Computational Studies of Organic Transformations in Molecular Sieves

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Abstract

This thesis reports the quantum chemical study of organic transformations inside the pores of alumino- and titano-silicate molecular sieves. Specifically, we have studied the conversion of methanol to gasoline, the MTG process, in the pores of Brönsted acidic alumino-silicates and the epoxidation of alkenes with hydrogen peroxide inside the pores of titanosilicates. In all cases, the cluster approach to the description of the molecular sieve has been adopted. Our calculations have clearly indicated the strengths and weakness of both the quantum chemical techniques and the cluster approximation and have resulted in suggested mechanisms for both the conversion of methanol and the oxidation of ethene. In the former case, a 'carbene-like' mechanism is suggested in agreement with that proposed by Hunter and Hutchings (Catalysis Today, 6, 279 (1990)). In the latter case, a pathway proceeding through a Ti$^{IV}$($\eta_2$-00H) complex is proposed; the mechanism is able to rationalise all experimental observations concerning this catalytic process. A study of the nature and coordination state of Ti$^{IV}$ centres in titanosilicates is also presented and it is noted that titanyl (Ti=0) groups may be present as labile species in the presence of protic solvents.
Acknowledgements

First and foremost, I am greatly indebted to Prof. Richard Catlow for support and guidance during the execution of this work. A better supervisor I could not have found. Although not formally involved in this work, I'd like to thank Sir Prof. J.M. Thomas for his enthusiasm and interest in the work on epoxidation catalysis. I am grateful to EPSRC for financial provisions and computer resources.

I would also like to thank Alexei Sokol for his ‘disgusting’ ways - may I meet more people like you. And Andy Davis, thanks for being at the other end of the pint glass when the going got tough. Of course Simon Carling was always there too - cheers mate!

I'd also like to thanks a number of people, for reasons too varied and detailed to list here; Rob Bell, Dewi Lewis, Grant Morrison, Furio Cora, Shyam Vyas, Jean Connisbee, Gopinathan Sankar, Richie Oldroyd, Carolyn Barker, Ben Slater, and everyone else at the Royal Institution.

Lastly, but most importantly, this thesis is dedicated to my parents; without mum and dad it would never have happened. Of course, my sisters played a large part too, without them, I may never have left home to go to university!
Contents

Abstract i
Acknowledgements ii
Preface 1

I Introduction 2
Part I Abstract 3

1 Molecular Sieves 4
1.1 Structure and topology 5
1.2 Chemical composition 10
1.3 Shape selectivity 13
1.4 Catalysis 14
1.5 Summary 16

2 Experimental Techniques 17
2.1 General 17
2.2 Experimental: Diffraction; X-ray, neutrons, electrons 20
2.3 Vibrational Spectroscopy 22
2.4 Nuclear Magnetic Resonance 26
2.5 X-ray Absorption (XAS) 30
2.6 Electron Spin Resonance (ESR) 33
2.7 Ultra-Violet and Visible Spectroscopy (UV-vis) 35
2.8 Summary 36

iii
## MTG: Formation of surface methyl-oxonium ion

### 6. Methodological Details
- Methanol Adsorption
  - Vibrational Spectrum of the Physisorbed Methanol
  - $^{13}$C NMR Spectrum of Physisorbed Methanol
- Ethanol Adsorption
- Surface Methylation:
  - Calculated Reaction Profiles
  - One and Two Methanol Molecules
- One dimethyl ether and one dimethyl ether and water
- Formation of Surface Methyl-oxonium ions - Summary and Discussion of Calculated Results

## MTG: Reaction of Surface Methyl-oxonium Ions

### 7. Methodological Details
- Surface Methyl-oxonium ion deprotonation
- Surface Methyl-oxonium Ion Reaction:
  - Formation of a Surface Ethyl-oxonium Ion
- Deprotonation and Reaction of Surface Methyl-oxonium ions - Summary and Discussion of Calculated Results

## Ti(IV) Partial Oxidation Catalysis

### III. Part III Abstract

## Ti$^{IV}$ Oxidation Catalysts:

### Literature Review
- General Observations
- The Nature of Ti$^{IV}$
  - TiO$_2$-SiO$_2$ mixed oxides
  - Crystalline Ti$^{IV}$-silicates
  - Ti$^{IV}$-silasequioxanes
  - The nature of Ti$^{IV}$: theoretical evidence
- Partial Oxidation Catalysis in Ti$^{IV}$-silicas:
  - Mechanistic Detail
  - Effect of Solvent
List of Figures

1.1 Example of zeolite structure faujasite (FAU) ........................................... 7
1.2 Secondary Building Units (SBUs)[12]. ...................................................... 9
1.3 An atomistic model of the MCM-41 structure [24]. ................................. 10
1.4 Formation of acidic/basic properties in zeolites .................................... 11
1.5 Different types of guest molecule shape selectivity displayed by molecular sieves ................................................................. 14
1.6 Schematic representation of the reaction profile .................................. 15

2.1 Spectroscopic ranges, energies and typical relaxation timescales. 19
2.2 Neutron diffraction structure of H_{2}O adsorbed in H-SAPO-34 [36]. ......... 21
2.3 Schematic illustration of the evolution of the ν, δ and γ modes of zeolitic ZO-H .B complexes ................................................................. 24
2.4 Evolution of the ν(ZO-H..B) band as a function of increasing basicity of the adsorbed base. ................................................................. 25
2.5 Illustration of the effect of CP and MAS on solid state NMR spectrum. ......... 29
2.6 {\textsuperscript{29}}Si NMR spectroscopic ranges of silicates with different numbers of A1 neighbours [29]. ......................................................... 30
2.7 Schematic representation of the XAS regions as function of incident radiation energy ................................................................. 31
2.8 Schematic representation of the process involved in obtaining a radial distribution function from EXAFS raw data. .............. 32
2.9 The isotropic ESR spectrum of a single unpaired electron ........................ 33
2.10 Typical ESR lineshapes for an asymmetric solid-state spin system. .......... 35
3.1 The process of forming a cluster from a molecular sieve framework ........................................................................................................... 57
3.2 One dimensional reaction coordinate showing ........................................ 58
3.3 The effect of taking a step that is too large in a transition state search. ............................................................. 60

4.1 BLYP/TZVP optimised structure of the water dimer. .................... 65
4.2 BLYP/TZVP optimised structure of the methanol dimer. .......... 69
4.3 HF optimised structures along the pathway for reaction of methanol at a methylated alumino-silicate Brönsted acid site. ....... 72

5.1 Change of reactants and products with contact time [176] .... 80
5.2 Formation of dimethyl ether from methanol at a alumino-silicate Brönsted acid site (ZOH) via a surface methyl-oxonium ion. ................................................................. 82
5.3 Carbene mechanism for C-C bond formation (from [177]). .... 83
5.4 The trimethyloxonium ion mechanism for methanol conversion. 85
5.5 Free radical mechanisms for C-C bond formation [86]. ......... 89
5.6 Surface methyl-oxonium ion mechanism [177]. .................... 91
5.7 CO catalysed mechanism via ketene [210]................................. 94
5.8 Calculated reaction coordinates for proton transfer from a Brönsted acid site model to adsorbed NH$_3$[100]. .... 97
5.9 11T faujasite model for CH$_3$OH physisorption at a Brönsted site. 99
5.10 Schematic potential surface for CH$_3$OH adsorption [62]. .... 102
5.11 3T model for CH$_3$OH physisorption at a Brönsted site. ....... 103
5.12 BP86/DZVP calculated reaction path for formation of surface methyl-oxonium ion from a single methanol molecule [173]. 105
5.13 BP86/DZVP calculated reaction path for formation of dimethyl ether from direct condensation of two adsorbed methanol molecules [143]. 106
5.14 BP86/DZVP calculated reaction path for formation of ethanol from two adsorbed methanols via a surface methyl-oxonium ion [174]. 107
5.15 BP86/DZVP calculated reaction path for formation of ethylmethyl-
ether from direct condensation of dimethyl ether and meth-
anol [174].......................................................... 108
5.16 Reaction scheme modelled by Chuvylkin et al.[233] ........... 109
5.17 C–H dissociation of methanol as predicted by Vetrivel et al.[234].110

6.1 BLYP/TZVP optimised structure of CH₃OH physisorbed via
two strong hydrogen bonds............................................ 116
6.2 BLYP/TZVP and BLYP/DZVP optimised structures along
the reaction path for formation of surface methyl-oxonium ions.122
6.3 MP2/6-31G**//HF/6-31G** and BLYP/DZVP optimised struc-
tures along the reaction path for formation of surface methyl-
oxonium ions...................................................... 125

7.1 BLYP/DZVP optimised reaction path for the formation and
deprotonation of a model surface methyl-oxonium ion. ......... 131
7.2 MP2/6-31G**//HF/6-31G** optimised reaction path for the
formation of adsorbed CH₂CH₂ from a surface methyl-oxonium
ion and methanol via a surface ethyl-oxonium ion in a step
wise manner......................................................... 136
7.3 MP2/6-31G**//HF/6-31G** optimised reaction path for the
formation of adsorbed CH₂CH₂ from a surface methyl-oxonium
ion and methanol via a surface ethyl-oxonium ion in a con-
certed manner...................................................... 138
7.4 Schematic representation of a probable mechanism for the
MTG process.......................................................... 141

8.1 Suggested model for titanyl species in TiO₂-SiO₂ mixed oxides
[259]................................................................. 150
8.2 Schematic representation of Ti⁴⁺ hydrolysis in TS-1 [263].... 151
8.3 Schematic representation of the hydrolysis of Ti-O-Si bonds
suggested on the basis of isotopic labeling experiments [269] 153
8.4 Schematic representation of the hydrolysis of Ti-O groups,
consistent with the isotopic labeling experiments of Bellussi
et al.[269].............................................................. 154

ix
8.5 Schematic representation of extraframework edge-sharing $[\text{TiO}_x]$ units as suggested in reference [282]. ................................................... 155
8.6 Schematic representation of a Ti$^\text{IV}$-octasilasequioxane showing only the tetrahedral T atoms. ................................................... 158
8.7 Schematic representation of the reactions studied by de Man and Sauer [42]. ............................................................................................ 159
8.8 Formation of titanium peroxo species. .............................................. 163
8.9 The effect of NaOH treatment on TS-1 as suggested in reference [295]. ................................................................................................... 169
8.10 Cis-hydroxo(alkylperoxo) complex, suggested as the active species on the basis of work on Ti=0 porphyrin catalysts [300]. 171
8.11 Suggested pathway for epoxide formation from a Ti$^\text{IV}(\eta_2$-$\text{O}_2$) complex as suggested by Notari [248]. .............................................. 174
8.12 Suggested pathway for epoxide formation from a Ti$^\text{IV}$-OOH...ROH complex as suggested by Clerici and coworkers [269, 298, 297]. 175
8.13 Suggested pathway for epoxide formation via a cyclic intermediate as suggested by Mimoun [307, 308] and Huybrechts et al. [309]. ................................................................................................... 176
8.14 Suggested pathway for epoxide formation via a bidentate Ti$^\text{IV}(\eta_2$-OOH) complex as suggested by Karlsen and Schöffel [293]. 178
8.15 Suggested pathway for epoxide formation via a short lived or restricted radical intermediate as suggested by Notari [5]. 179
8.16 Suggested pathway for alkane oxidation on TS-1 as suggested by Khouw et al. [295]. ................................................................. 180

9.1 BP86/DZVP optimised geometries of the surface Ti$^\text{IV}$ species before and after hydrolysis and hydration. 186
9.2 BP86/DZVP optimised geometries of the complexes relevant to Ti$^\text{IV}$ active-site formation via grafting. 188
9.3 BP86/DZVP optimised reaction path for the formation of a titanyl group. 191

10.1 Schematic representation of the nature of dehydrated Ti$^\text{IV}$ sites in titanosilicate catalysts. 197
10.2 BP86/DZVP optimised geometries along the pathway for reaction of ‘TiOH’ with ethene.........................198
10.3 BP86/DZVP optimised geometries along the pathway for reaction of ‘Ti=0’ with ethene.........................199
10.4 BP86/DZVP optimised geometries along the pathway for hydrolysis of the hydroxy function of ‘TiOH’ with H₂O₂.................................................................201
10.5 BP86/DZVP optimised geometries along the pathway for hydrolysis of the hydroxy function of ‘Ti(OH)₂’ with H₂O₂.................................................................202
10.6 BP86/DZVP optimised geometries along the pathway for hydrolysis of the siloxy function of ‘TiOH’ with H₂O₂.................................................................204
10.7 BP86/DZVP optimised geometries along the pathway for hydrolysis of the siloxy function of a modified ‘TiOH’ complex with H₂O₂.................................................................206
10.8 BP86/DZVP optimised geometries along the pathway for formation of a Ti(η₂-OOH) complex from ‘Ti=0’ with H₂O₂.................................................................207
10.9 BP86/DZVP optimised geometries along the pathway for ethene oxide formation from Ti(OH)(η₂-OOH) and CH₂CH₂.................................................................208
10.10 BP86/DZVP Kohn-Sham MO diagram describing the oxygen transfer step from a Ti⁴⁺(η₂-OOH) active site to ethene.................................................................210
10.11 BP86/DZVP optimised geometries along the pathway for deactivation of the active oxygen donating species, Ti(OH)(η₂-OOH), in the absence of an oxidisable substrate.................................................................213
10.12 BP86 estimated UV-vis absorption spectra showing that the model for the deactivated η₂-0₂ complex gives rise to the observed 260,000 cm⁻¹.................................................................215
10.13 Possible catalytic cycles for alkene epoxidation at Ti-OR sites based on the individual steps studied in the current work.................................................................217
10.14 Proposed mechanism for epoxidation at Ti-OR sites based on the current work and that in the open literature.................................................................222
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Some examples of reactions catalysed by molecular sieves</td>
<td>5</td>
</tr>
<tr>
<td>1.2</td>
<td>Structure types, pore dimensionalities and channel sizes of selected microporous molecular sieves</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>Examples of heteroatoms incorporated into molecular sieves.</td>
<td>12</td>
</tr>
<tr>
<td>1.4</td>
<td>Framework properties of regular molecular sieves [9].</td>
<td>13</td>
</tr>
<tr>
<td>3.1</td>
<td>Basis-Set definitions: polarisation functions are included in the definitions</td>
<td>54</td>
</tr>
<tr>
<td>4.1</td>
<td>Calculated and experimental properties of isolated water and the water dimer</td>
<td>64</td>
</tr>
<tr>
<td>4.2</td>
<td>Calculated and experimental properties of isolated methanol and the methanol dimer</td>
<td>67</td>
</tr>
<tr>
<td>4.3</td>
<td>DFT/BLYP calculated NMR absolute ($\sigma_{\text{iso}}$) and relative ($\delta_{\text{rel}}$) isotropic chemical shifts and anisotropies ($\Delta\sigma$) of the methanol monomer and dimer (in ppm)</td>
<td>68</td>
</tr>
<tr>
<td>4.4</td>
<td>Calculated energetics for the reaction shown in Figure 4.3 over a 1T model alumino-silicate Brönsted acid site: comparison of quantum chemical methods</td>
<td>73</td>
</tr>
<tr>
<td>4.5</td>
<td>Calculated energetics for the reaction shown in Figure 4.3 over a 1T and 5T model alumino-silicate Brönsted acid site: effect of cluster size</td>
<td>74</td>
</tr>
<tr>
<td>5.1</td>
<td>Calculated energies of methanol adsorption (energies in kJmol$^{-1}$)</td>
<td>101</td>
</tr>
<tr>
<td>6.1</td>
<td>Methodological Details</td>
<td>115</td>
</tr>
</tbody>
</table>
6.2 BLYP calculated (harmonic) frequencies for the bare acid site (ZOH) and the methanol–acid site complex compared to other studies and experiment. .................................. 118
6.3 Formation of Surface Methyl-oxonium ions: Summary of calculated activation barriers. ............................................. 127

7.1 BLYP/DZVP calculated energy changes for the deprotonation step of the reactions shown in Figure 7.1. ................. 132
7.2 BLYP/DZVP calculated properties of the optimised structures along the reaction coordinate for ZOCH₃ deprotonation shown in Figure 7.1. .............................................. 134

8.1 Individual Ti–O distance (R), their averages, and the distributions within various Ti⁴⁺ containing compounds (ΔR) [279]. 156
8.2 Selected results showing the influence of solvent on the oxidation of 1-octene using H₂O₂ over Ti–Al–β [9]. ............... 161
8.3 Selected results showing the influence of H₂O on the oxidation of 1-hexene and n-octane over TS-1 [295]. ................... 162
8.4 Selected results showing the influence of peroxide structure on the oxidation of allyl chloride over a TiO₂-SiO₂ coprecipitate at 80°C [296]. ......................................................... 166
8.5 Selected results showing the influence of additives on the epoxidation of 1-butene over TS-1 with H₂O₂ [297]. ............. 168
Preface

This thesis was begun at an exceptional time for the application of computational chemistry to problems in molecular sieves. The explosion of available computer resources, both in-house and national, as well as our increased awareness of methodological difficulties associated with the study of adsorption and reactivity, left us at a stage where we could start to make predictive contributions to the understanding of catalysis in molecular sieves.

The thesis is presented as three major parts. In the first, a detailed study of the strengths and weaknesses of common quantum chemical methods is presented, together with a broader discussion of molecular sieves, experimental and theoretical techniques (Part I). Although we know a great deal about the various quantum chemical methods, continued debate concerning their use in, for example, reactivity problems, warrants such a study. The second part of the thesis (Part II) concerns the computational study of the mechanism of Methanol to Gasoline (MTG) conversion, a prototypical Brönsted acid catalysed process that, despite being discovered over 20 years ago, is still not well understood. Lastly, Part III discusses the hugely topical Ti IV-silica epoxidation catalysts; the structure, coordination state, hydration, hydrolysis and reactivity of model active sites are studied and a mechanism for alkene epoxidation, consistent with all data in the open literature, is suggested. Further, our studies were able to indicate routes for improvement of the catalytic process.

