once the low coordinate sites are occupied, further Cl⁻ doping will result in the modification of the [Li]⁰ centre concentration as discussed above. Furthermore, experiment shows that chloride does not have a significant effect on the methane activity of the material. Rather, its prime effect is to radically increase the ethene selectivity.²⁰,²¹ These calculations are consistent with this observation. The addition of chloride will primarily modify the siting and concentration of [Li]⁰ centres and untrapped holes at low coordinate sites. Thus, if we consider that the untrapped holes on a (1 0 0) surface or some related defect are in fact ethene selective sites, then the effect of chloride on the ethene selectivity is rationalised by these calculations.

7.4.6.1.3 The effect of Chloride on Impurity Segregation

Another experimentally noted effect of the addition of Cl⁻ to MgO is to increase the surface segregation of the common impurity Ca²⁺,²⁰ which substitutes for Mg²⁺ in the lattice. It can therefore be supposed that chloride either interacts with the calcium ions or interacts with species to which the calcium may be bound. Calculations on defects containing Ca²⁺ and Cl⁻ have therefore been performed and the formation energies of the relevant defects are given in Table 7-18.
Table 7-18. Ca$^{2+}$ containing defect clusters

<table>
<thead>
<tr>
<th>Defect</th>
<th>Defect Energy (eV)</th>
<th>Bulk</th>
<th>Surface (1 0 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$ substitutional</td>
<td>6.93</td>
<td>5.17</td>
<td></td>
</tr>
<tr>
<td>[Ca$^{2+}$ O$^{-}$]$^+$</td>
<td>21.99</td>
<td>20.44</td>
<td></td>
</tr>
<tr>
<td>[Ca$^{2+}$ Cl$^{-}$]$^+$</td>
<td>25.44</td>
<td>22.04</td>
<td></td>
</tr>
<tr>
<td>[Ca$^{2+}$ O$^{-}$ Li$^+$]</td>
<td>37.46</td>
<td>35.36</td>
<td></td>
</tr>
<tr>
<td>[Ca$^{2+}$ Cl$^{-}$ Li$^+$] linear</td>
<td>40.77</td>
<td>37.30</td>
<td></td>
</tr>
<tr>
<td>[Ca$^{2+}$ Cl$^{-}$ Li$^+$] square</td>
<td>40.81</td>
<td>37.01</td>
<td></td>
</tr>
</tbody>
</table>

It has been established, both experimentally$^{63}$ and by theoretical calculations$^{64}$ that Ca$^{2+}$ will surface segregate, which is confirmed in these calculations by the large segregation energy;

$Ca^{2+}_{(bulk)} \rightarrow Ca^{2+}_{(surface)} \quad \Delta E = -1.76$eV \hspace{1cm} (7.30)

However, if (as is predicted) the surface has a high chloride concentration, this surface Ca$^{2+}$ species has a high probability of being on a lattice site adjacent to a Cl$^{-}$ defect. This charged defect is calculated to be slightly more stable than the isolated surface species:

$Ca^{2+}_{(100)} + Cl^{-}_{(100)} \rightarrow Ca^{2+}Cl^{-}_{(100)} \quad \Delta E = -0.16$eV \hspace{1cm} (7.31)

Thus, the migration Ca$^{2+}$ to the surface will now be marginally enhanced;

$Ca^{2+}_{(bulk)} + Cl^{-}_{(surface)} \rightarrow [CaCl]^{+}_{(surface)} \quad \Delta E = - 1.93$eV \hspace{1cm} (7.32)
A similar effect is also calculated for Li/MgO, where the presence of [Li]° adjacent to the Ca^{2+} produces a more stable defect than if they were isolated

\[ \text{Ca}^{2+}_{\text{bulk}} + [\text{Li}]^0_{\text{surface}} \rightarrow (\text{Ca}[\text{Li}]^0)^{2+}_{\text{surface}} \quad \Delta E = -1.99 \text{eV} \quad (7.33) \]

Therefore it is expected that Ca^{2+} segregates to a larger extent in Li/MgO (and therefore in Cl-Li/MgO) than in MgO simply by the presence of the [Li]° defects.

It has been demonstrated above that neutral [LiCl] centres are an important surface defect species. It is possible that Ca^{2+} will associate with this defect, resulting in a neutral defect, which is demonstrated by considering the following defect migration processes;

\[ \text{Ca}^{2+}_{\text{surface}} + [\text{LiCl}]_{\text{surface}} \rightarrow \begin{bmatrix} \text{Cl}^- & \text{Li}^+ \\ \text{Ca}^{2+} & \text{O}^{2-} \end{bmatrix}_{\text{surface}} \quad \Delta E = -0.11 \text{eV} \quad (7.34) \]

However, a linear defect containing Ca and the LiCl centre is unstable

\[ \text{Ca}^{2+}_{\text{surface}} + [\text{LiCl}]_{\text{surface}} \rightarrow \begin{bmatrix} \text{Ca}^{2+} & \text{Cl}^- & \text{Li}^+ \end{bmatrix}_{\text{surface}} \quad \Delta E = +0.18 \text{eV} \quad (7.35) \]

Thus, we have demonstrated how the formation of calcium containing defect clusters at the surface can enhance the surface segregation and concentration of calcium by increasing the thermodynamic stability of the impurity. The result is in agreement with experimental evidence for increased surface segregation in the presence of chloride.\(^{20}\)
7.5. Comments on the Reaction Mechanism

We shall now attempt to place the above results in the context of the reaction mechanism of partial oxidation of methane and the selectivity and activity of the MgO based catalysts. We shall also comment on the relative activity and selectivity of different possible active sites on the basis of their calculated stability.