Each part of the work is preceded with a separate abstract and the thesis concludes with a summary and some final remarks. It remains only to be noted that even within the 3 years devoted to this work, technological and methodological advances have proceeded at such a rate that the current work is already becoming dated. Who knows what we will be able to achieve in the next 3 years?
Part I

Introduction
Part I Abstract

This first Part of the thesis concentrates on introducing the basic ideas of molecular sieves and the experimental and theoretical tools used to study them. Chapter 1 introduces the reader to the structure, topology, and chemical composition of molecular sieves with an emphasis on Brönsted acidic and redox systems. These two themes play a central rôle throughout the work. Chapter 2 outlines common experimental techniques that have been applied to the study of framework materials with an emphasis on time-scales and studying organic intermediates in heterogeneous reactions. Chapter 3 then describes theoretical techniques, Hartree-Fock theory (HF), 2nd order Möller-Plesset theory (MP2) and density functional theory (DFT), that will be used in the current work. The problems of studying reactions in solids, particularly those arising from use of the cluster approximation and the difficulties encountered in locating transition states on the adiabatic potential energy surface are discussed. Finally, Chapter 4 reports theoretical results on the ability of the various methods to accurately predict ground and transition state properties. It is concluded that density functional theory can lead to activation barriers that are up to 30% underestimated and that MP2 corrected HF methods can lead to activation barriers that are up to 30% overestimated. Further, for the system studied, the size of the cluster fragment used to describe the zeolite appears to have little effect on the calculated energetics. The quality of predicted equilibrium state properties are much better.
Chapter 1

Molecular Sieves

Molecular sieves, i.e., zeolites and/or zeotypes, microporous, framework materials based on $\text{TO}_4$ corner sharing tetrahedra ($T$ commonly being $\text{Si}$, $\text{Al}$, or $\text{P}$ [1]) are now a major component of many important and potentially important industrial processes [2, 3, 4]. They have found extensive use as shape-selective heterogeneous catalysts as well as in separation problems and as catalyst supports; but it is their ability for catalysis that has attracted so much academic and industrial interest [2, 3, 4, 5, 6]. At the present time, however, a great deal of industrial catalysts are still homogeneous. These catalysts often show high toxicity, are difficult to transport, can corrode storage containers and need to be separated from any liquid phase products at the end of a catalytic cycle, an undesirable and costly complication. Molecular sieves, and in general any heterogeneous catalysts, do not suffer from the drawbacks associated with homogeneous systems described above, but are much more difficult to study and fine-tune. Their use is still, therefore, very much limited to bulk chemical application, e.g., they have been applied to hydrocarbon cracking [7, 8], isomerisation [7, 8], partial oxidations (where chiral purity is not a problem)[5, 9], MTBE formation [10, 11], see Table 1.1. Changes in environmental legislation and increasingly tight energy restrictions on industrial processes, together with improved understanding of solid-state systems has thus led to increasing interest in heterogeneous catalysis.

The next few sections will give a brief introduction to the structure, topologies and general properties of molecular sieves as background to the
Table 1.1: Some examples of reactions catalysed by molecular sieves

<table>
<thead>
<tr>
<th>Process</th>
<th>Example</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>n(C_{12}H_{18}) → n(C_{12}H_{18}) + ...</td>
<td>H-Y ethene + ...</td>
</tr>
<tr>
<td>cracking</td>
<td>oil</td>
<td></td>
</tr>
<tr>
<td>Disproportionation</td>
<td>2(C_6H_5CH_3) → C_6H_6 + C_8H_{10}</td>
<td>toluene H-ZSM-5</td>
</tr>
<tr>
<td>Alkylation</td>
<td>C_6H_5CH_3 + C_2H_4 → C_6H_5C_2H_5</td>
<td>benzene + ethene</td>
</tr>
<tr>
<td>Conversion</td>
<td>n(CH_3OH) → n(CH_2) + n(H_2O)</td>
<td>methanol H-ZSM-5</td>
</tr>
<tr>
<td>of methanol</td>
<td>methanol</td>
<td>gasoline + water</td>
</tr>
<tr>
<td>oxidation</td>
<td>C_3H_7 → C_3H_7O</td>
<td>propene TS-1</td>
</tr>
<tr>
<td>of alkenes</td>
<td>propene</td>
<td>propene oxide (epoxide)</td>
</tr>
<tr>
<td>oxidation</td>
<td>C_6H_5OH → C_6H_4(OH)_2</td>
<td>phenol TS-1</td>
</tr>
<tr>
<td>of phenol</td>
<td>phenol</td>
<td>catechol and hydroquinone</td>
</tr>
</tbody>
</table>

computational study that forms the basis of this thesis; methanol conversion to gasoline-range hydrocarbons and alkene epoxidation reactions over acidic and redox molecular sieves respectively.

### 1.1 Structure and topology

Molecular sieves, zeolites and zeotypes are built up from corner sharing T0_4 tetrahedra, the so-called primary building units. A molecular sieve with a specific topology or arrangement of primary building units is described generally by a three-letter code independant of its chemical composition
[1], see Table 1.2. To avoid ambiguity, we will make the distinction of us-

Table 1.2: Structure types, pore dimensionalities and channel sizes of selected microporous molecular sieves.

<table>
<thead>
<tr>
<th>Pore Size</th>
<th>Structure type</th>
<th>Named examples</th>
<th>Pore diameter (Å)</th>
<th>Channel dimensionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>small</td>
<td>LTA zeolite A</td>
<td>4.1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>medium</td>
<td>MFI ZSM-5, TS-1, VS-1</td>
<td>5.3 x 5.6; 5.1 x 5.5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MEL ZSM-11, TS-2, VS-2</td>
<td>5.3 x 5.4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MTT ZSM-23</td>
<td>4.5 x 5.2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EUO EU-1</td>
<td>4.1 x 5.7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AEL AlPO₄-11</td>
<td>3.9 x 6.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MTW ZSM-12</td>
<td>5.5 x 6.2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TON Theta-1, ZSM-22</td>
<td>4.4 x 5.5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>large</td>
<td>MOR mordenite</td>
<td>6.5 x 7.0; 2.6 x 5.7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BEA zeolite β</td>
<td>7.6 x 6.4; 5.5 x 5.5</td>
<td>1;2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AFI AlPO₄-5</td>
<td>7.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EMT hexagonal faujasite</td>
<td>7.1; 7.4 x 6.5</td>
<td>1;2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FAU zeolite X or Y</td>
<td>7.4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>extra large</td>
<td>AET AlPO₄-8</td>
<td>7.9 x 8.7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLO cloverite</td>
<td>13.2 x 4.0</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>VFI VPI-5</td>
<td>12.1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \): dimensionalities of different channel systems given separately.
number of possible three dimensional frameworks with channel structures extending throughout the crystals in one, two or three dimensions. For example, the ‘internally’ one-dimensional AFI structure can be described as a bunch of 7.3Å diameter hollow tubes, whereas the FAU structure consists of three orthogonal 7.4Å diameter channel systems which intersect in large cavities (13Å diameter supercages)[12], i.e., the framework has a three-dimensional character, see Figure 1.1. The dimensionality of a framework, in

Faujasite (FAU)

Figure 1.1: Example of zeolite structure faujasite (FAU) showing only the connected T centers.

the sense just described, is thus important in defining the molecular sieve’s transport character (with respect to guest molecules) and hence is a factor in determining any catalytic properties that the framework-type may display.

Of the infinite number of possible topologies mentioned above, only around a 100 have been realised (and characterised) in nature or synthetically [1] and of these only a handful have found industrial application [13].
The huge number of hypothetical molecular sieves however has fuelled a large and continuing research effort into the characterisation and understanding of the stability and formation of different structure types in an aim to promote the discovery of new materials. The reader interested in the rationalisation and prediction of the structure of molecular sieves is referred to the work of P. Cox[14] and D. Lewis [15, 16]. Reference [17] also contains an excellent discussion of the topologies of framework materials in terms of meshes, operators and sheets. A more illustrative way of characterising zeolite structure, however, is through the use of secondary building units or SBUs. Molecular sieve frameworks can be thought of as being built up of a finite or infinite number of such units, each vertex (in Figure 1.2) representing a $T_0_4$ tetrahedron [12]. The finite units which occur in tetrahedral frameworks are shown in Figure 1.2. In choosing these SBUs it is assumed that the entire framework is built up of only one of them and that there is an integral number of them in any one unit cell; for example, the FAU structure shown in Figure 1.1 is made up of 6-6 or 6-2 SBUs. They are also invariably non-chiral, a problem that has attracted a great deal of attention from the pharmaceutical industry.

Given a particular framework-type then, it is clearly both of academic and practical importance to understand the fundamental properties associated with it. For example, relative to the enzyme paradigm molecular sieves are more or less rigid inorganic structures, but it is known that adsorbed molecules can induce small structural changes due, in part, to the very flexible Si-0-Si framework units [18, 19]; benzene, for instance, is known to induce angle deformations of up to $7^\circ$ [20]. Thus, the well defined pore systems and the freedom to undergo small structural change enables molecular sieves to recognise, discriminate and organise guest molecules with a precision of less than 1Å [21] depending on the framework-type. We will discuss the shape selectivity of molecular sieves in more detail below. However, an equally important property of these materials which arises from their framework nature, and is of great importance for catalytic purposes, is their huge internal surface areas.

It can be seen from Table 1.2 that zeolites and zeotypes are typically microporous with channel diameters of up to 13Å. Recently, however, an
important new type of siliceous framework structure was discovered with mesoporous pores ranging from 25 to 100Å in diameter [22, 23]. This family of materials, an example of which is Mobil’s MCM-41, unlike the crystalline microporous materials, have long range structural order in only two dimensions. In addition, the detailed nature of the channel walls in these mesoporous sieves is poorly understood. Figure 1.3 shows a representations of this type of material. The mesoporous materials are of great interest to the pharmaceutical and fine chemical industries since they offer the benefits of a heterogeneous catalytic environment, retain a certain degree of guest molecule shape selectivity but have pore sizes which are large enough to make them useful in processes involving bulky reagents and products.

Having introduced structural features of molecular sieves, it is clear that the chemical composition of the sieve will influence its properties. This effect will be discussed next.
1.2 Chemical composition

Zeolites, i.e., (metallo)aluminosilicates, have structure defining tetrahedral sites occupied by Si and Al with Si:Al ratios from 1:1 to $\infty : 1$ (essentially purely siliceous). The different formal valencies of Si (tetravalent) and Al (trivalent) produces an overall negative charge for each Al incorporated into the framework which are typically balanced by alkali, alkaline earth or rare earth metal cations. Zeolites containing alkali cations show weak basic character whilst hydrated alkaline earth metal cations show acidic properties due to the production of Brønsted acid sites on dissociation of water, see Figure 1.4. Exchange of metal ions, also shown in Figure 1.4, for, what is in effect, protons, results in a Brønsted acidic material which has been compared to superacidic media. Use of this term to describe acidity in the solid state is, however, questionable as the unambiguous measurement of the Hammett acidity, $H_0$, (the formal definition of superacidity being that $H_0$ is less than -12 [25]) is very difficult.

Although Al derived Brønsted acid sites are by far the most common
type in molecular sieves, framework substitution in which the metals are tetrahedrally coordinated to oxygen has been reported for a number of metal cations and a number of framework structures. Table 1.3 shows selected examples of metal cations for which framework incorporation has been claimed. Clearly, substitution of trivalent ions will result in Brönsted acidity as shown above. Thus, molecular sieves can be tailored to have properties ranging from weakly basic (incorporating extraframework metal cations) to strongly acidic [26].

In addition to this ‘acidic degree of freedom’, the chemical composition of molecular sieves can have a profound effect on the hydrophobic/hydrophilic nature of the material [9]. For example, pure all-Si sieves have electrically neutral hydrophobic frameworks. Substitution of the framework Si for tetravalent ions such as Ti$^{IV}$ retains the framework neutrality and have little effect on its hydrophobicity. Substitution of trivalent ions such as Al$^{III}$, however, results in a charged, hydrophilic framework. Hydrophobicity will clearly have an effect on liquid-phase transformations catalysed by molecular sieves since reactants must be transported across a phase boundary (liquid → catalyst) to the active site and vice-versa for the products. Thus, an understanding of this effect is crucial for controlling aspects of the catalytic behaviour of molecular sieves. Table 1.4 shows the general hydrophobic properties of molecular sieves with different combinations of P, Al and Si in
Table 1.3: Examples of heteroatoms incorporated into molecular sieves (data taken from original table in reference [9]).

<table>
<thead>
<tr>
<th>Metal cation</th>
<th>Structure type</th>
<th>Metal cation composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>MFI, MEL, MTW, BEA, ZSM-48, MCM-41</td>
<td>Ti; Si</td>
</tr>
<tr>
<td></td>
<td>BEA, MOR</td>
<td>Ti; Al; Si</td>
</tr>
<tr>
<td></td>
<td>AEL, AFI, VFI</td>
<td>Ti; Al; P</td>
</tr>
<tr>
<td></td>
<td>AFI</td>
<td>Ti; Al; Si, P</td>
</tr>
<tr>
<td>V&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>MFI, MEL, ZSM-48, MTW NCL-1, AFI</td>
<td>V; Si</td>
</tr>
<tr>
<td></td>
<td>BEA</td>
<td>V; Si; (Al; B)</td>
</tr>
<tr>
<td></td>
<td>TON, EUO</td>
<td>V; Si; Al</td>
</tr>
<tr>
<td></td>
<td>AFI, AEL, VFI</td>
<td>V; Al; P</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>MFI, MEL, MTW, BEA, MOR, EUO, MTT FAU</td>
<td>Fe; Si</td>
</tr>
<tr>
<td></td>
<td>AFI, VFI</td>
<td>Fe; Al; P</td>
</tr>
<tr>
<td>Co&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>MFI</td>
<td>Co; Si</td>
</tr>
<tr>
<td></td>
<td>AEL, AFI, FAU, VFI</td>
<td>Co; Al, P</td>
</tr>
</tbody>
</table>

the framework. Although the general trends are clear, the detailed effect of solvent on the catalytic properties for any given substrate/catalyst system is poorly understood.

At this point, we have discussed mainly Brønsted acid sites in molecular sieves. Although this is still the largest industrial use of these materials it is far from being the only one. Another very active field is that of redox
<table>
<thead>
<tr>
<th>Molecular Sieve</th>
<th>Chemical Composition</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td>[Si(IV)O-Al(III).O-Si(IV)]&lt;sup&gt;-&lt;/sup&gt; H&lt;sup&gt;+&lt;/sup&gt; or M&lt;sup&gt;n+&lt;/sup&gt;</td>
<td>Negatively charged framework, hydrophilic, with ion exchange and acid sites.</td>
</tr>
<tr>
<td>Siliceous</td>
<td>[Si(IV)O-Si(IV).O-Si(IV)]</td>
<td>Neutral framework, hydrophobic, without ion exchange and acid sites.</td>
</tr>
<tr>
<td>AlPO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>[Al(III).O-P(V).O-Al(III)]</td>
<td>Neutral framework, hydrophilic, without ion exchange and acid sites.</td>
</tr>
<tr>
<td>SAPO</td>
<td>[Si(IV).O-Al(III).O-P(V)]&lt;sup&gt;-&lt;/sup&gt; H&lt;sup&gt;+&lt;/sup&gt; or M&lt;sup&gt;n+&lt;/sup&gt;</td>
<td>Negatively charged framework, hydrophilic, with ion exchange and acid sites.</td>
</tr>
</tbody>
</table>

Catalysts arising from incorporation of, e.g., V<sup>4+</sup>, Cr<sup>4+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Ti<sup>4+</sup> [9, 27, 5]. We will refer to these materials as 'redox molecular sieves'. These materials, with specific reference to Ti<sup>IV</sup>-silicas, will be discussed in more detail in later Chapters.

1.3 Shape selectivity

We have previously mentioned guest molecule selectivity in terms of the channel/intersection nature of molecular sieves. This section's aim is to define this effect more clearly.

Following Csisery [28], the ability of molecular sieves to discriminate
between molecules on the basis of shape and size can be separated into three
distinct types as shown in Figure 1.5. For the case of reversible reactions,
e.g., acid catalysed processes, all three forms of selectivity are active. For
irreversible processes, however, only reactant and transition state selectivity
is important, as in, e.g., oxidation catalysis.

1.4 Catalysis

With this background information, it is worth reiterating that industrial
interest in molecular sieves is primarily due to their capacity to act as hetero-
egeneous catalysts. Given that the computational work reported later in
this thesis concerns aspects of important catalytic processes, this section will
outline some basic ideas behind catalysis.

Catalysis, the effect of accelerating a chemical reaction that would either
not occur (within appreciable timescales) or occur more slowly, is the basis for much of today's manufacturing industry. Figure 1.6 shows a schematic reaction coordinate that highlights the effect. It is clear that, without the catalyst, the activation barrier for the process is prohibitively high, but that in the presence of the heterogeneous catalyst the reaction profile can change dramatically. In addition to the size and shape of the activation

![Reaction Coordinate](image)

**Figure 1.6:** Schematic representation of the reaction profile of an uncatalysed process (top line) and a catalysed one (bottom line). The y-axis represents free-energy in arbitrary units. The process associated with 1. is reactant adsorption; 2. reactant activation; 3. product desorption; 4. uncatalysed activation.

Barrier however, catalysis on heterogeneous systems also involves diffusion of the reactants to the active site and subsequent adsorption, as well as desorption and diffusion of the resulting products. Any one of these steps can control the effectiveness of the material for the catalytic conversion of a given substrate and a full understanding of all of these factors is a necessary pre-requisite to the specialist design and control of a catalytic process.

The work described in this thesis is only concerned with the calculation of the adsorption and activation of reactants and the desorption of reaction
1.5 Summary

This chapter has covered the nomenclature in common use to describe molecular sieves, their structural topology, chemical compositions and shape selectivities. Also discussed has been the effect of incorporating hetero-atom defects, particularly Al$^{3+}$ and Ti$^{4+}$, into the frameworks of the host, especially with respect to siliceous materials. The effect of incorporating hetero-atom defects was discussed with an emphasis on acidic and redox properties and on the molecular sieve's hydrophobicity/hydrophilicity. Finally, we presented an overview of catalysis in heterogeneous systems, emphasising the need for a better understanding of these materials.

The next two chapters will overview the common experimental and theoretical techniques used to study problems in molecular sieves as a foundation for the computational study of the methanol to gasoline and alkene epoxidation processes discussed thereafter.
Chapter 2

Experimental Techniques

Chapter 1 gave a brief overview of the structure, framework-type, chemical composition and general properties of molecular sieves, especially with respect to acidic (Al$^{3+}$) and redox (Ti$^{4+}$) incorporation into the framework of (siliceous) hosts. The present Chapter describes the common experimental techniques used to probe these and other important properties of molecular sieves. This Chapter is not intended as a prerequisite to the understanding of the computational work described in later Chapters but is, instead, intended to give a more general background to problems associated with studying structural and dynamical properties in these materials.