7.5.1 [Li]$^0$ centres

Experimentally, the [Li]$^0$ centre is considered to be the main active site for hydrogen abstraction from methane. However, it has also been shown that although this site activates both methane and ethane, other active sites are present at which ethane is more readily dehydrogenated. It should also be remembered that the C-H bond strength in methane is higher than in ethane (435 kJ mol$^{-1}$ and 410 kJ mol$^{-1}$ respectively), suggesting that if the [Li]$^0$ centre were equally active for both methane and ethane then much higher yields of ethene than achieved would be expected. Thus, other active sites must be present for the dehydrogenation of ethane and other surface catalysed reactions.

We shall now discuss the relative activity of the [Li]$^0$ centre and untrapped holes at both planar and step sites and attempt to relate this to possible reaction pathways.

We can consider that the more stable a catalytically active centre, the less active it will be. Conversely an unstable species is likely to be highly active and may indeed be simply reactive rather than catalytically active. We can apply these principles to the active sites here by considering the relative activity of these defects at the various surface topographic features.
Consider first the activity of the [Li]$^0$ centre. We have shown that the stability of this centre is highest at the low coordinate sites such as steps. Thus if the morphology of the catalyst results in the formation of many of such sites, we predict that the [Li]$^0$ centre will segregate to these sites. Thus the concentration of the most active hydrogen abstraction centres (from methane) is reduced and we may expect a decrease in the conversion of methane. However, although segregated, there will not be an appreciable decrease in the number of [Li]$^0$ centres since we find that this centre is still bound at the low coordination sites (that is, still more stable than the untrapped hole and lithium substitutional). Furthermore, the increased stability of these step [Li]$^0$ centres may result in them being less active for methane activation whilst maintaining their ethane activity. Thus we suggest that a morphology which promoted the siting of [Li]$^0$ centres at low coordinate sites will lead to an overall decrease in the activity of the catalyst but will increase ethene selectivity. However, if our assumption that a more stable active site will be less active, we might also postulate that there will be an increase in the activation energy of the reaction involved. Thus, it will be necessary to increase the reaction temperature to maintain the same methane conversion.

### 7.5.2 Untrapped Holes as Active Sites

Although less stable than when trapped in a [Li]$^0$ centre, our calculations have shown that it may be possible to generate untrapped oxygen holes. They also suggest that these untrapped holes may exist as small polarons on the surface and in particular at low coordinate sites. Any process which increases the population of untrapped holes, will, if these species are indeed active sites, increase the activity of catalyst. Our calculations on the effect of chloride doping provides such a mechanism. The formation of [LiCl] centres will lead to an increase in the number of untrapped holes. However, experimentally it is noted that it is not the methane activity of this catalyst which is primarily modified by
chloride doping. Rather it is the ethene selectivity which is increased.\textsuperscript{19-21} We might postulate therefore, that untrapped holes, or other defect centres formed as a consequence of holes becoming untrapped are active sites for ethane dehydrogenation.

### 7.5.3 Active Sites in Pure MgO

Although the activity of pure MgO is considerably lower than that of Li/MgO, it is still effective in the oxidative coupling of methane. However, little work has been done to identify active sites in this material. We shall therefore consider the results of our calculations on untrapped holes and chloride doping and attempt to elucidate possible active sites for methane conversion by pure MgO.

Oxygen holes can exist in binary oxides compensated, not as in the case of Li/MgO by dopant ions, but by intrinsic defects such as cation vacancies as illustrated by the following equation which shows the formation of $V_k$ centre:

\[
\text{Mg}_{(Mg)}^{2+} + 2h^+ \rightarrow \left[ \begin{array}{c} O^- \\ V_{Mg}^{2+} \\ O^2^- \end{array} \right] \quad (7.36)
\]

We calculate this defect to be bound by 3.2eV at the (1 0 0) surface. However, we should note again that this is an approximate result given the open-shell nature of this defect. Nevertheless, we can envisage how this defect may be active for ethane dehydrogenation. The geometry of the defect is similar to ethane molecule with a distance of 4.7Å between the two oxygen holes (in our simulations), compared to 2.3Å between the hydrogen atoms of ethane in an eclipsed conformation. Furthermore, we might expect its activity to be lower than that of the single untrapped hole since two holes are shared between three lattice sites, which may result in this type of defect being able to catalyse the dehydrogenation of the weaker ethane C-H bond and not that in methane. The low activity of pure MgO is in agreement with this argument. Furthermore, Burch and Tsang\textsuperscript{17} showed that pure MgO is more effective at converting ethane...
than methane. They showed that over the temperature range 500-750°C, ethane conversion is over twice that of methane and that ethene selectivity is also fourfold higher. Thus, defects such as the $V_k$ centre postulated here are likely active sites in pure MgO and furthermore will also be present in Li/MgO as ethane dehydrogenation sites.

### 7.5.4 Morphological Effects and Activity

The recent work by Hargreaves et al. has concluded that although the primary active site for ethane and ethene formation is located at the (100) surface they also propose from their morphology studies that the bottom of steps may also be active for hydrocarbon conversion. From our calculations we would expect that a chloride doped MgO catalyst will have a morphology in which the majority of chloride would be present at step sites. We therefore suggest that the proposed active sites at the bottom of the steps would be modified both from a steric viewpoint and also an electronic one. Since the ratio of ethene to ethane increases on the addition of $\text{Cl}^-$, we therefore conclude that bottom step sites are active only for methane coupling and not for ethane dehydrogenation, since otherwise we would expect a lowering in ethene production.