2.1 General

A very wide range of experimental methods have been applied to aspect of molecular sieve chemistry [29]. More often than not, 'physical chemistry' techniques have been applied, i.e., the sample is irradiated and a response is measured. It is clear that in order to study a specific event, the characteristic timescale of the method must be less than that associated with the event, a particularly critical factor in the study of reaction phenomena. With respect to any particular experimental method, there are four distinct times that must be considered (for more information see [30]),

1. the time during which a quantum of radiation or a particle takes to interact with a molecule,
2. the lifetime of the perturbed/excited state of the molecule,

3. the minimum lifetime that a species being studied must have in order for it to be seen as a distinct species,

4. the total time of an experiment in which the species is observed.

The time taken for radiation or a particle to interact with a chemical system is typically $10^{-16}$ to $10^{-18}$ s and each particle or photon therefore 'sees' the chemical system with an instantaneous structure and with fixed electronic, vibrational and rotational states.

The lifetime of the perturbed or excited states, for example, in NMR, is a critical factor in measuring the spectrum as it is the response associated with relaxation of this state that is actually measured. This lifetime is also important in experiments that measure very fast transitions, e.g., electronic spectroscopy, since large uncertainties in the energies of the relevant states make observation of the transition difficult, i.e., subject to severe spectroscopic broadening.

The third point is one that depends on the frequency scale of the spectrum. In vibrational spectroscopy, for example, with a resolution of $1\text{cm}^{-1}$, around $10^{10}\text{Hz}$, if two species interconvert such that their lifetimes are $< < 10^{-10}$ s then they will not be observed as unique entities.

Finally, the timescale of the experiment can often limit the time resolution attainable. For example, in diffraction studies, although each photon or particle is diffracted in around $10^{-18}$ s, the accumulation of data required from many particles can take minutes, hours or even days.

Thus, a definitive experimental timescale is difficult to assess. However, with the exception of diffraction experiments and taking into account the Uncertainty Principle, the relaxation times of the perturbed states is often a good guide to the limiting time resolutions obtainable with various experimental methods. Figure 2.1 indicates the energy ranges and typical relaxation times for a number of common spectroscopic techniques.

Structural problems are typically attacked using standard diffraction techniques (X-ray, neutron) although NMR, IR, UV-vis, ESR, XPS, and X-ray absorption experiments are also commonly employed. Diffraction
Spectroscopic Range

<table>
<thead>
<tr>
<th>Spectra/Transition Type</th>
<th>XAS</th>
<th>Electronic</th>
<th>Vibrational</th>
<th>ESR</th>
<th>NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxation Times</td>
<td>$10^{-15}$</td>
<td>$10^{-1}$</td>
<td>$10^{-2}$</td>
<td>$10$ (s)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.1: Spectroscopic ranges, energies and typical relaxation timescales for a number of common experimental methods and observed transitions.

techniques rely on the presence of long range order in the sample; however catalysis is often concerned with inherently local defect structures. Thus, NMR, IR, UV-vis, ESR, XPS, and X-ray absorption experiments have been applied to study local structural problems such as the nature of reactive defects in molecular sieves or the diffusion of organic adsorbates on extended surfaces. These local structure techniques, although very powerful, still suffer from the fact that they give averaged results in a temporal and/or spatial sense.

In addition to structural methods, a whole family of techniques exist to probe the bulk properties of materials such as, BET isotherm measurements, calorimetry, temperature programmed desorption, etc. which can be used to quantify pore size distributions, adsorption strength with respect to molecular probes, reaction profiles etc. The interested reader should consult [29, 30].

A brief description of the more common techniques and any relevant results pertaining to molecular sieve chemistry will now be highlighted.
2.2 Experimental : Diffraction; X-ray, neutrons, electrons

The structural data discussed in Section 1.1 has mostly been derived on the basis of single-crystal diffraction patterns or Rietveld refinement of powder diffraction patterns [29]. Often these studies are aided by computational predictions, an example being the structure solution of Nu-87 [31]. Diffraction studies have also been used to locate extra-framework cations in substituted molecular sieves, e.g., Na-X [32], and again, computational techniques have often aided in solving the experimental phase problem [33]. In time-resolved mode, and with the best instrumentation, a resolution of seconds (energy dispersive XRD) can be achieved, especially using intense synchrotron radiation, and numerous studies of crystal growth have been reported (although it has so far proved impossible to extract atomic structure from such rapid scans) [34, 35].

Diffraction techniques are based on the idea that X-rays, neutrons or electrons with a wavelength of the order of magnitude of internuclear distances, around $10^{-10}$ m or 1 Å, will be diffracted by an array of atoms, or more precisely by their electron cloud, nucleus, or coulomb well, producing an interference pattern. Solution of the measured interference or diffraction pattern to obtain the atomic structure, via, for example, the electron density distribution (X-rays) requires the solution of a phase problem which can, especially in the case of powders, be extremely demanding. However, the use of diffraction is now routine for many solid state problems.

X-rays (and electrons) suffer from the fact that the intensity of scattering is proportional to the atomic number of the scattering atoms. Thus, light nuclei in the presence of heavy nuclei, e.g., H, and similar nuclei, e.g., Al and Si, cannot easily be distinguished. X-ray diffraction will thus give averaged structures over Al-O-Si and Si-O-Si units and other techniques which give information on short range order, such as X-ray absorption, NMR and computational techniques, are therefore needed.

Electrons also suffer from being weakly penetrating and are mostly used for gas phase and surface problems. Neutrons on the other hand are highly penetrating (like X-rays) and show a discontinuous relationship between
scattering intensity and atomic number. Thus, Al and Si can be distin­
guished and the large neutron scattering amplitude of \(^{2}\)H makes the location of hydrogen positions possible. For example, Smith et al. [36] have made a detailed study of the location of Brönsted acid sites and their interaction with water in H-SAPO-34 (CHA structure) by Infra-red, NMR and neutron diffraction. Both of these problems, i.e., the unambiguous location of the charge balancing Brönsted proton and the location and nature of adsorbed H\(_2\)O has frustrated experimental [37, 38, 39] and theoretical workers for many years [40, 41]. The neutron diffraction study however was able to solve the structure of the dehydrated material and was able to locate proton (actually deuteron) positions in the chabazitic cage. Thus, they were able to show that in H-SAPO-34 adsorbed water exists as both hydrogen bonded water and as hydronium ions where the Brönsted proton has been completely transferred from the framework to the adsorbate, as shown in Figure 2.2.

Clearly then, neutron diffraction studies have a large rôle to play in fully understanding Brönsted acidic systems, but we is stress that the H-SAPO-34 study was only possible due to the simplicity of the CHA structure and due to the fortuitous long range order of the adsorbed water. The study of more

Figure 2.2: Neutron diffraction structure of H\(_2\)O adsorbed in H-SAPO-34 [36].
complicated host-adsorbate systems is still very much a challenge, and of course, diffraction experiment timescales, greater than seconds, precludes direct observation of reaction transients.

2.3 Vibrational Spectroscopy

Vibrational spectroscopy, especially Infra-red (IR) and Raman, but also inelastic neutron scattering, have been used extensively to probe the local structural properties of molecular sieves [29]; for example, the technique is routinely used to observe the 960 cm\(^{-1}\) band used as a fingerprint of Ti\(^{IV}\) incorporated into silicate frameworks [42, 43, 44] and the hydroxyl stretching frequencies used to study Brönsted acid sites [45, 46, 47]. These techniques have also been used to characterise framework modes but this is outside the interest of the present work. Fast, time-resolved vibrational spectroscopy, although becoming widely used in other fields has yet to be applied in earnest to reactivity problems in molecular sieves, although the widespread application of these methods can only be a matter of time (see, for example, [48, 49]).

Vibrational spectroscopy, the observation of the vibrational normal modes of a molecule or chemical system is based on the interaction of radiation (or particles) with some property of the system that changes during vibrational excitation [29, 30, 50]. For example, IR arises from the interaction of the oscillating electric vector of the electromagnetic radiation with an induced oscillating electronic dipole in the system of interest. Selection rules are thus based around the requirement that the excited vibrational mode leads to a change in the dipole of the system and for symmetrical systems the IR spectrum can shed light on molecular symmetry. Raman spectroscopy on the other hand is an inelastic scattering effect. It arises through the polarisation of an electron cloud by the oscillating electric vector of the incident radiation. The selection rules for allowed transitions are thus governed by the need for a change in the polarisability of the system to occur during vibrational excitation and just as in IR, the spectra of high symmetry species are very distinct. Inelastic neutron scattering is a similar technique with the advantage of having no symmetry selection rules. For more detailed
information of the theoretical basis for describing molecular vibrations, IR and Raman, see [51, 30, 50].

By far the most common use of vibrational spectroscopy in molecular sieve science has been to monitor the effect of adsorbed probe or reactant molecules [52, 53]. Typical examples are the monitoring of adsorbed pyridine [54, 55] for which the internal vibrational frequencies are characteristic of the type of acid site (Lewis or Brönsted) at which it is adsorbed. Another common use of vibrational spectroscopy is for monitoring the progress of chemical transformation, e.g., of methanol after adsorption onto H-form zeolites [56, 57, 58] (see also Chapter 5). The use of vibrational spectroscopy in solid-state systems has now reached a high level of maturity with developments like Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy (DRIFTS) enabling substantial gains in sensitivity and with expansion of the spectroscopic range into the Near Infra-Red (NIR) [59]. The relative simplicity of IR and Raman experiments has also facilitated the development and use of in-situ cells which allows systems to be studied under 'working conditions'. One major drawback of these techniques, however, is their complicated spectra and spectroscopic interpretation is always subject to debate.

The use of Raman spectroscopy for the study of heterogeneous problems is less widespread; a discussion is, however, given in the review article [60].

For the present discussion, the collected results of important vibrational spectroscopic studies of probe molecules in acidic zeolites will be summarised. Following Kustov [59], and as previously noted, the characterisation of Brönsted acidity using IR spectroscopy can be achieved by studying H-bonding effects of probe molecules with the Brönsted site or observing chemical transformations of adsorbed molecules at that site. The first method is based on measuring frequency shifts of the Brönsted –OH stretching vibrations upon H-bond formation with adsorbed molecules. Lewis acid sites have less well defined specific vibrational features and investigation of such centres is often through observation of changes in the internal modes of adsorbed probes (for more details see, for example, [59]).

Returning to Brönsted acidity, the three types of localised vibrations of zeolitic Brönsted acid sites are (after [52]),
Figure 2.3: Schematic illustration of the evolution of the $\nu$, $\delta$ and $\gamma$ modes of zeolitic ZO-H...B complexes as a function of the hydrogen bonding strength of the adsorbed base, B (after [52]). The complex effects on the band shape of the broad $\nu$(ZO-H...B) arising from resonance effects are omitted as are internal modes of the adsorbed base.

$\nu$(ZO...B) stretch,
$\delta$(ZO...B) in-plane bend,
$\gamma$(ZO...B) out-of-plane bend,

where ZOH represents the zeolitic Brönsted site (see Figure 1.4) and B represents the adsorbed (Basic) probe molecule. With respect to the unperturbed Brönsted O-H stretching mode, $\nu$(ZO-H), H-bonding interactions with weakly basic probe molecules, i.e., those that do not result in proton transfer to the adsorbate or other chemical transformations, give rise to the following effects,
Figure 2.4: Evolution of the $\nu(ZO-H..B)$ band as a function of increasing basicity of the adsorbed base, B (after [52]).

1. a downward shift in $\nu(ZO-H)$ proportional to the strength of hydrogen bonding interaction,

2. a simultaneous increase in the half width of $\nu(ZOH)$, observed to be roughly $\frac{3}{2} \Delta \nu(ZOH)$,

3. a corresponding increase in the peak intensity.

The shifts towards lower frequencies, $\Delta \nu(ZO-H)$, on hydrogen bond formation can vary between tens of cm$^{-1}$ and $\sim$2000 cm$^{-1}$ with simultaneous half-width of the perturbed $\nu(ZO-H)$ increasing from a few tens up to around 1500 cm$^{-1}$. The in and out-of-plane ZO-H bending modes are also shifted to
higher frequencies and broadened on formation of Brönsted acid–adsorbate complexes. After Zecchina et al. [52], the evolution of the three ZO–H bands on increasing the H-bonding strength of an adsorbate is shown schematically in Figure 2.3. The effects of these changes on the observed spectra are, however, omitted. The schematic spectra highlight two important effects,

1. Spectra (d–e): resonance of the perturbed $\nu$(ZO–H) with the $2\delta$(ZO..B) overtone of the perturbed in-plane bend will give rise to a Fermi resonance effect and the appearance of an Evans window in the broad $\nu$(ZO–H..B) band (see also Figure 2.4). The spectra in this region thus take on an A-B-C pattern of three broad peaks: $\nu$(ZO–H..B) containing an Evans window and $\delta$(ZO..B). $\gamma$(ZO..B) is usually obscured by intense skeletal modes of the molecular sieve.

2. Spectra (f–g): will give rise to anharmonic coupling of $\nu$(ZO–H..B) with $\delta$(ZO..B) and $\gamma$(ZO..B) which is known to alter deeply the band profile.

Figure 2.3 also neglects to show the internal vibrational modes of the probe molecule which will, of course, complicate the observed spectra further.

Finally then, Figure 2.4 shows, again schematically, the ZO-H spectroscopic features observed when a number of different strength basic probes are adsorbed at the Brönsted acid site. We will return to the question of spectroscopic interpretation as regards the nature of methanol adsorption in molecular sieves in Chapters 5 and 6. At this point it is worth noting that the Fermi resonance interpretation, although widely accepted in other fields, is still debated in the solid-state community [61, 46, 62, 63, 58]. However, recent computational results of methanol [64] and acetonitrile adsorption [65] has lent strong backing to the Fermi resonance model.

### 2.4 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR), i.e., the measurement of the perturbation of the energy levels of nuclei possessing a magnetic moment when an external magnetic field is applied to the system, has taken a central rôle in
the study of defects in molecular sieves for many years and with the development of reliable in-situ cells [66, 67, 68], studies of the reactivity of organic molecules at defect sites in molecular sieves has also enjoyed considerable success.

Unlike the case of solutions, the NMR spectra of solids are typically featureless and very broad with the chemical shift and spin-spin couplings that characterise solution spectra often being obscured [29, 67]. The overriding drive in solid-state NMR experiments therefore is to manipulate the spin systems in order to remove or average characteristic interactions, simplifying the spectrum and allowing ‘chemical’ information to be retrieved.

Briefly then, the dominant nuclear spin interactions that are important in obtaining and understanding NMR spectra are [29],

1. the Zeeman interaction, $H_Z$: an effect which arises from the interaction of the nuclear magnetic moment with an applied static magnetic field. This effect is responsible for the initial splitting of the nuclear energy levels and determines the frequency of observation of a particular nucleus at a given magnetic field strength.

2. the Dipolar interaction, $H_{DP}$: this effect arises from the interaction of nuclear spins. It is directional and has a $1-3\cos^2\Theta$ dependence, where $\Theta$ is the angle between the internuclear vectors and the applied magnetic field direction; it also has an $r^{-3}$ dependence which make nearest neighbour interactions dominant.

3. the Chemical Shift effect, $H_{CS}$: this effect is caused by the modification of the applied magnetic field felt by the nucleus due to its surrounding electron density. It depends on the orientation of the chemical system with respect to the magnetic field (the anisotropic part again has a $1-3\cos^2\Theta$ dependence) and is dependent on the applied field strength.

4. the spin-spin coupling interaction, $H_{SC}$: the effect is due to an indirect electron coupled nuclear spin-spin interaction. It is orientation dependent with respect to the two nuclear spin vectors.
5. the Quadrupolar interaction $H_Q$: this effect arises from the interaction of the nuclear spins with the electric field gradient at the nucleus. It is dependent on the nuclear quadrupolar moment, i.e., it is important for systems containing nuclei with non-integral spins, e.g., $^{27}\text{Al}$ and $^{1^7}\text{O}$, and as such is relevant to the majority of NMR observable nuclei.

The magnitude of the effects discussed above, and thus their relative importance, in Hertz, are shown below:

$$
\begin{matrix}
H_Z & H_D & H_{GS} & H_{SC} & H_Q \\
10^6 - 10^9 & 0 - 10^5 & 0 - 10^5 & 0 - 10^4 & 0 - 10^9
\end{matrix}
$$

In the solid state, the orientation dependence of the interactions is not averaged to zero by molecular tumbling and special experiments are required in order to extract information from the spectrum. Of particular importance in this respect is Magic Angle Spinning (MAS) NMR, i.e., by rotating the sample at the Magic Angle of 57.44° to the applied magnetic field, at a rate faster than the interaction frequency (see above), the chemical shift anisotropy as well as any residual dipolar interactions (not turned off by decoupling) is removed ($<1-3\cos^2\Theta>$ $\rightarrow$ 0) giving high resolution 'solution-like' spectra. In addition, cross-polarisation (CP) can be used to enhance the signal to noise ratio by increasing the magnetisation of the dilute nuclei from a magnetisation reservoir of an abundant spin system, e.g., $^1\text{H}$. Figure 2.5 illustrates the enormous effect that MAS and CP techniques can have on the resolution and intensity of solid-state NMR spectra.

With this background, a few examples of the application of NMR applied to molecular sieve problems will be described. NMR has been used extensively to study acid site topologies in aluminas and zeolites and the interested reader is referred to the article of Blumenfield and Fripiat [69]. The earliest studies were made on Si and Al distributions in zeolites and related minerals since the $^{29}\text{Si}$ chemical shifts are sensitive to both the degree of polymerisation of Si, i.e., the number of bridging oxygens around it, and to the number of next nearest Al neighbours [29]. As an example, schematically shown in Figure 2.6 is the dependence of the $^{29}\text{Si}$ chemical shift on the number of Al neighbours [29]. This information is more difficult to extract from $^{27}\text{Al}$ NMR due to the problem of 'invisible' Al, i.e., that fraction of $^{27}\text{Al}$ in a
position of low local symmetry for which the quadrupolar interaction causes extreme spectroscopic broadening [70].

NMR has also been used to extract data on internuclear distances. For example, [71, 72, 73] have all used $^1$H NMR to obtain an Al···H distance of Brönsted acid sites in H-zeolites in the range of 2.37 to 2.48Å. Similar studies have shown that this distance depends on the number of oxygen atoms of the structural ring that the Brönsted sites is a part of [74].

Some of the most exciting developments in solid-state NMR, however, involve following the progress of organic reactions in microporous sieves using in-situ MAS NMR cells. Although this method is limited to the time taken to record the NMR signal (around 10$^{-6}$ seconds), great success has been achieved observing, for example, in-situ guest molecule shape selectivity [75] and, in favourable cases, it has been able to shed light on reaction mechanisms, e.g., the work of Haw and coworkers on the methanol to gasoline process [76, 77, 78]. The subject of the methanol to gasoline process will be dealt with in more detail in Part II.
2.5 X-ray Absorption (XAS)

The use of X-ray radiation in spectroscopy has become widespread in recent years, particularly with the development of synchrotron sources which provide a broad-band tunable source of intense radiation in the X-ray region. The present section will, however, only discuss extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) as these two related techniques have been widely applied to the problem of defect/active site characterisation in molecular sieves, i.e., to probe local structural properties.

When X-rays pass through a material of thickness \(x\) the loss in intensity follows an exponential law, \(\exp(-\mu x)\) where \(\mu\) is the linear absorption or extinction coefficient. When the X-ray energy \(h\nu\) becomes equal to or greater than the binding energy of a core electron in a specific atomic centre, the electron is emitted from the core in a photoelectric process. At this point, there is a sharp increase in the observed absorption coefficient known as
Figure 2.7: Schematic representation of the XAS regions as function of incident radiation energy.

the absorption edge. This 'low energy' part of the spectrum is known as the X-ray absorption near edge spectrum or XANES. As the photon energy increases, the absorption coefficient becomes modulated in an oscillatory fashion, and this region of the spectrum is known as the EXAFS region. A schematic representation of the X-ray absorption spectrum is shown in Figure 2.7.

Briefly then, the XANES absorption edge shows fine structure associated with the various electronic transitions that can occur from the core states to empty or partially filled states, governed primarily by the dipole selection rules. However, in systems (particularly those containing transition metals), with distorted local symmetry about the absorbing atom and those with non-centrosymmetric symmetry, e.g., tetrahedrally coordinated centres, the lowest unoccupied states are mixed p-d states and a transition can often be observed as a 'pre-edge feature'. The p-d character of the lowest unoccupied states depends on the absorbing centre, its local geometry and the orbital overlap with ligand orbitals, i.e., it is dependent on the distance between the absorbing centre and its ligands. Thus, near edge features, in theory, contain a great deal of information about the absorbing centre. In practice, however, this information can only be extracted using correlations with well defined systems and XANES features are typically
used as fingerprints. For example, XANES is very often used to characterise tetrahedral coordination which displays a strong pre-edge feature (the equivalent energy transition in octahedral systems is dipole forbidden). For more detail concerning the theory of application of XANES see Bianconi et al. [79].

EXAFS on the other hand occurs at higher X-ray energies as compared to the XANES region and is a final state effect arising from interference of the outgoing photoelectron 'with that fraction of itself' that has been backscattered from neighbouring atoms. Thus, the oscillatory behaviour of the measured absorption (due to this interference behaviour) contains information about the local structure around the excited atomic centre. In a similar manner to X-ray diffraction, the observed (reciprocal space) EXAFS pattern of a particular absorbing centre can be Fourier transformed, on solution of a phase problem, to give the radial distribution of the electron density (in real space) around that centre. This process is schematically shown in Figure 2.8. Extraction of a physical model for the local structure around the absorbing centre is then performed by fitting a calculated EXAFS spectrum of a model to the data observed.

Figure 2.8: Schematic representation of the process involved in obtaining a radial distribution function from EXAFS raw data.

The continuing development of EXAFS theory and its implementation in readily available codes, as well as technical developments such as Quick EXAFS (QuEXAFS) which allows data to be collected in only a few minutes, have made accurate structure analysis (±0.02Å for the first shell, ±0.1Å for the second), and dynamics studies of relatively slow phenomenae, routine.
There are now numerous examples of the use of EXAFS in the field of molecular sieves and catalysis. For example, one important application has been to the study of $T_1^{IV}$ incorporation in siliceous hosts, a subject that is discussed in more detail in Chapter 8. Another example is its application to the study of $\text{Al}^{3+}$ sites in zeolites. Koningsberger et al.\cite{80} have studied several zeolite-Y materials with $\text{Al}$ XANES and EXAFS and have observed a number of correlations in the $\text{Al}-\text{O}$ distance, the XANES intensity and the observed acidity of the zeolite. For example, they have shown that $r(\text{Al}-\text{O})$ decreases in the order $\text{H-Y} > \text{NH}_4-\text{Y} > \text{Na-Y}$ while the XANES (1s-3p transition) intensity decreases in the same order. These observations were found to correlate well with the calculated electron density on the $\text{Al}$ centre (and thus the Brønsted site's acidity) based on the results of cluster calculations. Use of XAS therefore could provide a fast and reliable method of probing zeolite acidity.

2.6 Electron Spin Resonance (ESR)

Although ESR has been applied in a limited fashion to the work described later in this thesis, it will be discussed here in order to highlight the fact that open shell systems can be important in solids, particularly in defective or transition metal substituted molecular sieves.

![Figure 2.9: The isotropic ESR spectrum of a single unpaired electron coupled equivalently to six $I = 1/2$ nuclei (benzene radical anion).](image)

The technique of electron spin resonance spectroscopy \cite{30, 50} can only
be applied to systems with one or more unpaired electrons. In the presence of an applied magnetic field, $B_o$, the normally degenerate electron spin energy levels of the unpaired electron are split according to the strength of the magnetic field, $B_o$, the Landé g-factor, which plays a similar rôle in ESR to the chemical shift in NMR, and the electronic spin state. In the presence of neighbouring ‘spinning’ nuclei the perturbed spin system can interact with the nuclear magnetic moment of the nuclei by one of two dominant mechanisms (the magnitude of this coupling being described by a hyperfine coupling constant, $a_i$):

1. nuclear-electron spin coupling, which is analogous to the nuclear dipole-dipole coupling observed in NMR experiments and in a similar fashion decays as $r^{-3}$ between the electron and nuclear position and is anisotropic.

2. Fermi contact interaction - a non-classical interaction between the nuclear moment and the magnetic field produced at the nucleus by the electron spin. It is thus limited to $s-$electrons which have a finite density at the nucleus.

The isotropic ESR spectrum for a single electron interacting equivalently with six $I = 1/2$ nuclei (benzene radical anion) is shown schematically in Figure 2.9. Note that the ESR spectrum is shown in first derivative form. This is a consequence of the measurement procedure. In the solid-state, the anisotropy of the hyperfine coupling constant and the Landé g-factor become relevant and, analogous to similar problems in NMR, can lead to severe spectroscopic broadening and complications. Figure 2.10 shows a typical absorption line shape for an anisotropic resonance.

Thus, ESR can give information (if the very often complicated spectrum can be interpreted) about the number and type of ‘spinning’ nuclei coupled to the electron via the hyperfine coupling constants, about the molecular orbital occupied by the unpaired electron, again via the hyperfine coupling constants, and in a (usually) fingerprint fashion, ESR can identify species via their Landé g-tensor components in a similar manner to chemical shifts in NMR. However, due to spectroscopic broadening that occurs from fast
ESR has had a significant impact on the subject of open shell defects in molecular sieves [81, 82, 83] as well as on the understanding of open shell transition metal incorporated systems [84, 85]. Relevant to the current work, however, is its contribution to the study of the methanol to gasoline process. Clark et al. [86], on the basis of radical trap experiments, have postulated a number of radical pathways for the conversion of methanol over Brönsted acidic zeolites. This work will be discussed further in Chapter 5.

2.7 Ultra-Violet and Visible Spectroscopy (UV-vis)

UV-vis spectroscopy is mostly concerned with the transfer of electrons from valence shell orbitals or bands. The most common form of this technique is in absorption experiments where resonant absorption of a photon leads to electronic excitation of the system. This type of measurement can give (in addition to information on the energy gap between electronic states) information concerning the vibrational states of the excited electronic state. For more information on alternative UV-vis experiments and selection rules, we refer to reference [30]. As noted previously, electronic transitions take
place in around $10^{-15}$s and it is therefore the Uncertainty Principle (and technological difficulties) which limits the achievable time resolution.

For solids, electronic absorption bands are usually broad with little structure due to the overlapping of many vibrational sub-bands and due to the short lifetime of the excited states (high probability of photon re-emission). The latter leads to large Uncertainties in the energy levels and thus causes spectroscopic broadening. Use of UV-vis spectroscopy in molecular sieve problems therefore is mostly limited to fingerprinting roles, especially where transition metals are involved; ligand to metal charge transfer bands are often used to detect types of ligands, coordination and ligand to metal bonding. For example, UV-vis spectroscopy has been used to probe the nature of oxygen binding to Ti$^{IV}$ in Ti-silica catalysts [44, 5] and to detect whether extra-framework titania particles are present [87]. UV-vis spectroscopy has also been used extensively to study defects in molecular sieves and the reader is referred to reference [88].

2.8 Summary

This chapter has given a brief overview of some commonly used experimental techniques employed in molecular sieve research, such as NMR, XAS, diffraction and vibrational spectroscopy. Examples of their application have been outlined in order to give insight into the strengths and limitations of each method. The next Chapter continues with a discussion of the theoretical methods used in the work reported in later Chapters.
Chapter 3

Computational Techniques

The study of organic reactivity in molecular sieves reported later in this thesis is computational in nature and therefore knowledge of the computational techniques, their approximations, inherent limitations and strengths is required. Further, since we are involved primarily with reactivity, i.e., the formations and rupture of chemical bonds, a quantum mechanical description is crucial. Thus, this Chapter forms an introduction to quantum mechanical ideas as applied to chemical problems; the traditional Hartree-Fock (HF) and Möller-Plesset (MP) theories and the recent incarnations of Density Functional Theory (DFT).

In addition, the study of reactivity in solid state systems raises a number of questions concerning the strategy employed to describe the active site, i.e., should a cluster, a periodic array or some variety of embedded cluster approach be used. The current work is based on the cluster approximation and this methodology is described and discussed.

Finally, Transition State Theory is considered briefly and methods for locating transition state structures are outlined.

3.1 General

The mathematical description of a molecule including both quantum mechanical and relativistic effects is a formidable problem. For most chemical systems therefore a simpler approach is adopted starting from the non-
relativistic Schrödinger equation

\[ \hat{H} \Psi_{n,v}(r,R) = E_{n,v} \Psi_{n,v}(r,R), \quad (3.1) \]

where \( \hat{H} \) is the Hamiltonian operator for the system, \( \Psi_{n,v}(r,R) \) is the wavefunction containing all information about the system with \( n \) and \( v \) labelling electronic and nuclear quantum numbers respectively. \( E_{n,v} \) is the energy of the system in the state described by \( \Psi_{n,v} \). In general \( \Psi_{n,v}(r,R) \) is a complex function of both electronic \( (r) \) and nuclear position \( (R) \). Solution of equation (3.1) is generally too difficult for practical purposes and recourse is made to the Born-Oppenheimer approximation [89]; see also, for example [90, 91]. Born and Oppenheimer were able to show that an approximate solution of the wave equation (3.1) for a polyatomic system can be found by assuming that the nuclear and electronic motions are separable, i.e., that because the electronic mass is several thousand times smaller than that of the nuclei, electronic motion is a slowly varying function of nuclear position and to a good approximation

\[ \Psi_{n,v}(r,R) \approx \psi_n(r;R) \phi_{n,v}(R), \quad (3.2) \]

where \( \psi_n(r;R) \) is the electronic wavefunction dependent on electronic position and quantum number, parametrically dependent on the nuclear coordinates and independent of the nuclear quantum number. \( \phi_{n,v}(R) \) is the nuclear wavefunction. With this approximation two separate Schrödinger equations can be written, the first describing the electronic motion,

\[ \hat{H}_{el} \psi_n(r;R) = E_n(R) \psi_n(r;R), \quad (3.3) \]

where the electronic energy \( E_n(R) \) is a function of nuclear position and electronic quantum number. The second equation describes the motion of the nuclei on this potential energy surface,

\[ \hat{H}_{nuc} \phi_{n,v}(R) = E_{n,v} \phi_{n,v}(R). \quad (3.4) \]

Solution of the electronic wave-equation (3.3) at various points on the potential energy surface is required in order to describe phenomena such as electronic transitions, electron and proton transfer processes and bond breakage and formation. These problems are dealt with by the various quantum
chemical techniques. In contrast, problems such as predicting vibrational frequencies, sublimation energies, crystal structures etc. can often be dealt with using a classical or semi-classical approximation to the ground state potential energy surface $E_0(R)$. The functional form used to describe the potential energy surface is fitted to experimental or quantum chemical data and is generally of a mathematical form that is much easier to handle computationally than that of a quantum mechanical description. The obvious advantage of this approach is that larger systems can be studied and dynamics simulations can be carried out more readily. Obviously, effects which depend explicitly on electronic structure cannot be reproduced by such methods.

Since the current work is based upon the search for reaction mechanisms, quantum chemical methods are a necessity. The following sections detail the techniques, approximations, and notations common in modern quantum chemistry.

### 3.2 Quantum Chemical Techniques

Most modern quantum chemistry methods differ in their strategies to determine the electronic energy resulting from the Born-Oppenhiemer approximation. Despite this variation the basic description of a system of atoms is very often that of Molecular Orbital Theory in which one-electron functions or molecular orbitals are used to approximate the full many-electron wavefunction. A molecular spin-orbital $\psi_i(x, y, z, \xi)$ is a function of the spatial and spin coordinates of a single electron,

$$
\psi_i(x, y, z, \xi) = \phi_i(x, y, z)\eta_i(\xi), \quad (3.5)
$$

where $\phi$ is the spatial and $\eta$ the spin wavefunction. $\eta$ can be one of two spin functions $\alpha$ or $\beta$. The $|\psi_i|^2$ are generally interpreted as the probability distribution of an electron in space, integrating to unity and with the actual spin-orbitals usually constrained to be orthogonal, i.e.,

$$
\langle \psi_i | \psi_j \rangle = \delta_{ij}. \quad (3.6)
$$

The simplest type of $n$ electron molecular orbital wavefunction that satisfies the fundamental (fermionic) requirement of antisymmetry is a normalised
single (Slater) determinant, $\Psi$,

$$\Psi = \frac{1}{\sqrt{n!}} \det \begin{vmatrix} \psi_1(1) & \psi_2(1) & \ldots & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & \ldots & \psi_n(2) \\ \vdots \\ \psi_1(n) & \psi_2(n) & \ldots & \psi_n(n) \end{vmatrix}, \quad (3.7)$$

where numbers in parentheses label electrons. In the case of a restricted closed-shell wavefunction, a given spatial function would appear twice, each associated with a different spin component. On expansion, the single determinant wavefunction becomes a sum of spin-orbital products, the square of each term corresponding to a probability distribution of $n$ independent electrons in space. This type of wavefunction is also known as an antisymmetrised product,

$$\Psi = \frac{1}{\sqrt{n!}} A |\psi_1(1)\psi_2(2)\ldots\psi_n(n)|, \quad (3.8)$$

where the antisymmetriser $A$ is defined as,

$$A = \sum_p (-1)^p \hat{P}(1,2,...n). \quad (3.9)$$

The operator $\hat{P}$ permutes pairs of electron labels. Antisymmetry introduces partial correlation of the functions describing electrons of like spin, an effect known as exchange, but electron-correlation derived from interaction of electrons with different spins is not explicitly included in a single-determinantal wavefunction.

For practical reasons the individual molecular orbitals are usually expressed as linear combinations of fixed one-electron basis functions, $\chi_\mu$ (see page 52), the molecular orbitals thus being written as:

$$\phi_i(r) = \sum_\mu c_{i\mu} \chi_\mu(r), \quad (3.10)$$

where the coefficients $c_{i\mu}$ define the $\phi_i$. More often than not, the one electron basis functions are taken to be atomic orbitals or functions that closely resemble them, giving the linear combination of atomic orbitals (LCAO) method. In the limit of a complete set of expansion functions
the LCAO method can describe the molecular orbitals making up a single-determinantal wavefunction exactly, i.e., the Hartree-Fock limit. In practice, however, one must truncate the basis set expansion leading to the possibility of large errors in the wavefunction.

Given an appropriate form for the many-electron wavefunction, some method of determining the coefficients in the LCAO expansion is required. This can be achieved using perturbation theory but it is more common to use variational procedures based on the wavefunction, e.g., Hartree-Fock theory [90, 91] or the charge density, e.g., Kohn-Sham density functional theories [92] (although at this level DFT is an exact theory and an exact many-electron wavefunction can, in principle, be recovered). These two methods, HF and DFT, as well as Möller-Plesset theory, are discussed in more detail below.