### 7.5.5 Catalyst De-activation

Experimentally it has been noted that not only is lithium lost during the reaction but also that deactivation is accompanied by the formation of a lithium carbonate phase. However, when chloride is added, both the loss of lithium and carbonate formation is reduced. Both these effects can be rationalised in terms of the results of our calculations. Lithium loss can be considered as occurring during reaction or as a result of evaporation of lithium ions from the surface, both from planar surfaces and step sites. We have seen that the $[\text{LiCl}]$ centres are more strongly bound than $[\text{Li}]^0$ centres and therefore
lithium loss from such centres will be reduced. Carbonate formation is postulated to be the effect of CO$_2$ absorbing onto [Li]$^0$ centres followed by aggregation of such sites to form a Li$_2$CO$_3$ phase.$^{1,2}$ The presence of clusters or ‘microgalaxies’ of [Li]$^0$ centres will promote this process, but will be inhibited by the presence of [LiCl] centres. We have seen how mixed clusters of [LiCl] and [Li]$^0$ centres are stable (equation 7.26). Thus formation of an extended layer of absorbed CO$_2$ on [Li]$^0$ centres will be interrupted, reducing the probability of the formation of a Li$_2$CO$_3$ phase.

7.6. Summary

We have demonstrated the surface segregation and stability of the proposed main methane activation site, the lithium trapped hole defect. The untrapped hole has been calculated to be stabilised at low coordinate sites, although less favourable than the [Li]$^0$ centre. Calculations on the doping of Li/MgO with Cl$^-$ is shown to modify the concentration and siting of the oxygen hole containing defects. Cl$^-$ is calculated to be strongly surface segregated. Furthermore the Cl$^-$ substitutional will segregate to low coordinate sites, competing for these sites with the untrapped oxygen holes. The stability of a [LiCl] defect centre will lead to in competition for Li$^+$ at the surface, resulting in a lowering of the [Li]$^0$ centre concentration and the formation of new oxygen hole containing defects. We have elucidated from the calculations and experimental data that oxygen hole defects at step sites have a low activity for methane activation and that these and other hole containing defects on the (1 0 0) surface are active for ethane dehydrogenation.
7.7. References


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Chapter 8

Quantum Mechanical Studies of Hydrogen Abstraction from Methane by MgO Catalysts
8.1. Introduction

Extensive experimental work has been carried out on the partial oxidation of methane by MgO based catalysts. Furthermore, much effort has been placed on the elucidation of the reaction mechanism and of the nature of the catalytic active site. Thus, in comparison to most other catalytic systems, the catalyst and the reaction are reasonable well understood. Spectroscopic studies have identified the key process to be the abstraction of a hydrogen from a methane molecule and that the likely active site for this is a lithium trapped oxygen hole.\textsuperscript{1-7} Furthermore, kinetic and thermochemical studies have shown that this hydrogen abstraction is the rate limiting step in the reaction.\textsuperscript{2,8-12} However, although the overall reaction of oxidative coupling is a relatively simple one, there are many other surface and gas phase reactions and processes which make it difficult to obtain any detailed information about any one particular process. In particular this makes the determination of thermodynamic parameters such as the reaction enthalpy and the activation energy of the reaction difficult. Thus many theoretical studies have been carried out to determine these parameters with particular emphasis on the process of hydrogen abstraction by oxygen holes.

Quantum mechanical techniques have gained extensive use in the study of structural properties and, more recently, reactivity in solids.\textsuperscript{13,14} In particular we may investigate reaction pathways including both the geometry and energetics of reaction intermediates and activation energies.

The interest in the catalytic properties of MgO and the relatively well defined surface structure has led to a variety of quantum mechanical studies of the properties and activity of MgO based materials. Much work has been done on the chemisorption of small molecules on the perfect surface and over defects at the surface. These studies include H\textsubscript{2}\textsuperscript{15,16}, CO\textsuperscript{15} and CO\textsubscript{2}\textsuperscript{17} adsorption onto the (1 0 0) surface, H\textsubscript{2} dissociation over V centres,\textsuperscript{18} Cl\textsubscript{2} adsorption,\textsuperscript{19,20} the
vibrational spectra of CO$_2$ and the adsorption and dissociation of H$_2$ over non-planar sites. Numerous studies of the reaction of methane on the surface of MgO have been performed. Earlier work tended to utilise the semi-empirical approaches. Some of the most extensive work has been carried out by Børve and Pettersson and Børve who extended their initial study of the gas phase reaction of metal oxide dimers and methane to the reaction at the MgO (1 0 0) surface and at non-planar sites. The surface reactions were considered using quantum mechanical clusters embedded in point charge arrays to represent the Madelung field of the solid.

Although the geometries of the quantum mechanical clusters have been optimised in these studies, this has been done in a point charge array which is considered as an unrelaxed termination of the bulk, whereas even a non-defective surface is modified from that given by such a simple termination. We have already seen how both experimental studies and atomistic simulation studies (see Chapter 7) show the (1 0 0) surface of MgO to be rumpled. Although relatively small, this rumpling has an appreciable effect on the Madelung field at the surface. Surface reconstruction in other materials can be much more significant, for example the interlayer distances at the surfaces of Al$_2$O$_3$ change by up to 30%. Furthermore, the surfaces under consideration will not be perfect surfaces; they will be defective, the species under investigation being point defects. The lattice relaxations surrounding a defect have been shown to be substantial in ionic solids (see Chapter 7 and references therein) and thus will result in important modifications to the electrostatic field of the lattice at the defect site. Lattice relaxation is known to have a considerable effect on calculated reaction pathways as demonstrated by Pope et al. who found that the neglect of these effects almost doubled the reaction enthalpy of H$_2$ dissociation by a V centre.

This study will utilise the results of the surface simulation techniques discussed in Chapter 7 as a basis for the construction of point charge arrays. We shall
show the effect of surface relaxation on the reaction enthalpies and intermediate geometries.

8.2. Methodology

Ab-initio Hartree-Fock calculations will be used to study the abstraction of hydrogen from methane by an oxygen hole. The open-shell nature of this process requires a suitable treatment of unpaired spins and all calculations will be performed using the Unrestricted Hartree-Fock (UHF) method. Electron correlation will be included by using second-order Moller-Plesset theory (MP2). The GAMESS code has been used for all the calculations presented here.

8.2.1 Basis Sets

The basis function used for the Mg and O atoms of the MgO cluster were those developed by Nada and co-workers, which were optimised to reproduce the structure of the ionic crystal. The basis set of oxygen was further optimised for describing a O species, by varying the most diffuse functions to minimise the energy of a OMg\textsubscript{4} cluster in a perfect point charge array (described below). The basis sets for MgO are given in Table 8-1. The carbon and hydrogen atoms were described using the double zeta basis sets of Dunning which were augmented with diffuse d and p functions on the C and H respectively. These are given in Table 8-2.
Table 8-1 - MgO basis sets. The $l$ type basis consists of an $s$ and $p$ basis with the same exponent with the first and second contraction coefficients respectively.

<table>
<thead>
<tr>
<th>Type</th>
<th>Exponent</th>
<th>Contraction Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$s$</td>
<td>68370.000 0.0002226</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9661.000 0.0019010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2041.000 0.0110420</td>
<td></td>
</tr>
<tr>
<td></td>
<td>529.600  0.0500500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>159.170  0.1690000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>54.710   0.3669500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.236   0.4008000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.791    0.1487000</td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>143.700 -0.0067100 0.00807</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.270  -0.0792700 0.06401</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.661   -0.0808800 0.20920</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.726   0.2947000  0.34600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.598   0.5714000  0.37310</td>
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</tr>
<tr>
<td>$l$</td>
<td>0.688   1.0000000 1.00000</td>
<td></td>
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<tr>
<td>$l^2$</td>
<td>0.332   1.0000000 1.00000</td>
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<table>
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<th>Type</th>
<th>Exponent</th>
<th>Contraction Coefficients</th>
</tr>
</thead>
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<td>$s$</td>
<td>8020.000 0.0010800</td>
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</tr>
<tr>
<td></td>
<td>1338.000 0.0080400</td>
<td></td>
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<td>255.400  0.0532400</td>
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<td>69.220   0.1681000</td>
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<td>23.900   0.3581000</td>
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<td>9.264    0.3855000</td>
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<td>1.212    0.0728000</td>
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<td>$l$</td>
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<td>10.470  -0.0915000 0.06960</td>
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<td>3.235   -0.0402000 0.20650</td>
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</tr>
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<td></td>
<td>1.217   0.3790000  0.34700</td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>0.500   1.0000000 1.00000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.191   1.0000000 1.00000</td>
<td></td>
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</table>

continues...
Table 8-2. Basis sets for Methane. DZ is the standard Dunning double-\(\zeta\) basis set.\(^{33}\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Basis</th>
<th>Augmented function</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>DZ</td>
<td>d</td>
</tr>
<tr>
<td>H</td>
<td>DZ</td>
<td>p</td>
</tr>
</tbody>
</table>

\(\text{Table 8-2. Basis sets for Methane. DZ is the standard Dunning double-\(\zeta\) basis set.}^{33}\)
8.2.2 Point Charge Arrays

Point charge arrays (or blocks) were constructed to represent the (1 0 0) surface, as discussed in Chapter 4. The size of the array determines the accuracy to which the Madelung energy and field of the infinite crystal are represented. A thorough investigation by Foot\(^\text{34}\) of the effect of array size showed that at least three layers of atoms with a layer dimension of at least 7x7 atoms are required to describe satisfactorily the Madelung field and to reproduce the dissociation energy of a surface hydroxide. We have therefore ensured a good representation of the lattice by using arrays of 9x9 ions to a depth of 5 layers.

Four different arrays were constructed which reflect the varying treatment of defects at the surface. All the blocks were constructed centred on an oxygen site. The four arrays were as follows (with each being subsequently referred to by the label in parentheses):

1. **Perfect Surface (PERF)**
   
The surface is treated as a termination of the bulk crystal with no relaxation of the resulting (1 0 0) surface being considered - the same treatment as used by previous workers.\(^{25}\)

2. **Relaxed Surface (RUMPL)**
   
The perfect (1 0 0) surface was simulated using the atomistic simulation techniques previously described, with the resulting relaxed coordinates being used to construct the array. Figure 8-1 shows a closeup of the surface rumpling in this surface representation.