3.2.1 Hartree-Fock Theory

Hartree-Fock theory is concerned with finding the energetically best variational single-determinant electronic wavefunction. If the many-electron non-relativistic Hamiltonian is defined in atomic units as

\[ \hat{H} = \sum_i \hat{h}_i + \sum_{i>j} \frac{1}{r_{ij}}, \]  

(3.11)

where \( \hat{h}_i \) is a one electron operator for the \( i \)th electron moving in the field of the nuclear charges \( \{Z_A\} \),

\[ \hat{h}_i = -\frac{1}{2} \nabla_i^2 + \sum_A \frac{Z_A}{r_{iA}}, \]  

(3.12)

then an estimate of the energy of the system described by a normalised antisymmetrised wavefunction \( \Psi \) is

\[ E = \int \Psi^* \hat{H} \Psi \, d\tau, \]  

(3.13)

and it can be shown that

\[ E = \int \Psi^* \hat{H} \Psi \, d\tau \geq E_{\text{exact}}, \]  

(3.14)

where \( E_{\text{exact}} \) is the energy resulting from exact solution of equation (3.3) and \( d\tau \) indicates integration over all spin and spatial variables. This is the
variational principle applied to an antisymmetrised product wavefunction. For a system described by a closed-shell antisymmetrised product of $N$ orthonormal spin-orbitals, the energy can also be written in terms of integrals,

$$E = 2 \sum_{i} h_{ii} + \sum_{ij} (2J_{ij} - K_{ij}), \quad (3.15)$$

where the indices label doubly occupied molecular orbitals and the nuclear-field orbital energies ($h_{ii}$), the coulomb integrals ($J_{ij}$), and the exchange integrals ($K_{ij}$) are defined as,

$$h_{ii} = \int \psi_i^*(1) \hat{h} \psi_i(1) \, dv(1) \quad (3.16)$$

$$J_{ij} = \int \frac{\psi_i^*(1) \psi_j^*(2) \psi_i(1) \psi_j(2)}{r_{12}} \, dv(1) \, dv(2) \quad (3.17)$$

$$K_{ij} = \int \frac{\psi_i^*(1) \psi_j^*(2) \psi_j(1) \psi_i(2)}{r_{12}} \, dv(1) \, dv(2). \quad (3.18)$$

Total spin is accounted for by the form of the wavefunction, not by spin dependencies in the Hamiltonian, and $E$ is therefore spin independent. In order that $E$ may reach its absolute minimum it is necessary (but not sufficient) that $\delta E = 0$ for an arbitrary variation in any of the molecular orbitals. Varying the molecular orbitals under orthonormality constraints leads to an expression for the variation in the energy of the system which when set to zero leads to a set of equations, the Hartree-Fock equations, which the 'best' molecular orbitals must satisfy, i.e., (in canonical form),

$$\hat{f} \psi_i = \epsilon_i \psi_i, \quad \forall i, \quad (3.19)$$

where $\epsilon_i$ are the Hartree-Fock molecular orbital energies and the operator $\hat{f}$ is the Fock operator given by,

$$\hat{f}(1) = \hat{h}(1) + \sum_{i} (\hat{j}_i(1) - \hat{k}_i(1)). \quad (3.20)$$

$$= \hat{h}(1) + \hat{\epsilon}^{\text{HF}}(1).$$

In equation (3.21) $\hat{h}(1)$ is the one-electron kinetic and nuclear attraction operators for electron 1, $\hat{j}_i(1)$ is the coulomb and $\hat{k}_i(1)$ the exchange operator.
defined as,

\[ j_i(1) = \int \frac{\psi_i^*(1) \psi_i(1)}{r_{12}} dv(1) \]  

(3.21)

\[ k_i(1) = \int \frac{\psi_i^*(1) \psi_j(1)}{r_{12}} dv(1). \]  

(3.22)

Thus the problem of finding the 'best' antisymmetrized product of orthonormal spin-orbitals reduces to that of solving the eigenvalue problem of the Fock operator \( \hat{f} \). Note, however, that the Hartree-Fock energy is not simply the sum of eigenvalues of the Fock operator as this procedure would double count many two-electron integrals.

In all but the simplest cases numerical solution of the Hartree-Fock equations is extremely difficult and approximations for the 'best' molecular orbitals are introduced. As mentioned above, one widely used approach is to use linear combinations of atomic orbitals \( \chi_\mu \) (LCAO method),

\[ \psi_i(r) = \sum_\mu c_\mu \chi_\mu(r). \]

The problem of finding the best LCAO molecular orbitals is then one of varying the coefficients until the energy reaches its absolute minimum, giving rise to the equation,

\[ Fc = \epsilon Sc, \]

(3.23)

where the overlap matrix \( S \) has elements \( S_{pq} = \int \chi_p^* \chi_q dv \), \( F \) is the Fock matrix in the atomic orbital basis, \( c \) is the matrix of expansion coefficients and \( \epsilon \) is the matrix of molecular orbital energies. These equations were simultaneously proposed by Roothan [93] and Hall [94] and form the basis of modern Hartree-Fock quantum chemistry procedures. Because the wavefunction and energies depend on the matrices \( S \) and \( F \), the Roothan-Hall equations are usually solved iteratively. An initial guess for the coefficients is used to construct \( S \) and \( F \), and equation (3.23) is solved to give a new set of coefficients which are compared with the original set. Guided by this comparison a new set of coefficients is chosen and the procedure repeated until some predetermined convergence criteria are met. The technique is known as the LCAO self-consistent field method.
The present discussion has focused on restricted closed-shell wavefunctions which are known to behave incorrectly at bond dissociation limits. This can be remedied by introducing unrestricted open-shell methods in which each electron is described by its own spatial function thus giving rise to a set of coupled Hartree-Fock equations for alpha and beta electrons; the latter must be solved simultaneously. Although this approach allows greater variational freedom in the calculation, the wavefunction is not an eigenfunction of the total electron spin operator \( \hat{S}^2 \) and is subject to spin contamination. The work reported in Parts II and III use restricted, closed shell methods although it is pointed out that the reactions under study never involve reaching a bond’s dissociation limit.

The Roothan-Hall equations formally scale as \( N^4 \) where \( N \) is the number of atomic basis functions as the Fock matrix contains contributions from four-center two-electron integrals. Methods to introduce electron correlation either by perturbation theory or multi-determinant methods scale with even larger powers; for example, second-order Møller-Plesset perturbation theory (see Section 3.2.2) formally scales as \( N^5 \). This behaviour is a major set back to Hartree-Fock and post Hartree-Fock methods. However, new algorithms designed to assess quickly the size of two-electron integrals and discard those that are insignificant has allowed the practical scaling of Hartree-Fock methods to be reduced to as low as \( N^{2.2} \) for very large systems [95]. More recently, there has also been a great deal of interest in accurate linear scaling methods [96, 97]. Although these procedures introduce the possibility of studying larger systems and/or using more extended basis sets, it does nothing to correct for the lack of electron-correlation. The Hartree-Fock codes used in the present work are Gaussian-94 [98] and Cadpac 6.0 [99]. Gaussian-94 uses an SCF convergence criteria of \( 10^{-8} \) on changes in elements of the density matrix, a geometry optimisation convergence criteria of 0.00045 Hartree bohr\(^{-1}\) maximum force, 0.0003 Hartree bohr\(^{-1}\) RMS force, 0.0018 bohr maximum displacement and 0.0012 RMS displacement. Cadpac 6.0 uses an SCF convergence criteria of \( 10^{-6} \) on changes in elements of the density matrix, and a geometry optimisation convergence criteria of \( 10^{-4} \) Hartree bohr\(^{-1}\) maximum force. Unless explicitly stated otherwise, these defaults will be used throughout.
Some of the problems associated with basis set truncation and electron correlation are highlighted in a review by Allavena et al. [100] who show that for studies of ammonia adsorption on zeolite fragments, extended basis sets and electron correlation are required to produce even a qualitatively correct potential energy surface. Sauer et al. [62] have also noted that electron correlation is required to calculate vibrational frequencies that are comparable with those recorded experimentally for methanol adsorbed in acidic zeolites. An important point for the current work is the failure of HF theory to predict accurately the energy of transition state structures due, probably, to the inability of single determinant wavefunctions to describe the complex state to state mixing that occurs at these points [101]. Recourse to some form of (electron) correlated wavefunction is therefore necessary. The next section describes a traditional perturbation theory method of including the effects of electron correlation into the calculations.

3.2.2 Möller-Plesset Perturbation Theory

The basis of Möller-Plesset theory is the use of Rayleigh-Schrödinger (RS) perturbation theory to incorporate the effect of excitations, i.e., electron correlation, into the HF wavefunction.

The RS approach involves separating the true Hamiltonian, $\hat{H}$, into a zeroth order term, $\hat{H}_0$, and a perturbation, $\hat{V}$. Introducing an ordering parameter, $\lambda$, we have

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}. \quad (3.24)$$

The problem then is to solve,

$$\hat{H}\Psi = (\hat{H}_0 + \lambda \hat{V})\Psi = E\Psi. \quad (3.25)$$

$\hat{H}_0$ is chosen such that the eigenfunctions and eigenvalues of the zeroth order term are already known, i.e.,

$$\hat{H}_0|\psi^{(0)}\rangle = E^{(0)}|\psi^{(0)}\rangle. \quad (3.26)$$

The exact eigenfunctions and eigenvalues of $\hat{H}$ can then be expanded in a Taylor series about $\lambda$,

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots, \quad (3.27)$$

45
\[ \Psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots \]  

(3.28)

Substituting (3.27) and (3.28) into equation (3.25) and equating coefficients of \( \lambda^n \) gives,

\[
\begin{align*}
\hat{H}_0 |\psi^{(0)}\rangle &= E^{(0)} |\psi^{(0)}\rangle & n = 0, \\
\hat{H}_0 |\psi^{(1)}\rangle + \hat{V} |\psi^{(0)}\rangle &= E^{(0)} |\psi^{(1)}\rangle + E^{(1)} |\psi^{(0)}\rangle & n = 1, \\
\hat{H}_0 |\psi^{(2)}\rangle + \hat{V} |\psi^{(1)}\rangle &= E^{(0)} |\psi^{(2)}\rangle + E^{(1)} |\psi^{(1)}\rangle + E^{(2)} |\psi^{(2)}\rangle & n = 2,
\end{align*}
\]

(3.29)

where \( n \) is the order of the perturbation. Solving these equations for \( E^{(n)} \) gives rise to

\[
\begin{align*}
E^{(0)} &= \langle \psi^{(0)} | \hat{H}_0 | \psi^{(0)} \rangle & n = 0, \\
E^{(1)} &= \langle \psi^{(0)} | \hat{V} | \psi^{(0)} \rangle & n = 1, \\
E^{(2)} &= \langle \psi^{(0)} | \hat{V} | \psi^{(1)} \rangle & n = 2.
\end{align*}
\]

(3.30)

The problem is then to solve (3.29) for \( \psi^{(n)} \) and use (3.30) to extract the \( n \)th order eigenvalues corrections. For example, to second order,

\[
(E^{(0)} - E_n^{(0)}) |\psi^{(2)}\rangle = \hat{V}|\psi^{(1)}\rangle - E^{(1)}|\psi^{(1)}\rangle,
\]

(3.31)

\[
E^{(2)} = \sum_{z>0} \frac{|\langle \psi^{(0)} | \hat{V} | \psi^{(2)} \rangle|^2}{E^{(0)} - E_n^{(0)}},
\]

(3.32)

where \( z \) runs over excited states of the Hartree-Fock solution. Expressions for the higher order terms are similarly obtained.

For the specific case of the expansion of the correlation energy \( \hat{H}_0 \) is taken to be the Hartree-Fock Hamiltonian, \( \text{i.e.} \), the Hamiltonian for which the Hartree-Fock wavefunctions are exact eigenfunctions,

\[ \hat{H}_0 = \sum_i \hat{f}(i), \]

(3.33)

where \( \hat{f}(i) \) are the Fock operators (see equation (3.21)). Use of RS perturbation theory on \( \hat{H} \) separated in this manner was first described by Möller and Plesset [102] and is known as Möller-Plesset (MP), or many body, perturbation theory. The operator describing the perturbation then becomes

\[ \hat{V} = \hat{H} - \hat{H}_0 = \sum_{i<j} \tau_{ij}^{-1} - \sum_i v_{\text{HF}}(i). \]

(3.34)

In this formulation, the Hartree-Fock energy is \( E^{(0)} + E^{(1)} \) and the first correction to this description is the 2nd order term which incorporate double
excitations into the Hartree-Fock wavefunction. The second order energy correction requires only the zeroth and first order eigenvalues and eigenfunctions, i.e., the HF result, and are relatively simple to calculate. It is not surprising therefore that use of second order MP (MP2) theory has become so popular for including the effect of electron correlation into ab-initio calculations. A number of calculations in the present work use MP2 single point energy calculations at HF optimised geometries. This recipe is denoted HF/basis//MP2/basis where the level of theory after the '//' denotes that used to obtain geometries and that before denotes the theory used to calculate energies at these geometries.

Given this background it is important to recognise the limitations of Möller-Plesset theory. For example, it is not a variational approach and therefore the energies are not bounded from below. Indeed, for many systems MP2 corrected energies overshoot the exact energy, i.e., the estimate of the correlation energy can be too large [103], and it has been reported that the MP series can actually diverge [104]. Other authors have done extensive comparisons of ab-initio methodologies; for example, Smith and Radom [105] studied gas phase acidities and found that the quality of MP2 results depends strongly on the basis set employed and the problem studied. They also noted that pure density functional theories gave very similar results on average and that hybrid density functional theories gave consistently superior results. Density Functional Theory will be discussed in the next section.

3.2.3 Density-Functional methods (DFT)

An alternative quantum chemical method that implicitly includes the effect of electron correlation is that of Density Functional Theory (DFT). For an excellent discussion of the basis of Density Functional Theory, the reader is referred to the monograph of Parr and Yang [92]. For a more general discussion, we refer to reference [106].

Modern DFT began with the seminal work of Hohenberg and Kohn [107] who were able to prove that the total ground state electronic energy and all ground state properties of a system are functionals of the electronic density,
Kohn and Sham's \([108]\) contribution was to say that given an arbitrary \(N\)-electron atom or molecule with total electron density \(\rho\), then there is a corresponding reference system of \(N\) independent, non-interacting electrons (in a non-interacting one body potential \(v^{KS}\)) with the same density \(\rho\). Using this reference system, the total electronic energy (omitting the nuclear-nuclear attraction term), can be written,

\[
E[\rho] = T_\rho + \int \rho V_{\text{nuc}} v^3 + \int \int \frac{e^{(r_1)\rho(r_2)}}{r_{12}} dr^3 r_1 dr^3 r_2 + E_{\text{XC}}
\]

\[
E[\rho] = T_\rho[\rho] + E_N[\rho] + E_J[\rho] + E_{\text{XC}}[\rho],
\]

where \(T_\rho\) is the kinetic energy of non-interacting electrons, \(E_N\) is the electron-nuclear interaction, \(E_J\) is the classical electron-electron coulomb term and \(E_{\text{XC}}\) is the so-called exchange-correlation energy. This definition of the energy is, in fact, the starting point for Kohn-Sham DFT and improvements in the theory involve improving this functional. This is in contrast to more traditional methods which begin with an essentially exact Hamiltonian and seek to improve the solutions by improvements in the form of the approximate wavefunction. Equation (3.36) also defines \(E_{\text{XC}}\) and it is clear that it contains a great deal of information, for example, all two-body exchange and dynamical correlations and the kinetic energy contributions arising from electron interactions. To perform DFT calculations of the electronic energy one must optimise the energy with respect to variations in the density, and, in a similar way as for HF theory, it can be shown that for an approximate density \(\bar{\rho}\),

\[
E[\bar{\rho}] \geq E[\rho],
\]

\(i.e.,\) a variational principle based on the density exists (Hohenberg-Kohn theorem).

Proceeding with the Kohn-Sham approach, the non-interacting one particle orbitals, \(\psi_i\) (cf. Hartree-Fock molecular orbitals), of the reference system, constrained such that

\[
\rho = \sum_i^N |\psi_i|^2,
\]
will satisfy a one particle Schrödinger equation,

$$-\frac{1}{2} \nabla^2 \psi_i + v^{KS} = \epsilon_i \psi_i,$$

(3.39)

with

$$v^{KS} = v_{nuc} + v_{el} + v_{XC}.$$  

(3.40)

Equations (3.39), the Kohn-Sham equations, are analogous to the Fock equations (3.19) and (3.21) with $\hat{v}^{HF}$ replaced by $v^{KS}$ (with the exception that $v_{nuc}$ is part of $\hat{h}$, not $\hat{v}^{HF}$, in the current notation). In equation (3.40) $v_{nuc}$ is the electron-nuclear potential,

$$v_{el}(r_1) = \int \frac{\rho(r_2)d^3r_3}{r_{12}}, \text{ and}$$

(4.1)

$$v_{XC} = \frac{\delta E_{XC}}{\rho}.$$  

(3.42)

Thus, as in the case of the Fock equations (3.19), self-consistent solution of the Kohn-Sham equations (3.39) will give rise to the Kohn-Sham optimal molecular orbitals, $\psi_i$, which, through equations (3.38) and (3.36), will give the ground state energy for the specific functional (3.36). As in the case of HF theory described above, expansion of $\psi_i$ into an atomic orbital basis will lead to a set of equations analogous to the Roothan-Hall equations (3.23).

Up to this point, the theory is exact. However, only a number of global limiting properties and constraints on $E_{XC}$ are known, and it is the search for the 'best' $E_{XC}$ that has attracted enormous attention in recent years [109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122].

The workhorse of DFT quantum chemistry applications (also suggested by Kohn and Sham [108]) is the 'local spin-density' (LSDA) or 'local density' approximation (LDA) for which the exchange-correlation energy density, $\epsilon_{XC}$, in the exact expression,

$$E_{XC}^{LDA} = \int \epsilon_{XC}[\rho_\alpha(r), \rho_\beta(r)]d^3r,$$

(3.43)

is approximated by that of a uniform electron gas with the spin densities $\rho_\alpha$ and $\rho_\beta$ equal to their local atomic or molecular values. $\epsilon_{XC}$ has been
well characterised by Monte-Carlo simulations and a popular parametrisation of $\epsilon_{XC}$ from this type of study is that due to Vosko, Wilk and Nusair [123]. LDA typically gives good geometries, vibrational frequencies and single-particle properties for many systems (not including hydrogen bonded systems) but seriously overestimates bond energies [106, 111, 116].

An improvement on LDA is the generalized gradient approximations (GGAs) in which $E_{XC}$ is approximated by,

$$E_{XC}^{GGA} = \int f[\rho_\alpha(r), \rho_\beta(r), \nabla \rho_\alpha(r), \nabla \rho_\beta(r)] d^3 r, \quad (3.44)$$

where $E_{XC}^{GGA}$ now depends on the actual spin densities (the LDA part) and their gradients (the GGA part) at any given point $r$. The GGAs therefore are often referred to as gradient corrections to the local exchange-correlation potential. $E_{XC}^{GGA}$ (as well as $E_{XC}^{LDA}$) is usually separated into exchange and correlation contributions and a number of them have now been reported, e.g., the Becke-88 potential for exchange [109], and the Perdew-Wang-86 potential for correlation [110]. For a detailed comparison of the basis of the number of different GGA see [116].

Use of $E_{XC}^{GGA}$ is known to improve estimates of bond energies, barriers to chemical reactions, hydrogen bond geometries etc. although these so-called pure DFT methods have not yet reached a stage where they can be trusted to produce results of chemical accuracy for many systems [106, 114, 124]. A number of studies have, however, compared results (particularly geometries) to those of MP2 quality [40]. It is also noted that current popular GGAs do not explicitly contain all terms describing van der Waals interactions.

Another recent contribution to the field has been the development of hybrid DFT techniques. These methods incorporate part of the exact HF exchange through use of the reference orbitals $\psi_i$ and the adiabatic connection method [113, 118]. Hybrid DFT methods have been shown to give results which are consistently better than those obtained with pure DFT methods at the expense, unfortunately, of computer time. Approximations to $E_{XC}$ which incorporate $\nabla^2 \rho$ in the expansion have also been developed [120, 119, 122] but are not yet in common use. Linear scaling techniques have also received a great deal of attention [125, 126].

A great deal of the DFT calculations reported in the present work uses
the Cray Research code DGauss 3.0 [127] and it is therefore of relevance to
discuss some of its more important features. DGauss uses Gaussian linear-
combinations-of-atomic-orbitals (LCAO) to expand the Kohn-Sham refer­
cence orbitals $\psi_i$. A Gaussian auxiliary basis set [128] is also employed to
form an approximate density $\tilde{\rho}$,

$$\rho \approx \tilde{\rho} = \sum_k c_k \chi_k, \quad (3.45)$$

defined by minimising (subject to charge conservation),

$$\Delta = \int (\rho - \tilde{\rho}) \frac{1}{\tau_{12}} (\rho - \tilde{\rho}) d\tau_1 d\tau_2. \quad (3.46)$$

Due to the locality of all of the terms in the energy expression (3.36), this
approximate density can be used to reduce the four-centre integrals (in terms
of an atom centred basis) into three centre integrals with little comprom­
ise to the quality of the results (this trick cannot be employed in standard
HF and hybrid DFT implementations due to the non-local nature of exact
exchange). DGauss thus scales as $N^3$ where $N$ is the number of basis func­
tions employed (compare with $N^4$ and $N^5$ formal scaling for HF and MP2
theory respectively). DGauss3.0 also has the ability to calculate analytical
second derivatives, a critical requirement for efficiently locating transition
states of chemical reactions. The program uses the Vosko-Wilk-Nusair [123]
parametrisation of the local exchange-correlation potential and can employ
the gradient correction of Becke for exchange [109] with either the gradient
correction of Perdew and Wang [110] or Lee-Yang-Parr [121] for correlation.
These combinations give rise to the BP86 or BLYP gradient corrected func­
tionals respectively. DGauss also uses DFT energy optimised basis sets [129]
which have been shown to give better results than standard HF basis sets and
for which the basis set superposition error is small [130]. Unless stated oth­
erwise the DGauss calculations all use SCF convergence criteria of $5.0*10^{-5}$
on changes in the gradient of the orbital coefficients and $5.0*10^{-7}$ Hartrees
on the energy, a 'medium' integration grid and a geometry optimisation
criterion of $8.0*10^{-4}$ Hartree bohr$^{-1}$.

Gaussian 94 and Cadpac 6.0 also have the ability to perform DFT cal­
culations using standard 4-centre 2-electron integral schemes, i.e, scaling
formally as $N^4$. Unless stated otherwise, calculations will use default integration grid qualities, 'fine' for Gaussian 94, 'medium' for Cadpac 6.0. SCF and geometry convergence criteria are the same as for HF.

3.2.4 Basis sets and superposition error

The present work uses linear combinations of atomic orbitals, $\chi_\mu$, to represent the molecular orbitals $\psi_i$. Recall then,

$$\psi_i(r) = \sum_\mu c_{\mu i} \chi_\mu(r).$$

The atomic orbitals are in turn represented by atom centered Gaussian functions. Primitive Cartesian Gaussian-type orbitals (CGTOs) have the general form,

$$\chi_\mu(r) = N x^i y^j z^k e^{-\zeta(r-r_A)^2}, \quad (3.47)$$

where $A$ labels the atom it is centered upon, $N$ is a normalisation constant and the remainder of the preexponential term describes angular dependence, the orbital angular quantum number being equal to $i + j + k$. Gaussian functions do not have the same behaviour as hydrogenic wavefunctions at the nucleus or at large distances but have the advantage that they produce integrals that can be handled very efficiently. In order to obtain a better description of atomic wavefunctions using Gaussian functions it is usual to combine several together as follows,

$$\chi_\mu(r) = N x^i y^j z^k \sum_i d_i e^{-\zeta(r-r_A)^2}. \quad (3.48)$$

These orbitals are called contracted Gaussian-type orbitals, the $d_i$ being the contraction coefficients which are usually fixed at some preoptimised value.

Minimal basis sets have a number of contracted functions equal to the number of atomic orbitals occupied in a neutral atom. A double-zeta basis (DZ) has twice this number and so on. In order to describe polarisation and diffusivity of the electron density in the molecular environment, it is often necessary to include functions of higher angular momentum than are present in the neutral atom. For example, a polarisation function on hydrogen would be a 'p' type function. Naturally, larger basis sets offer greater variational
freedom and lead to less severe errors from basis set incompleteness. The present work relies heavily on valence double-zeta basis sets which describe atomic core regions with the same number of basis functions as there are occupied atomic orbitals in the neutral atom, and which describe the atomic valence regions with twice as many orbitals as in the neutral atom. For example, the 6-31G** basis set has six primitive Gaussians contracted to form core functions, two sets of three and one contracted Gaussians to describe valence functions and polarisation functions on heavy atoms (first asterix) and hydrogen atoms (second asterix). The DZVP basis, a double-zeta valence set with polarisation on heavy atoms is analogous. The DZVP basis supplied within DGauss [129] is written as (41) for H–He, (621/41/1) for B–Ne and (6321/521/1) for Al–Ar where, e.g., (621/41/1) means there are 3 contracted s-, 2 contracted p-, and 1 contracted d-functions. The s-functions consist of 6, 2, and 1 primitive Gaussians, the p-functions consist of 4 and 1 primitive Gaussians, and the d-function is a single primitive Gaussian. The basis sets used in the present work are shown in Table 3.1.

Basis sets used in molecular and ionic calculations are often far from complete due to the practical necessity of truncating the atomic orbital expansion (equation 3.10). Each subsystem in a complex or cluster calculation will then tend to use basis functions of other subsystems in order to lower their energies (the basis set superposition error). This nonphysical contribution to stabilization energy can be estimated using the Boys-Bernardi counterpoise method (see ref. [19] for more detail). Briefly, this involves calculating the energy of subsystem A with all of its own basis functions plus the basis functions of the other subsystems (say B), the latter without their electrons and nuclei. The energy obtained, $E_{A(B)}$, will be lower than the energy $E_A$ calculated with the basis functions of A alone, the difference being defined as the basis set superposition error (BSSE), $\epsilon_A$,

$$
\epsilon_A = E_A - E_{A(B)}.
$$

(3.49)

Subsystem B also has a superposition error associated with it,

$$
\epsilon_B = E_B - E_{B(A)}
$$

(3.50)
Table 3.1: Basis-Set definitions: polarisation functions are included in the definitions

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
</tr>
<tr>
<td>DZVP [129]</td>
<td>{41}</td>
</tr>
<tr>
<td>DZVP2 [129]</td>
<td>{621/41/1}</td>
</tr>
<tr>
<td>TZVP [129]</td>
<td>{311/11}</td>
</tr>
<tr>
<td>SAD++ [131]</td>
<td>{411/22}</td>
</tr>
<tr>
<td>diffuse</td>
<td>s: 0.01 p: 0.01</td>
</tr>
<tr>
<td>TZ2P [132]</td>
<td>{311/11}</td>
</tr>
<tr>
<td>6-31G** [90]</td>
<td>{31/1}</td>
</tr>
</tbody>
</table>
Instead of calculating the interaction energy of subsystems $A$ and $B$ as
\[
\Delta E_{AB} = E_{AB} - E_A - E_B,
\]
(3.51)
a corrected interaction energy $\Delta E_{AB}^c$ is calculated as
\[
\Delta E_{AB}^c = E_{AB} - E_{A(B)} - E_{B(A)}.
\]
(3.52)
This has the advantage that the difference is taken between energies obtained using the same basis set. The corrected interaction energy can also be written as
\[
\Delta E_{AB}^c = \Delta E_{AB} + \epsilon_A + \epsilon_B.
\]
(3.53)
Basis set superposition energy can only be reduced by using large, well balanced basis sets.

3.3 Strategies for study of solid materials

The present work involves the elucidation of reaction coordinates and we must therefore employ a quantum chemical technique. These techniques fall into two broad classes, those that exploit the translational symmetry of the solid material (periodic models) or those that use finite fragments or clusters. The former approach, using crystal orbital techniques, although more appealing, is very computationally demanding since electron-electron integrals have to be evaluated for the current and all neighbouring unit cells [19]. Despite this problem, the increase of fast computer technology and efficient algorithms have enabled substantial progress to be made and several programs are now widely available, e.g., Crystal [133, 134, 135, 136], Castep [137], DSolid [138]. The crystal orbital approach has more difficulties handling systems for which translational symmetry is lost, e.g., when defects are present, since recourse to supercell calculations is often necessary. However, codes are available which attempt to treat defects in extended solids in a purely quantum mechanical way [139] or using a hybrid (semi) classical/quantum mechanical approach [140, 141].

Finite models are more straightforward, although inherently approximate. A fragment of the bulk crystal that is thought to be representative
of an active site or defect is cut out from the crystal structure. This fragment is then employed in an electronic structure calculation. For zeolites and alumino-silicate systems, valence electrons are well localised as lone and bonding pairs and the finite model is not too severe an approximation although it does lead to neglect of long range dispersion and electrostatics [19]. Use of finite fragments to model sorption and reaction phenomena in zeolites raises several issues concerning approach and technique including [17]:

1. The validity of different quantum mechanical techniques with different levels of approximation.

2. The minimum size of cluster required to simulate the sorption or active site.

3. The different ways of fixing the geometry of the boundary atoms for these clusters.

4. The initial choice of geometry and orientation of the adsorbate/reactant over the active site.

It is common to treat the unsaturated bonds at the boundary of a finite fragment of alumino-silicate by either embedding in an array of point charge and/or by terminating with hydrogens or similar atoms in order to give an overall neutral system, see Figure 3.1.

The practice of embedding modest sized charged alumino-silicate fragments in an array of point charges has generally been discouraged for sorption studies as it leads to unrealistic artefacts [142].

The cluster approximation using hydrogens to saturate open valencies is the method of choice in the current work as this enables standard molecular quantum chemistry packages to be used, analytical second derivatives to be obtained efficiently and consequently advanced geometry searching algorithms to be employed (see Section 3.4). Analytical second derivatives are currently unavailable within periodic quantum chemistry codes and it is this limitation that has prevented them from having more bearing on the field of reactivity in molecular sieves and in solids in general.
3.4 Strategies for study of reaction mechanisms

Transition state theory describes chemical reactions in terms of the rate of passage of a molecular system through a first order saddle point (the transition state) on the potential energy surface connecting reactants and products (see for example [101]). Transition state, or activated complex, theory generally assumes that,

1. all molecules that cross through the transition state from the reactant side proceed to form products,

2. an equilibrium distribution of reactants is always maintained,

3. the molecules at the transition state are in thermal equilibrium with the reactants.

Transition state theory is ideally suited to molecular orbital theory as the latter can be used to locate the transition states and minimum energy structures involved in a reaction and, through statistical thermodynamics, can predict activation energies, enthalpies and free-energies, as well as rate and equilibrium constants. Although we consider that the cluster approx-
imation and the quantum chemical methods used in the current work are not sufficiently accurate to justify application of statistical thermodynamics ideas, a number of studies of reactivity in molecular sieves have used such approaches [143, 144].

In order to apply the ideas of transition state theory to the computational study of chemical reactions it is therefore necessary to locate the minimum and maximum (transition state) structures on the potential energy surface that are involved in the process; see Figure 3.2 for an example in a one-dimensional system. For this purpose it is common to apply advanced

![Figure 3.2: One dimensional reaction coordinate showing 1st order transition state (TS) and minima (M).](image)

geometry search algorithms that make use of the derivatives of the energy with respect to atomic positions. These Newton-Raphson or Quasi-Newton Raphson techniques will be summarised below.

Expanding the energy at the current position $x_k$ as a Taylor series gives:

$$E(x_k) = E(x_k) + (x - x_k)E'(x_k) + \frac{1}{2} \left((x - x_k)^T E''(x_k) (x - x_k)\right) + \ldots,$$

where the expansion is only shown to second order, $E'(x_k)$ is the gradient of the energy with respect to atomic positions at $x_k$ and $E''(x_k)$ is the second derivative of the energy with respect to atomic positions, the Hessian matrix. The Newton-Raphson or Quasi-Newton Raphson techniques (the latter used in the present work) assume that the potential energy surface is close to
quadratic (the Taylor expansion for \( E(x_k) \) is truncated at second order). Using this approximation, the first derivative, \( E'(x) \), becomes

\[
E'(x) = E'(x_k) + (x - x_k)^T E''(x_k). \tag{3.55}
\]

However, at a stationary point on the potential energy surface \( x = x^* \), e.g., at minima or transition states, \( E'(x^*) = 0 \) and we get:

\[
x^* = x_k - E'(x_k)E''^{-1}(x_k). \tag{3.56}
\]

This is the Newton-Raphson method, and as seen, it requires the inverse Hessian matrix. For a purely quadratic function this method will find the stationary point in a single step, in more 'real' systems however more steps are generally required. For a positive definite Hessian matrix (all positive eigenvalues) the Newton-Raphson method will find a minimum energy structure; for Hessian matrices with negative eigenvalues, however, the scheme will result in a transition state structure, i.e., the Newton-Raphson step will lead to an increase in energy along the direction of the eigenmodes of the Hessian with negative eigenvalues. The Newton-Raphson method requires \( E''^{-1}(x_k) \) at every point in the geometry search and is therefore prohibitively expensive for most cases of interest when using quantum mechanical approaches. An alternative approach which is employed in nearly all modern codes is the Quasi-Newton method which builds up \( E''^{-1} \) in successive geometry steps such that,

\[
\lim_{k \to \infty} H_k = E''^{-1}. \tag{3.57}
\]

Thus, at each geometry step, the new positions, \( x_{k+1} \), are obtained from the current position, \( x_k \), the gradient, \( E'(x_k) \), and the current approximation to the inverse Hessian, \( H_k \),

\[
x_{k+1} = x_k - H_k E'(x_k). \tag{3.58}
\]

This formula is exact for a quadratic function but 'real' systems often require a line search between \( x_{k+1} \) and \( x_k \) to locate the stationary point, i.e. to estimate the step size. Having moved to a new position, \( x_{k+1} \), \( H_k \) is updated from its value at the previous step according to a number of
formulae, common examples being those due to David-Fletcher and Powell (DFP), Broyden-Fletcher-Goldfarb and Shanno (BFGS) and Murtaugh-Sargent (MS). For quadratic functions of \( M \) variables these methods will converge to the stationary point in \( M \) steps.

Figure 3.3: The effect of taking a step that is too large in a transition state search - the transition state is missed and the 'path of shallowest ascent' is lost.

Initially the inverse Hessian, \( H \) is often set to the unit matrix, \( I \), and careful estimation of the step size is then crucial for an efficient minimisation. For transition state searches however, a fairly accurate estimate of the inverse Hessian at each step in the search is required in order to correctly determine the 'path of shallowest ascent' and the step size. Figure 3.3 shows the result of a step size which is too large, i.e., the transition state is missed. For transition state searches therefore it is often necessary to start from a structure in the vicinity of the transition state and for which the Hessian has the correct local structure, i.e., a single negative eigenvalue. Search algorithms used in the present work, i.e., in the Gaussian 94 suite [145] and in DGauss 3.0 [127], also implement 'trust radius' schemes in order to make efficient estimates of the optimum step size based on current confidence levels in the quadratic approximation and the Hessian at the current point. In addition, for transition states searches it is more common (and is the case in DGauss 3.0) to use the DFP updating scheme as this allows
the character of the Hessian to change during the search \[127\]. For more information on optimisation algorithms see \[146, 101, 147, 148, 145\].

The discussion of search algorithms presented above assumes that a good initial structure for the transition states is available. This is not always trivial and a number of methods have been developed that seek to aid in obtaining this initial guess \[146, 101\], for example, the linear (LST) and quadratic synchronous transit (QST) techniques which seek to find a guess to the transition state structure that lie between two supplied structures. Both LST and QST procedures can generate reasonably good initial guesses for a transition state structure provided that the reaction path is not too complex \[101\]. The transition states in the current work, have, however, been located on the basis of chemical intuition and the use of low quality, \textit{e.g.}, small basis set, calculations.

3.5 Summary

This Chapter has described the theoretical methods applied in the current work to problems of organic reactivity in molecular sieves. The cluster method has been introduced and discussed in relation to periodic models and we have stressed the need for accurate second derivatives of the energy with respect to the nuclear displacements for the efficient location of transition states on the potential energy hypersurface. In addition, Quasi-Newton geometry search algorithms have been described with an emphasis on the difficulties encountered in locating transition state structures.

The next Chapter reports some results aimed at benchmarking the quantum mechanical methods described above and used in later Chapters to problems involving the calculations of intermolecular interactions, vibrational frequencies, activation barriers and NMR properties. Such a study is fundamentally important if calculations on more difficult problems are to be fully understood.
Chapter 4

Calibration of Computational Techniques

The previous Chapter dealt, in some detail, with the quantum chemical techniques that will be used in the study of organic reactivity in molecular sieves reported in Parts II and III of this thesis. To complete Part I we now report benchmark calculations of test systems in order to gain detailed insights into the strengths and weaknesses of the specific quantum chemical recipes used in our calculations.

We will start with a discussion of the calculation of binding energies, vibrational and NMR properties of equilibrium structures of the water and methanol dimers. These systems are of direct relevance to the Methanol to Gasoline Process over H-zeolites where methanol, water and/or mixtures of both are likely to be present and where hydrogen bonding effects are critical. Subsequently, the calculated energetics of a possible reaction pathway for formation of ethene from methanol over 1T and 5T alumino-silicate clusters will be discussed in order to obtain some information on cluster size effects and the ability of the various quantum chemical methods to predict the properties of transition states. The details of this process will be discussed further in Part II.
4.1 Equilibrium Properties

The water and methanol dimers have been chosen as test cases for the current study of equilibrium properties as both of these have been the subject of numerous studies, e.g., references [149, 150], and contain aspects of chemical interest, e.g. hydrogen bonds, that are relevant to both the Methanol to Gasoline and Alkene Epoxidation processes.