3. **Oxygen Hole Surface (OHOLE)**
   
   An atomistic simulation was performed on a small polaron defect on the (1 0 0) surface. Fully relaxed coordinates are again used to construct the array. Figure 8-2 shows a close-up of the ion displacements surrounding the oxygen hole.
4. Lithium Trapped Hole Surface (LIHOLE)

As above, an atomistic simulation was carried out on a lithium trapped hole defect centre on the (1 0 0) surface. The lithium ion was located next to the oxygen hole on the surface. Figure 8-3 shows the ion displacements around the lithium trapped hole defect.

As discussed in the relevant sections of chapter 7, the electron gas potentials used in the simulations studies overestimate the lattice parameter of the perfect lattice of MgO. Thus all the interionic distances in the blocks (with the exception of the PERF block which is not constructed from relaxed coordinates) are scaled so that the lattice parameter is the same as the experimental value of 2.105Å.

The resultant blocks were then optimised so as best to represent the Madelung charge and field at the central oxygen atom by using a constrained least squares minimisation procedure, which was restricted to optimising the corner atoms and with the symmetry of the block being retained.
Figure 8-1. Close-up of the RUMPL surface block showing the surface rumpling.
Figure 8-2. Close-up of the ion displacement surrounding the oxygen hole defect in the OHOLE surface point charge array.
Figure 8-3. Close-up of the ion displacement surrounding the lithium trapped hole defect in the LIHOLE surface model. The lithium ion is to the left of the oxygen hole.
8.3. Results and Discussion

8.3.1 Gas Phase Reaction

We shall consider first the structure of the reactants and products in the gas phase and the reaction of a gas phase O· ion with a methane molecule, which will allow us to assess the suitability of the basis sets for this study and to determine the energies of the gas phase species.

For the reaction

\[ \text{CH}_4(g) + \text{O}(g) \rightarrow \text{CH}_3(g) + \text{OH}(g), \]  

(8.1)

we have calculated the energetics and geometry of the end products and of the transition state. Consider first the geometry of the methane molecule and the methyl radical (Figures 8-4 and 8-5). The C-H bond length (Table 8-3) is 1.083Å and 1.070Å respectively which are in reasonable agreement with experimental values. Further improvements in the geometry of methane have been shown to require extensive expansion of the basis set\(^{35}\) and would result in a large increase in the computer time required. If we now consider the bond dissociation of both methane,

\[ \text{H}_3\text{C} - \text{H}(g) \rightarrow \Delta E \rightarrow \text{CH}_3(g) + \text{H}(g), \]  

(8.2)

and of the hydroxide species

\[ \cdot \text{O} - \text{H}(g) \rightarrow \Delta E \rightarrow \text{O}(g) + \text{H}(g). \]  

(8.3)

we see (Table 8-4) that at the Hartree-Fock level (UHF) that the bond energy is underestimated. However, the values obtained at the MP2 level using the same basis functions are within 6\% of the experimental values\(^{36}\) which is entirely acceptable for the purposes of the present study. Thus it is evident that the performance of the basis sets used for the gas phase species, with respect to
geometry and bond energies is acceptable once the effects of electron correlation are included.

\begin{align*}
\text{Energy} &= -40.212178 \text{ a.u.} \\
\text{Energy} &= -39.572493 \text{ a.u.}
\end{align*}

Figure 8-4. UHF Geometries and Energy of the methane and methyl radical.

\begin{align*}
\text{Energy} &= -40.383142 \text{ a.u.} \\
\text{Energy} &= -39.712902 \text{ a.u.}
\end{align*}

Figure 8-5. MP2 UHF Geometries and Energy of the methane and methyl radical.
Table 8-3. Calculated bond lengths. (Experimental values from The Tables of Interionic Distances of The Chemical Society\textsuperscript{37}).

<table>
<thead>
<tr>
<th></th>
<th>Calculated C-H bond length (Å)</th>
<th>Experimental (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF</td>
<td>MP2</td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{3}-H</td>
<td>1.083</td>
<td>1.088</td>
</tr>
<tr>
<td>CH\textsubscript{2}-H</td>
<td>1.070</td>
<td>1.078</td>
</tr>
<tr>
<td>\cdot-O-H</td>
<td>0.951</td>
<td>0.974</td>
</tr>
</tbody>
</table>

Table 8-4. Gas phase bond dissociated energies. Experimental values from Vedeneyev\textsuperscript{36}.

<table>
<thead>
<tr>
<th></th>
<th>ΔE\textsubscript{bond dissociation} (kJ mol\textsuperscript{-1})</th>
<th>Experimental (kJ mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF</td>
<td>MP2</td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{3}-H</td>
<td>371.6</td>
<td>447.9</td>
</tr>
<tr>
<td>\cdot-O-H</td>
<td>328.3</td>
<td>468.1</td>
</tr>
</tbody>
</table>

We now consider the reaction pathway of the hydrogen abstraction reaction. It is intuitively apparent that the mode of the reaction is for the methane to approach the oxygen hole along the direction of one of the C-H bond, giving the system C\textsubscript{3v} symmetry. Using the transition state locating algorithms within the GAMESS package, we have followed this reaction pathway and located the transition state at a saddle point in the reaction energy hypersurface. All the bond distances were optimised as was the angle made by the abstracted hydrogen, the carbon and the remaining hydrogen atoms. However, the symmetry of the system was constrained so that the angle between the
hydrogens in the methyl umbrella are equivalent and also the O- and the
dissociating C-H bond were constrained to be linear. The reaction profile and
the geometry of the saddle point are shown in Figure 8-6.