Table 4.1 shows results for selected properties of the water molecule and its dimer, the BLYP/TZVP optimised structure of the latter being shown in Figure 4.1. A general description of the basis set expansions are given in Table 3.1, Section 3.2.4. Although there have been many theoretical studies of water and its dimer, far beyond the MP2/VTZ(2df, 2p) level shown in Table 4.1, our present aim is to gauge the quality of DFT and MP2//HF descriptions with respect to experiment and to MP2 calculations for which gradient-corrected DFT methods have often been compared; cases where higher quality calculations differ markedly from the MP2 results shown will be noted.

It is clear from Table 4.1 that the interaction energies (ΔE) are all in reasonable agreement with the experimental value of 22.8 ± 2.9 kJmol⁻¹, although the uncorrected MP2//HF calculation overestimates the strength of interaction. Correction of the energy for BSSE using the counterpoise method (see Section 3, Chapter 3.2.4) appears to lead to an interaction energy that is appreciably too low when the larger basis sets are used, i.e., for the BLYP/TZVP and BLYP/SAD++ cases. Given that use of the SAD++ basis set at the MP2 level (for which detailed results are not presented) also leads to an underestimation of ΔE, it must be concluded that the error, at least in the BLYP/TZVP and BLYP/SAD++ cases, is probably due to an overestimation of BSSE.

With the exception of the energetics, all of the BLYP calculations which employ a basis set including polarisation functions on hydrogen atoms give similar results. Addition of polarisation functions on hydrogen atoms leads to changes in the vibrational frequencies of up to 60 cm⁻¹. A similar effect is observed for the BP86 calculations although it is noted that the current BP86 results and those of Sim et al.[150] show marked differences (probably
Table 4.1: Calculated and experimental properties of isolated water and the water dimer. Unless labelled, all calculated frequencies are harmonic and all experimental frequencies are anharmonic. Energies ($\Delta E$) are in kJmol$^{-1}$, distances ($r$) in Å, dipole moments ($\mu$) in Debye, angles in degrees and frequencies ($\nu, \delta$) in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Property</th>
<th>DFT</th>
<th>MP2//HF $^a$</th>
<th>MP2 $^b$ [149]</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DZVP$^d_{\text{BLYP}}$</td>
<td>TZVP$^d_{\text{BLYP}}$</td>
<td>DZVP$^2_{\text{BLYP}}$</td>
<td>SAD++$^{cp}_{\text{BLYP}}$</td>
</tr>
<tr>
<td>$\Delta E$ $^c$</td>
<td>26.4</td>
<td>22.7</td>
<td>24.1</td>
<td>18.9</td>
</tr>
<tr>
<td>$\Delta r_{\text{dim}}$</td>
<td>0.0092</td>
<td>0.0094</td>
<td>0.0091</td>
<td>0.0078</td>
</tr>
<tr>
<td>$\nu_{\text{E}}$</td>
<td>3517</td>
<td>3539</td>
<td>3558</td>
<td>3542</td>
</tr>
<tr>
<td>$z$</td>
<td>3689</td>
<td>3708</td>
<td>3742</td>
<td>3718</td>
</tr>
<tr>
<td>$\mu_{\text{dim}}$</td>
<td>172</td>
<td>169</td>
<td>184</td>
<td>176</td>
</tr>
<tr>
<td>$\mu_{\text{mon}}$</td>
<td>0.979</td>
<td>0.974</td>
<td>0.976</td>
<td>0.975</td>
</tr>
<tr>
<td>$\zeta_{\text{h}}$</td>
<td>2.17</td>
<td>2.08</td>
<td>2.05</td>
<td>1.81</td>
</tr>
<tr>
<td>$\nu_{\text{sym}}$</td>
<td>104.4</td>
<td>104.9</td>
<td>104.4</td>
<td>104.3</td>
</tr>
<tr>
<td>$\nu_{\text{asym}}$</td>
<td>3621</td>
<td>3651</td>
<td>3683</td>
<td>3666</td>
</tr>
<tr>
<td>$\delta_{\text{sym}}$</td>
<td>3757</td>
<td>3765</td>
<td>3799</td>
<td>3770</td>
</tr>
<tr>
<td>$\delta_{\text{asym}}$</td>
<td>1666</td>
<td>1621</td>
<td>1605</td>
<td>1595</td>
</tr>
</tbody>
</table>

$^a$: MP2//HF indicates [energy] // [geometry and properties]. HF vibrational frequencies were scaled by the standard factor of 0.89 [90].

$^b$: D2P - double-$\zeta$ basis with triple-$\zeta$ contractions on O. VTZ(2df,2p) - valence triple-$\zeta$ with extra functions on (O,H).

$^c$: Values are free of thermal and zero-point energies. Parentheses indicate BSSE corrected values.

$^d$: Reference [149] and references therein.

$^{ha}$: harmonic frequency [157]; $^{ah}$: anharmonic frequency [158]

dg: DGauss calculation; cp: Cadpac calculation.
Figure 4.1: BLYP/TZVP optimised structure of the water dimer. Distance is in Å.

due to algorithmic and basis set differences).

Of particular importance to the molecular sieve community is the shift of hydroxyl frequencies on formation of hydrogen bonds, $\Delta \nu_{\text{OH}}$, see Section 2.3, Chapter 2. The ability of pure DFT methods to accurately describe hydroxyl groups has been questioned by a number of authors [40, 124, 150] and $\Delta \nu_{\text{OH}}$ has therefore been calculated for the water system. In order to avoid ambiguities arising from the coupling of the asymmetric and symmetric hydroxyl stretches of the water monomer ($\nu_{\text{asy}}$ and $\nu_{\text{sym}}$), $\Delta \nu_{\text{OH}}$ is defined as,

$$
\Delta \nu_{\text{OH}} = \frac{(\nu_{\text{asy}} + \nu_{\text{sym}})}{2}.
$$

(4.1)

The BP86 predictions for $\Delta \nu_{\text{OH}}$ of -214, -222 and -237 cm$^{-1}$ [150] are substantially larger than the BLYP results of -169 to -184 cm$^{-1}$ and the MP2 results of -112 and -133 cm$^{-1}$. MP4 results, reported by Bleiber and Sauer [149], suggest that the shift should probably be even less, at about -107 cm$^{-1}$. Although the experimental results for $\Delta \nu_{\text{OH}}$ show a large spread, use of ab-initio results to aid in spectroscopic band assignment has led to the conclusion that $\Delta \nu_{\text{OH}}$ for the water dimer should be at the lower end of the experimental range. With this in mind, the 0.89 scaled HF frequencies appear to be in excellent agreement with experiment. It is clear however that the pure DFT functionals tested, especially BP86, should be used with care when predicting vibrational properties.

Is is also evident from Table 4.1 that pure DFT calculations give bond lengths that are too long by about 0.01Å with respect to experiment and the MP2 results (HF results in bonds that are too short by around 0.02Å);
and give harmonic frequencies that are often in good agreement with experimental anharmonic frequencies, i.e., that are too low. In agreement with previous calculations [ ] Table 4.1 indicates that the B3LYP functional gives rise to substantial improvements in all calculated properties (at the expense of computer time), although the persistent error in $\Delta \nu_{\text{OH}}$ should be noted.

Table 4.2 gives similar information for properties of the methanol dimer; the BLYP/TZVP optimised structure is shown in Figure 4.2. The general observations are similar to those discussed above for the water system. Again, the largest basis set DFT calculations lead to the lowest interaction energy, although in this case all of the BSSE corrected energies are in agreement with experiment. The error in the DFT calculated values of the shift, $\Delta \nu_{\text{OH}}$, on dimer formation are not as large as those for water, possibly due to the fact that only one hydroxyl is involved in the case of the methanol dimer whilst two strongly coupled hydroxyls are involved in the case of water. A substantial basis set dependence of the calculated vibrational frequencies is, however, observed (compare BLYP/DZVP and BLYP/TZVP cases). Unlike the water system, the 0.89 scaled HF vibrational frequencies of the dimer show large errors leading to a greatly underestimated $\Delta \nu_{\text{OH}}$ on dimer formation. Bond lengths are slightly too large when calculated by the BLYP and BP86 methods and calculated harmonic frequencies are too low - comparable with experimental anharmonic frequencies. Analogously to the water calculations, HF predicts bond lengths that are too short. For the methanol system, different implementations of DFT result in calculated properties (compare columns 2 and 4 of Table 4.2) that show discrepancies, although the differences are not great.

For the methanol monomer/dimer case we have also probed the effect on the calculated properties of tightening SCF and gradient convergence criteria and increasing the quality of the integration grid. Comparison of the 4th and 5th columns of Table 4.2 shows, that for the BLYP functional at least, the results are essentially converged at the lower, default-level of SCF and gradient convergence and of integration grid quality.

In addition to the 'traditional' properties discussed above, there has been recent interest in calculating NMR properties in order to aid interpretations of complicated spectra [62, 67]. With this in mind, the $^1$H and $^{13}$C NMR
Table 4.2: Calculated and experimental properties of isolated methanol and the methanol dimer. Unless labelled, all calculated frequencies are harmonic and all experimental frequencies are anharmonic. Energies (ΔE) are in kJmol⁻¹, distances (r) in Å, dipole moments (µ) in Debye, angles in degrees, and frequencies (ν, δ, τ) in cm⁻¹.

<table>
<thead>
<tr>
<th>Property</th>
<th>DFT</th>
<th>HF//MP2</th>
<th>MP2 [149]</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DZVP dg (BLYP)</td>
<td>TZVP dg (BLYP)</td>
<td>DZVP cp (BLYP)</td>
<td>6-31G**</td>
</tr>
<tr>
<td>ΔE</td>
<td>17.3</td>
<td>12.4</td>
<td>15.8</td>
<td>15.4</td>
</tr>
<tr>
<td>νdonor; dimer</td>
<td>3518</td>
<td>3517</td>
<td>3489</td>
<td>3483</td>
</tr>
<tr>
<td>Δν dimer</td>
<td>133</td>
<td>150</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>rO–H monomer</td>
<td>2.90</td>
<td>2.90</td>
<td>2.90</td>
<td>2.91</td>
</tr>
<tr>
<td>rOH monomer</td>
<td>0.979</td>
<td>0.974</td>
<td>0.980</td>
<td>0.979</td>
</tr>
<tr>
<td>rC=O monomer</td>
<td>1.445</td>
<td>1.448</td>
<td>1.447</td>
<td>1.446</td>
</tr>
<tr>
<td>rH monomer</td>
<td>1.102</td>
<td>1.098</td>
<td>1.101</td>
<td>1.100</td>
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<tr>
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<td>117.5</td>
<td>108.1</td>
<td>107.5</td>
<td>107.5</td>
</tr>
<tr>
<td>μ monomer</td>
<td>1.819</td>
<td>1.831</td>
<td>1.824</td>
<td>1.819</td>
</tr>
<tr>
<td>νC=O monomer</td>
<td>3651</td>
<td>3667</td>
<td>3649</td>
<td>3643</td>
</tr>
<tr>
<td>νC=O monomer</td>
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<td>3024</td>
<td>3064</td>
<td>3062</td>
</tr>
<tr>
<td>δC=O monomer</td>
<td>2972</td>
<td>2958</td>
<td>2983</td>
<td>2977</td>
</tr>
<tr>
<td>νC=O monomer</td>
<td>2919</td>
<td>2919</td>
<td>2925</td>
<td>2919</td>
</tr>
<tr>
<td>τC=O monomer</td>
<td>1358</td>
<td>1345</td>
<td>1342</td>
<td>1334</td>
</tr>
<tr>
<td>νC=O monomer</td>
<td>988</td>
<td>962</td>
<td>995</td>
<td>990</td>
</tr>
<tr>
<td>τC=O monomer</td>
<td>361</td>
<td>293</td>
<td>328</td>
<td>324</td>
</tr>
</tbody>
</table>

a: HF frequencies scaled by the factor 0.89 [90].
b: SCF convergence of 10⁻⁶ on elements of the density matrix, gradient convergence of 10⁻⁶ Hartee bohr⁻¹ and a 'high' integration grid quality.
c: Frequencies were corrected for anharmonicity. Their final estimate for Δν, after higher correlation and BSSE corrections, is -126 cm⁻¹.
f: gas-phase [162, 161]. g: force constant calculation [161].
Table 4.3: DFT/BLYP calculated NMR absolute ($\sigma_{iso}$) and relative ($\delta_{TMS}$) isotropic chemical shifts and anisotropies ($\Delta\sigma$) of the methanol monomer and dimer (in ppm).

<table>
<thead>
<tr>
<th>Species</th>
<th>Quantity</th>
<th>DZVP/DZVP</th>
<th>TZVP/TZVP</th>
<th>TZ2P/TZVP</th>
<th>TZ2P*//TZVP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>IGLO</td>
<td>LORG</td>
<td>IGLO</td>
<td>LORG</td>
</tr>
<tr>
<td>Monomer</td>
<td>C</td>
<td>$\sigma_{iso}$</td>
<td>122.9</td>
<td>119.2</td>
<td>140.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta\sigma$</td>
<td>63.5</td>
<td>63.9</td>
<td>66.5</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$\sigma_{iso}$</td>
<td>35.7</td>
<td>26.8</td>
<td>37.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta\sigma$</td>
<td>16.9</td>
<td>29.7</td>
<td>-14.9</td>
</tr>
<tr>
<td>Dimer</td>
<td>acceptor C</td>
<td>$\sigma_{iso}$</td>
<td>123.9</td>
<td>118.0</td>
<td>138.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta\sigma$</td>
<td>54.7</td>
<td>61.7</td>
<td>78.4</td>
</tr>
<tr>
<td></td>
<td>donor C</td>
<td>$\delta_{TMS}$</td>
<td>48.2</td>
<td>50.4</td>
<td>52.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_{iso}$</td>
<td>125.7</td>
<td>121.3</td>
<td>139.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta\sigma$</td>
<td>-16.3</td>
<td>42.5</td>
<td>79.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\delta_{TMS}$</td>
<td>46.4</td>
<td>47.1</td>
<td>51.0</td>
</tr>
</tbody>
</table>

a: uncontracted basis set
spectra of methanol and its dimer were calculated for the BLYP/DZVP and BLYP/TZVP optimised structures. NMR spectra were calculated using the individual gauge localised orbitals (IGLO) [163] and the localised orbitals/local origin (LORG) [164] methods as implemented in DGauss 3.0, and using the gauge invariant atomic orbitals method (GIAO) [165] as implemented in Gaussian-94. All methods involve introducing a local gauge origin to define the vector potential of the external magnetic field. The latter method applies a local gauge origin for each atomic orbital at the atomic centre. The former two methods approximate the GIAO method by applying gauge factors to localised molecular orbitals. Following Haase and Sauer [62], absolute isotropic chemical shifts ($\sigma_{\text{iso}}$) have been related to relative shifts ($\delta_{\text{TMS}}$) using the formula,

$$\delta_{\text{TMS}}(\text{complex}) = \delta_{\text{TMS}}(\text{CH}_3\text{OH}) + \sigma_{\text{iso}}(\text{CH}_3\text{OH}) - \sigma_{\text{iso}}(\text{complex}), \quad (4.2)$$

where, $\delta_{\text{TMS}}(\text{CH}_3\text{OH})$ is taken as the experimental $^{13}\text{C}$ NMR gas phase value of 49.2 ppm [166] and the $\sigma_{\text{iso}}$ are calculated; i.e., we use methanol as an internal standard.

Calculated NMR isotropic chemical shifts ($\sigma_{\text{iso}}$) and anisotropies ($\Delta\sigma$) for methanol and its dimer are shown in Table 4.3. As it is difficult to compare calculated absolute chemical shielding constants for discrete gas phase species with experiment, the current aim is to gain information on the use of different methods for calculating these magnetic properties and
the problem of convergence of these calculated properties with basis set size. The notation basis-1//basis-2 will be used to signify, respectively, the basis set used for calculation of the magnetic properties and that used for optimisation of the relevant structure.

It is clear that a large basis set (TZ2P) is required in order to get reasonable agreement between results of chemical shielding constants and anisotropies from IGLO and LORG calculations. Smaller basis sets lead to substantial differences in the isotropic shifts and very poor descriptions of the individual components of the chemical shift tensor (highlighted by the value of the anistropies). However, even when employing the TZ2P basis set, the IGLO and LORG results are not converged with respect to those from GIAO calculations. The improved convergence of these magnetic property calculations with the GIAO method has been noted previously [165], and indeed, Table 4.3 indicates that in order to approach convergence of the absolute IGLO, LORG and GIAO results, an extremely flexible basis set is required. Although the calculated absolute chemical shifts for carbon (unlike those for hydrogen) have not converged at the TZ2P//TZVP level, the relative shifts, $\delta_{\text{TMPS}}$, of the methanol dimer's carbon centres have (to within about 0.2 ppm). Use of different auxiliary basis sets (DGauss) or higher quality integration grids and convergence criteria (results not shown) was found to have little effect on the absolute chemical shifts and anistropies.

4.2 Transition State Properties and Cluster Size Effects

Following the discussion of the ability of different quantum chemical methods and basis sets to predict the properties of equilibrium structures, this section will look at similar questions concerning transition state structures. Specifically, the section aims to address the uncertainty in the methods for calculating activation barriers for processes on alumino-silicate clusters.

Two elementary reaction steps have been chosen for this purpose, as shown in Figure 4.3. The first step, formation of a surface bound ethoxy group, can be considered to be 'covalent' in nature whilst the second step,
deprotonation of the ethoxy species to form adsorbed ethene, is 'ionic' in nature. All structures were fully (geometry) optimised without use of symmetry constraints. Figure 4.3 shows only HF optimised structures, although HF, LDA, BLYP, BP86 and B3LYP structures are all within 0.2Å and a few degrees of each other, i.e., are qualitatively similar.