The energy change, $E_r$, for this reaction at the UHF level is endothermic by 51 kJ
mol$^{-1}$. However, experimental studies$^{38}$ have found the gas phase process to be
exothermic and an estimate from the experimental bond dissociation energies
(Table 8-4) also suggests that the reaction should be exothermic by 29 kJ mol$^{-1}$. These
differences can be attributed mainly to the neglect of correlation energy in
these calculations. Figure 8-7 shows the reaction pathway and saddlepoint
gallery for the gas phase reaction at the MP2 level. The reaction is now
exothermic and in reasonable agreement with that estimated from experimental
bond dissociation energies. Of particular note is the dramatic decrease in the
activation energy of the transition state, confirming the need for correlation
effects to be included for such processes where bonds are being broken.

The geometry of the reaction intermediate at the UHF level is product-like. The
O-H bond length approaches that of the gas phase OH, whilst the methyl
moiety is approaching the planar geometry of the methyl radical. However, the
C-H bonds lengths remain similar to those in methane; the increase in bond
order, leading to a shortening of these bonds would not be expected to occur
until the reacting C-H bond had fully disassociated. However, at the MP2 level
the transition state geometry resembles more closely a physisorbed methane
molecule. The angle of the C-H bonds are closer to tetrahedral and the
dissociating bond is shorter. Thus it is apparent that the methane molecule does
not need to approach as close as predicted at the UHF level. Furthermore, it is
clear that the electron correlation effects result in a weaker bond which
dissociates more readily. At the UHF level the bond has not dissociated even
though the O-H species is almost fully product-like and the C-H bond has
stretched considerably. Conversely, at the MP2 level the bond is about to
dissociate at a much shorter C-H distance and whilst the OH species is less
product-like. The results are in good agreement with those of Børve and
Pettersson,$^{24}$ which calculated distances of 1.35Å and 1.21Å for the O-H and C-H
bonds respectively and an angle of 107° in the methyl moiety. Thus, it is clear from this study of the gas phase reaction that correlation effects are crucial in obtaining an accurate picture of the reaction pathway.

Figure 8-6. Gas phase reaction profile and the transition state geometry at the Hartree-Fock level (UHF).
Figure 8-7. Gas phase reaction profile and the transition state geometry at the MP2 level.
8.3.2 The Surface Reaction

We shall now consider the surface reaction

\[ \text{CH}_4(g) + O_{(surface)} \rightarrow \text{CH}_3(g) + \text{OH}_{(surface)}. \]  

(8.4)

In this study we have explicitly considered only a single O ion in the surface surrounded by point charges. The use of this smallest possible cluster may lead to an inadequate description of the electronic states of the surface. However, we hope to gain an initial insight into the effect of surface relaxation on the reaction from this study. It will become clear that a more extensive study is required to fully characterise the reaction pathway.

The reaction pathway has been calculated for each of the four different representations of the surface discussed above (section 8.2.2). All the calculations presented in this section are at the correlated MP2 level which we have shown above to be essential in obtaining reasonable reaction energies.

8.3.2.1 O stability

We shall consider first the effect of including the surface on the stability of the hole site. Table 8-5 gives the energy of the O in the various surface blocks. We see that the energy of the hole in the surface is considerably lower than it is in the gas phase; this effect is a consequence of the presence of the lattice. The effect of allowing lattice relaxation is clearly evident from these energies. We see that the more realistic the surface for the O defect, the lower the energy of the defect. Thus the simple termination is the least realistic and is consequently the least stable environment for the defect. Allowing surface rumpling lowers the energy somewhat. However, it is in the surface block calculated from the lattice points for a oxygen hole that the oxygen hole is most stable. Indeed, this effect is considerable, with the OHOLE surface being 1203 kJ mol\(^{-1}\) and 940 kJ mol\(^{-1}\) more stable than the PERF and RUMPL surface respectively. This clearly demonstrates the importance of lattice relaxation on the stability of defects.
However, the energy of the hole in the block constructed from the results for the lithium trapped hole is higher than we might expect, an effect which can most likely be attributed to the reduced lattice charge at the nearest cation site (the lithium site). We would expect however, that calculations on a larger cluster, where in particular the lithium is treated explicitly, would remove this apparent anomaly by allowing the hole to partially delocalise. It could also be considered that the O$^-$ is in fact less stable in this configuration. However, atomistic simulation results have demonstrated the stabilising effect of lithium on the untrapped hole. Therefore we conclude that an inadequate surface model will result in the surface species having higher energies than in a realistic surface model.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PERF</td>
<td>-273.5947451</td>
</tr>
<tr>
<td>RUMPL</td>
<td>-273.7014362</td>
</tr>
<tr>
<td>OHOLE</td>
<td>-274.0530668</td>
</tr>
<tr>
<td>LIHOLE</td>
<td>-273.6070431</td>
</tr>
</tbody>
</table>

*Table 8-5. The energy of the O$^-$ defect in the different surface blocks. Energies are given in atomic units (a.u.).*

**8.3.2.2 O-H bond dissociation**

The inclusion of the point charge representation of the surface modifies the bond length and the bond dissociation energy of the OH product (Table 8-6). Again, we find that the relaxation of the surface has a pronounced effect on the results. The more realistic the surface model, the weaker the bond, which is a result of
the oxygen hole being more stable in this surface description and therefore is destabilised on bonding to the hydrogen. We can conclude from these results that an inadequate surface description, in addition to giving higher energies for the cluster, results in an overestimate of the bond energies within the cluster.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Bond Length / Å</th>
<th>$E_{\text{dissoc(OH)}}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(gas phase)</td>
<td>0.974</td>
<td>468.1</td>
</tr>
<tr>
<td>PERF</td>
<td>0.966</td>
<td>411.8</td>
</tr>
<tr>
<td>RUMPL</td>
<td>0.966</td>
<td>420.0</td>
</tr>
<tr>
<td>OHOLE</td>
<td>0.955</td>
<td>377.5</td>
</tr>
<tr>
<td>LIHOLE</td>
<td>0.953</td>
<td>378.6</td>
</tr>
</tbody>
</table>

Table 8-6. Equilibrium bond length and dissociation energy of the ’OH product in the different surface models. All results at the MP2 level. Gas phase results are also given for comparison.

8.3.2.3 Surface Effects on the Reaction Pathway

For each surface, we have determined the reaction pathway and the transition state geometry. However, before discussing the result it is important to note the differences between these calculations and those on the gas phase reaction pathway discussed previously.

8.3.2.3.1 Methyl Rotation

The surface possess a symmetry which requires us to include an additional degree of freedom in the incoming methane molecule. We have included the effect of the rotation of the methyl moiety about the O-H-C axis by considering the two extremes of this rotation. Figure 8-8 shows the two configurations
considered. These are the two extremes for the unique rotational configurations when we consider the untrapped oxygen hole. For each surface we have located the transition state with $\theta = 0^\circ$. The methyl moiety was then rotated to $\theta = 15^\circ$ and the remaining parameters re-optimised. In all cases the $\theta = 0^\circ$ geometry had a slightly lower energy (<0.0001 a.u. difference). For the lithium trapped hole we would have to consider further rotational configurations since this defect has a lower symmetry. However, given the results for the other sites and the fact that we are not considering the lithium ion explicitly, an approximation which is likely to have a more pronounced effect, these other configurations have been ignored. For this defect we have considered the case with the hydrogen directed along the axis of the lithium trapped hole defect. We therefore did not perform a new saddlepoint search with the rotation included since the effect appears negligible. We conclude that given the almost barrierless rotation that the methyl moiety will continue to rotate even when chemisorbed at the hole.

\[
\begin{align*}
\text{Mg} & \quad \text{Mg} \\
& | \\
& | \\
& | \\
\text{H}^3 & \quad \text{H}^2
\end{align*}
\]

*Figure 8-8. Rotational symmetry of the methyl group. The two unique position for the untrapped hole surfaces are shown at $\theta = 0^\circ$ and $\theta = 15^\circ$.*
8.3.3 Surface Reaction Profiles

The reaction profile and transition state geometry for each surface block are presented in Figures 8-9—8-12 and Tables 8-7 and 8-8 show the geometries and energetics respectively. We shall discuss the effect of surface relaxation on the results.

The overall reaction for all the different surfaces is now exothermic. Thus, even if the results are not exact, we can conclude that the long range interaction between the surface hole and the surrounding lattice have a substantial effect by making the reaction exothermic. Moreover, the results show that the embedding of the hole in the surface also influences the activation barrier of the reaction. There is a clear difference between the two non-defective surface blocks (PERF and RUMPL) and the blocks which arise from relaxation about a defect (OHOLE and LIHOLE). In the former (Figures 8-9 and 8-10), the O-H bond length is much longer than in the latter (Figures 8-11 and 8-12) whilst the angle between the hydrogens of the methyl moiety are slightly larger indicating repulsive interactions with the surface. With the OHOLE and LIHOLE surfaces however, the methane approach is much closer and there appears to be a reduction in the repulsion felt by the hydrogens of the methyl umbrella, resulting in a decrease in the angle between the hydrogens and the surface, giving the methyl moiety a geometry which is more akin to the end product methyl radical. We also find large changes in the energetics of the reaction (Table 8-8). In the non-defective blocks, the activation barriers are relatively small and the enthalpy change, $E_r$, of the order of 50 kJ mol$^{-1}$. However, in the defective surfaces the activation energies are of the order of 3.5 times higher whilst the enthalpy change is reduced by a similar factor, again confirming the importance of lattice relaxation.

When we consider the two different surface types - non-defective and defective - we see further evidence of the effect of relaxation on the activation energy and also on the stability of the final products. Since the gas phase energies remain the same for all the reactions, it is the stability of the surface hydroxide that
controls the overall reaction enthalpy. Consider first the non-defective surfaces. We have already seen that the hole and the O-H species become more stable as the surface is allowed to rumple, which results in the rumpled surface reaction being more exothermic than that for the PERF surface (Table 8-8). However, the rumpling process increases the activation barrier, albeit marginally. We note further that the distance from the surface to the carbon of the methyl moiety has increased by 0.05Å at the transition state suggesting repulsion between the hydrogen atoms of this species and the now rumpled surface. These results indicate that although small, surface relaxation processes are important in calculating surface reaction profiles. The effect of surface relaxation on reaction enthalpies in such quantum mechanical calculations is likely to be small if the surface under consideration is non-defective and that surface reconstruction is minimal. However, the active site under consideration here is a defect and the lattice relaxation around a defect can be considerable. The consequences of this lattice relaxation on the activity of the active site is clearly demonstrated by our results.

The results for the defective surfaces (OHOLE and LIHOLE) are slightly surprising in that they predict a higher activation barrier than the other models. However, this can be considered as further evidence that the inclusion of surface relaxation effects is crucial if accurate activation barriers and reaction enthalpies are to be calculated. Børve and Pettersson\(^{25}\) report an exothermic reaction with \(E_R = -16.3\) kJ mol\(^{-1}\) and \(E_A = 26.3\) kJ mol\(^{-1}\) for a lithium trapped hole centre in an Mg\(_2\)O\(_5\) cluster at the CCI+Q\(^t\) level, with which our results are in reasonable agreement. However, Børve and Pettersson treated the surface as a perfect termination of the surface with no lattice relaxation. Thus, although their cluster was larger and the calculations more rigorous, the resulting energies may be in error due to the effects noted above.

\(\text{CCI}^+Q^t\) level, with which our results are in reasonable agreement. However, Børve and Pettersson treated the surface as a perfect termination of the surface with no lattice relaxation. Thus, although their cluster was larger and the calculations more rigorous, the resulting energies may be in error due to the effects noted above.

\(^{t}\) Contracted Correlation Interaction (CCI) method\(^{39}\) with the Davidson correction\(^{40,41}\) (+Q) for higher excitations. Correlation energy is included in this treatment.
Our calculated reaction enthalpy is in reasonable agreement with the work of Børve and Pettersson. However, the activation barrier is some four times greater than their value. Thus we may conclude that the lattice relaxation has a more pronounced effect on intermediate states than on the reaction limits. This conclusion is partly supported by the comparison made by Børve and Pettersson of the gas phase and surface reaction of a lithium trapped hole species. They find only a small change in the reaction enthalpy (-13.8 kJ mol$^{-1}$ and -16.3 kJ mol$^{-1}$ for the gas phase and surface reaction respectively) whilst the effect on the activation barrier is more significant (20.0 kJ mol$^{-1}$ and 26.3 kJ mol$^{-1}$ respectively). Our calculations also show this trend when comparing the defect surfaces and the gas phase (Table 8-8). However, as noted before, the non-defective surface increase the overall reaction enthalpy.

Whilst the minimal size of the quantum mechanical cluster used in this work will have a major bearing on the quantitative results, this study has clearly demonstrated the major influence that the relaxation of the lattice at surface defects has on such calculations. Treating a perfect surface as a termination of the bulk crystal may have only a small effect on the energetics and geometry of the reaction pathway, although this will only hold if surface reconstruction is minimal. However, when defective surfaces are considered, we found large differences in reaction enthalpies and pathways dependant on the treatment of the lattice relaxations. We conclude that more realistic surface point charge arrays are necessary to enable accurate reaction pathways to be determined. The results of surface simulations using effective interatomic potentials provide a means of generating such models. Further work is required in this area to provide a comprehensive description of this process. The present work re-enforces the need to consider carefully the embedding procedures used in such calculations.
### Table 8-7. Structural parameters at the transition state for the different surfaces. Gas phase values are also included for comparison. \( H(O) \) is the hydrogen being abstracted from the methane.

<table>
<thead>
<tr>
<th></th>
<th>O-H((O))</th>
<th>C-H((O))</th>
<th>C-H</th>
<th>( \angle \text{HCO} (^\circ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase</td>
<td>1.127</td>
<td>1.336</td>
<td>1.088</td>
<td>106.5</td>
</tr>
<tr>
<td>PERF</td>
<td>1.494</td>
<td>1.211</td>
<td>1.080</td>
<td>105.2</td>
</tr>
<tr>
<td>RUMPL</td>
<td>1.580</td>
<td>1.180</td>
<td>1.080</td>
<td>105.9</td>
</tr>
<tr>
<td>OHOLE</td>
<td>1.257</td>
<td>1.244</td>
<td>1.080</td>
<td>105.1</td>
</tr>
<tr>
<td>LIHOLE</td>
<td>1.250</td>
<td>1.280</td>
<td>1.080</td>
<td>105.0</td>
</tr>
</tbody>
</table>

### Table 8-8. Energy changes for the different surfaces. \( E_A \) and \( E_R \) are the activation energy and overall reaction enthalpy respectively. Gas phase values are also included for comparison.

<table>
<thead>
<tr>
<th></th>
<th>( E_A ) (kJ mol(^{-1}))</th>
<th>( E_R ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase</td>
<td>49.1</td>
<td>-18.4</td>
</tr>
<tr>
<td>PERF</td>
<td>24.3</td>
<td>-49.0</td>
</tr>
<tr>
<td>RUMPL</td>
<td>29.7</td>
<td>-64.0</td>
</tr>
<tr>
<td>OHOLE</td>
<td>87.9</td>
<td>-16.2</td>
</tr>
<tr>
<td>LIHOLE</td>
<td>92.0</td>
<td>-18.2</td>
</tr>
</tbody>
</table>
Figure 8-9. Reaction profile and the transition state geometry with the PERF surface.
Figure 8-10. Reaction profile and the transition state geometry with the RUMPL surface.
$E_A = 87.9 \text{ kJ mol}^{-1}$

$E_R = -16.2 \text{ kJ mol}^{-1}$

Figure 8-11. Reaction profile and the transition state geometry with the OHOLE surface.
Figure 8-12. Reaction profile and the transition state geometry with the LIHOLE surface.
8.4. References


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