Table 4.4 shows the calculated energy changes along the reaction path shown in Figure 4.3, i.e., using a 1T cluster, \((\text{HO})_2\text{Al}(\text{X})\text{H}, \text{X} \text{ being H, CH}_3 \text{ or CH}_2\text{CH}_3\). It is immediately clear that there is a large variation in the calculated energetics, especially as regards HF, HF/MP2 and pure DFT methods. It is well known that HF theory overestimates activation barriers due to the weakness that single-determinant wavefunctions show in describing adiabatic transition states for which complicated electron correlations (ground-excited state mixings) are crucial [101]. This effect can be seen in Table 4.4. MP2 correction of the HF energies at the HF stationary points helps to remedy this problem but the MP2//HF energy changes are still up to \(\sim 125 \text{ kJmol}^{-1}\) larger (in magnitude) than those arising from pure DFT. In order to understand better which method is more appropriate, and in the absence of experimental activation barriers for these processes, the calculations were repeated using the B3LYP/6-31G** recipe. This method has been shown to be superior to pure, gradient-corrected DFT and MP2//HF methods [167] and will be considered, for the present purpose, to produce the 'exact' energies; Table 4.4 shows the results. It is apparent then that pure DFT gives a lower bound and MP2//HF gives an upper bound to the energy changes, i.e. with an error of \(\pm 30\%\) respectively.

Further points to note from this study are first, the surprising accuracy of the BLYP//LDA combination which really only fails to describe the weak Z0Et...H2O interaction \(\langle \Delta E_3 \rangle\) and secondly, the fact that differences in the MP2//HF and pure DFT results are much larger for the 'covalent' first step than the 'ionic' second step.

Table 4.5 compares the MP2//HF results for the reaction shown in Figure 4.3 over 1T and 5T alumino-silicate clusters. Clearly the energy changes are very close, the errors being smaller than those associated with using MP2//HF or pure DFT methodologies. We conclude therefore that the dominant contribution to the energy differences comes from changes in local
Figure 4.3: HF optimised structures along the pathway for reaction of methanol at a methylated alumino-silicate Brønsted acid site (ZOMe) modelled by a 1T cluster. The first step involves formation of a surface ethoxy group (ZOEt) while the second step involves deprotonation to form adsorbed ethene and a new Brønsted acid (ZOH). The labels refer to intermediates (int-) and transition states (ts-).
Table 4.4: Calculated energetics for the reaction shown in Figure 4.3 over a 1T model alumino-silicate Brönsted acid site: comparison of quantum chemical methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_1$</td>
</tr>
<tr>
<td>HF/6-31G**</td>
<td>514</td>
</tr>
<tr>
<td>MP2/6-31G**//HF/6-31G**</td>
<td>465</td>
</tr>
<tr>
<td>BLYP/DZVP//LDA/DZVP</td>
<td>386</td>
</tr>
<tr>
<td>BLYP/DZVP//BLYP/DZVP</td>
<td>382</td>
</tr>
<tr>
<td>BP86/DZVP//BP86/DZVP</td>
<td>383</td>
</tr>
<tr>
<td>B3LYP/6-31G**//B3LYP/6-31G**</td>
<td>409</td>
</tr>
</tbody>
</table>

bonding and that it is more important to use an accurate quantum chemical method than it is to use large, computationally expensive clusters. This conclusion does not, of course, take into account the effect of non-local electrostatic, polarisation or steric constraints on the cluster due to the host framework. These effects have been analysed in some detail by Sherwood et al. [141] using a new QM/MM approach. They concluded that the steric constraints imposed by the framework on the cluster geometry made the largest impact on the calculated reaction profile.

4.3 Summary

The ability of different quantum chemical techniques to describe equilibrium properties of the water and methanol dimers have been studied. The quality of the predicted equilibrium geometries can be ordered as follows: HF $<$ BP86 $<$ BLYP $<$ MP2 $\approx$ B3LYP, although the differences are not huge. As previously reported, bond lengths are overestimated by around 0.01Å [168, 169, 170, 171, 172] and underestimated by around 0.02Å [90] by
Table 4.5: Calculated energetics for the reaction shown in Figure 4.3 over a 1T and 5T model alumino-silicate Brønsted acid site: effect of cluster size.

<table>
<thead>
<tr>
<th>Method</th>
<th>Cluster</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Delta E_1$</td>
</tr>
<tr>
<td>HF/6-31G**</td>
<td>1T</td>
<td>514</td>
</tr>
<tr>
<td></td>
<td>5T</td>
<td>504</td>
</tr>
<tr>
<td>MP2/6-31G**//HF/6-31G**</td>
<td>1T</td>
<td>465</td>
</tr>
<tr>
<td></td>
<td>5T</td>
<td>465</td>
</tr>
</tbody>
</table>

pure DFT and HF methods respectively. The calculated interaction energies of the water and methanol dimers are also similar, and again, the quality of the results can be ordered as HF < MP2//HF ≈ pure DFT < MP2 ≈ B3LYP although it is noted that basis set superposition can lead to considerable error when calculating these relatively weak interactions. Of particular importance is the observation of errors in the calculated vibrational frequencies using pure DFT and HF theories. Pure, gradient-corrected DFT results in harmonic vibrational frequencies that are often in good agreement with anharmonic experimental frequencies, i.e., that are too low, but compound errors lead to shifts of $\nu_{\text{OH}}$ on hydrogen bond formation that are too large. In this context, BP86 is particularly poor, especially when multiple, coupled OH groups are present. Scaled HF harmonic frequencies, whilst often in good agreement with experiment, show large errors in the case of hydrogen-bonding situations as can be seen, for example, in the large $\nu_{\text{OH}}$ of the donor molecule of the methanol dimer which leads to a very small shift on dimer formation.

Turning to the calculations of NMR properties, convergence of chemical shifts using the BLYP functional and all three IGLO, LORG and GIAO methods is found to be difficult for carbon, with absolute shifts ($\Delta \sigma$) prob-
ably not fully converged using the large uncontracted TZ2P basis set. The situation for hydrogen is much better. Relative chemical shifts ($\delta_{\text{NMR}}$) for carbon are, for practical purposes, converged at the TZ2P//TZVP level. As previously reported [165] the GIAO method leads to the best convergence of the calculated NMR properties.

The calculation of transition state properties, particularly activation barriers, was shown to be more difficult than calculation of equilibrium properties. MP2//HF and pure DFT methods were shown to give, respectively, upper and lower bounds to activation barriers (using the assumption that the B3LYP/6-31G** method represents the 'exact' result). Geometries at all levels, HF, BP86, BLYP, LDA and B3LYP were found to be within 0.2Å and $\sim 10^\circ$ of each other. In addition, it has been shown that for the 'covalent' and 'ionic' reaction steps tested, cluster size effects are negligible indicating that the dominant contribution to the barrier is from local changes in bonding.

In conclusion, the pure, gradient-corrected DFT results give, on average, better geometries than the HF method (although they are all qualitatively similar), give harmonic frequencies that are comparable to experiment, i.e., that are too low, but that are more trustworthy than 0.89 scaled HF frequencies and give equilibrium interaction energies in reasonable agreement with experiment, B3LYP, MP2//HF and MP2 calculations. Reactions profiles are bounded from above by MP2//HF and from below by pure DFT (by $\pm 30\%$) and cluster size effects appear small. Part II will now look in some detail, using 3T and 4T clusters, BLYP and HP//MP2 methods, at aspects of the Methanol to Gasoline Process. Part III will follow with extensive study at the BP86 level of Ti(IV)-silicate partial oxidation catalysis.
Part II

The Methanol to Gasoline (MTG) Process
Part II Abstract

This Part of the thesis describes quantum chemical calculations on possible reaction paths for formation of the first C-C bond from methanol reacting over Brönsted acidic zeolites. The discussion begins with a detailed survey of previous experimental and theoretical literature (Chapter 5). Chapters 6 and 7 continue with BLYP/DZVP and MP2/6-31G**//HF/6-31G** cluster calculations of the methyl-oxonium ion pathway for methanol conversion within the cluster approximation. It is concluded that the current quantum chemical methods and models are not sufficiently accurate to determine the dominant reaction mechanism, although it is suggested that a probable pathway for initial C-C bond formation is as shown in Scheme 1, with steps 3 and 4 being rate determining.

![Scheme 1](image)

Comparison of the calculated activation barriers with experiment is difficult but it is noted that both the current calculations and those of Blaskowski
and van Santen [173, 143, 144, 174] lead to activation energies for the rate determining step that are substantially larger than those observed experimentally. We suggest that this problem is due to a combination of approximate theoretical methods and models and to the difficulty in interpreting thermodynamic data from experiment.
Chapter 5

MTG : Literature Review

5.1 The Methanol to Gasoline (MTG) Process : General

The MTG process was first reported in the mid 1970s[175] and has since attracted a great deal of research in an attempt to elucidate the detailed mechanism of this Brønsted acid catalysed reaction. The reasons behind such interest stem, in part, from the obvious industrial interest in having an efficient alternative to crude oil based sources for the production of gasoline range hydrocarbons. However, there is also great academic interest in understanding the mechanism of this prototypical Brønsted acid catalysed process.

Despite all efforts, mechanistic detail concerning the formation of the first C–C bond during methanol conversion has been elusive. We will begin our computational study of the MTG process by first reviewing the most important literature concerning mechanistic aspects of the reaction, derived both from experiment and theory, that has been reported over the last 20 years.

5.2 Experimental literature studies

The following sections are structured in order to compare and contrast the various proposed mechanisms for the methanol to gasoline (MTG) process
over highly siliceous, intermediate pore size, acidic zeolites, e.g., \( \text{H-ZSM-5} \). Other catalysts are also known to be active for this reaction, for example, zinc halide supported aluminium sulphates, phosphorous pentoxides, poly-phosphoric acid and \( \text{WO}_3 \) supported on \( \gamma \)-alumina. However, only \( \text{H-ZSM-5} \) has an extended lifetime for the process without formation of excessive methane.

General observations about the MTG process will be followed by a sequential discussion of the various mechanisms.

5.2.1 General observations and primary products.

Experimental measurements have shown that a wide variety of products in the \( \text{C}_1-\text{C}_5 \) hydrocarbon range are formed in the MTG process over \( \text{H-ZSM-5} \). The selectivity of the process appears to vary with feed rate, temperature, catalyst preparation and methanol/water partial pressures. Figure 5.1 shows the change of reactants and products with catalyst contact time for methanol reacting over \( \text{H-ZSM-5} \) at 371°C (Chang and Silvestri [176]).

![Figure 5.1: Change of reactants and products with contact time [176]](image)
We note that the process is subject to an induction period with methanol, dimethyl ether or a mixture of both reacting to form hydrocarbons. These observations were made as early as 1977 but it was not until 1992 that clear spectroscopic evidence was reported for this initial methanol, water, dimethyl ether equilibrium (via in-situ solid state NMR [76]).

In order to extract information pertinent to the formation of initial products, conditions of very low conversion need to be studied. Even under these conditions, studying initial events is still difficult as secondary reaction of the primary products appears to be faster than their formation [177, 178]. Difficulties also arise from the heterogeneous nature of the process. The problem of identifying the first formed hydrocarbon products has been tackled by chemical studies in two ways,

1. Extrapolation of data based on ethene/propene product ratio. Haag et al.[179] used this procedure to suggest that methane and ethene were primary products. Extrapolation however has been severely criticized (see page 283 of reference [177]),

2. Use of less reactive alcohols, ethers, esters etc. than methanol after the observation that H–ZSM–5 could convert a wide range of chemical species to hydrocarbons [176]. Hutchings et al. [180]) used this approach to infer that methane and ethene were the first formed hydrocarbons.

As noted, spectroscopic observation of the formation of ethene and ethylmethyl ether at the onset of hydrocarbon formation (523K) was first reported by Munson et al.[76] using in-situ solid state NMR spectroscopy. They suggested the in-pore ethene, methanol and ethylmethyl ether equilibrium shown below (although their observation was dependent on catalyst activation and water content).

\[
\text{CH}_3\text{CH}_2\text{OCH}_3 \rightleftharpoons \text{CH}_3\text{OH} + \text{CH}_2 = \text{CH}_2
\] (5.1)

A more detailed discussion of reaction mechanisms reported in the open literature will now be presented.
5.2.2 Mechanisms of initial C-C bond formation.

Many mechanisms have been proposed for formation of the initial C-C bond during methanol conversion. Before they are discussed, however, we shall comment on experimental measurements of the energetics of methanol conversion. Due to the difficulties encountered in analysing calorimetric or similar experiments in terms of individual reaction events, few such studies have been reported. Two however are worthy of note.

Bandiera and Naccache [181] studied the dehydration of methanol over dealuminated H-Mordenite at 473 to 573K. Their analysis, in terms of a Langmuir-Hinshelwood model resulted in an estimate of 80 kJmol⁻¹ for the true activation barrier for dimethyl ether formation. They interpreted their results in terms of a reaction involving neighbouring zeolitic acid and basic sites as shown in Figure 5.2. In the Figure 5.2, species II represents

\[
[2\text{CH}_3\text{OH} + \text{ZOH}] \rightarrow [\text{ZOCH}_3 + \text{CH}_3\text{OH} + \text{H}_2\text{O}]_{\text{ads}} \rightarrow [\text{ZOH} + \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}],
\]

Figure 5.2: Formation of dimethyl ether from methanol at a alumino-silicate Brönsted acid site (ZOH) via a surface methyl-oxonium ion (ZOCH₃) as suggested by Bandiera and Naccache [181].

the surface methyl-oxonium with the second methanol molecule adsorbed on an adjacent basic lattice oxygen. This process has now been studied in some detail theoretically and will be discussed in Section 5.3. Bandiera and Naccache also observed that product H₂O and CH₃OCH₃ competed for adsorption on the zeolitic acid sites at low (473K) temperatures, explaining the effect of H₂O on the observed induction time for catalysis (see Figure 5.1).

More recently, Jayamurthy and Vasudevan [182] have reported a temperature programmed surface reaction study of methanol conversion over H-ZSM-5. Their method was able to delineate two main steps for hydrocarbon formation which they interpreted as:

1. dehydration of methanol to form dimethyl ether and
2. conversion of dimethyl ether to generate hydrocarbons.
The activation barriers associated with each step (based on observation of the temperature at which \( \text{H}_2\text{O} \) is desorbed) were 108 and 195 \( \text{kJmol}^{-1} \) respectively. Further, Jayamurthy and Vasudevan reported methanol/dimethyl ether coadsorption experiments to show that it was unlikely that methanol played any rôle in the second step of the reaction.

We will continue with a discussion of a number of popular reaction mechanism that have received some measure of experimental verification.

5.2.2.1 The Carbene Mechanism.

A series of proposals by different workers (see the discussion in [177]) led to the suggestion that a carbene pathway could be operative during methanol conversion over H-ZSM-5. Chang and Silvestri [176] concluded that \( \alpha \)-elimination of water by the concerted action of acid and base sites within the zeolite pores could lead to formation of a \( \text{C}_1 \) carbene species \( \cdot \text{CH}_2 \). They believed that insertion of this carbene into the \( \text{C}-\text{O} \) bond of methanol or dimethyl ether was likely to be responsible for the initial \( \text{C}-\text{C} \) bond (as opposed to carbene polymerisation). See Figure 5.3.

\[
\text{B}^- + \text{H-CH}_2\text{-OH} + \text{H-B} \rightarrow \text{B-H} + \cdot \text{CH}_2 + \text{H}_2\text{O} + 
\]

\[
\cdot \text{CH}_2 + \text{CH}_3\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OH}
\]

Figure 5.3: Carbene mechanism for \( \text{C}-\text{C} \) bond formation (from [177]).

Ethene could then be formed as in Equation 5.1 or by dehydration of ethanol as in Equation 5.2, shown below [76].

\[
\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_2 = \text{CH}_2 \quad (5.2)
\]

Chang and Chu (ref. 41 of [177]) provided indirect evidence on the mechanism by trapping the reactive \( \text{C}_1 \) intermediate from \( ^{13}\text{C} \) labelled methanol with unlabelled propane. They employed conditions under which they considered propane to be unreactive. Analysis of the i/n ratio (branched to straight chain ratio) and the isotopic distribution of the butane products were thought to be consistent with the insertion of a carbene into the \( \text{C}-\text{H} \)
bond of propane. This experiment has been the subject of a great deal of
criticism, specifically, the assumption that propane is not inert under the
reaction conditions employed [183].

Chemical modelling experiments have been attempted in order to investi­
gate the behaviour of carbenes as reactive intermediates. Lee and Wu [184]
used CH₂N₂ as a carbene source. They found that although CH₂N₂ generates
CH₂CH₂ in the absence of H-ZSM-5 its formation is enhanced in its presence.
However, Olah et al. [185] in attempting to induce singlet carbene insertion
into the C-O bond of trimethyloxonium, (CH₃)₃O⁺, salts, showed that CH₂N₂
is more likely to be protonated by the acidic zeolite, methylating a second
CH₂N₂ to form a C-C bond, i.e., opposing this experimental ‘evidence’ for the
carbene mechanism.

More recent studies of the MTG process over H-ZSM-5 and WO₃/γ-Al₂O₃
have also criticized the carbene mechanism. Hunter and Hutchings [186] co­
fed H₂/CH₃OH over WO₃/γ-Al₂O₃ and H-ZSM-5 under a range of conditions and
conversions. They found in all cases that methane selectivity was similar to
selectivities in the absence of H₂. This suggests that free :CH₂ is not present
as it is known to readily insert into H₂. They also demonstrated that the
reaction is mechanistically different over the two catalysts (see also ref. 29
and 52 of [177]). Thus, although free carbene species are probably not
present during methanol conversion, surface stabilised carbene species may be.
It is quite possible that the two types of carbene (singlet and triplet)
have different properties. In fact, some early ab-initio quantum chemical
studies by Drenth et al. [187] indicated that carbenes can be stabilised in
the zeolite framework.

5.2.2.2 The trimethyloxonium (TMO) ion mechanism.

This mechanism was proposed by van den Berg et al. [188] and Olah [189] for
methanol conversion over H-ZSM-5 and WO₃/γ-Al₂O₃ respectively. However,
as previously noted, Hutchings and Hunter have since shown that the process
displays mechanistic differences over the two catalysts [186, 190, 191].

The mechanism involves formation of a trimethyloxonium ion, (CH₃)₃O⁺,
as a crucial intermediate, as shown in Figure 5.4, and the central question is
whether the conjugate base form of the acidic zeolite is basic enough to deprotonate a non-bonded intermediate to form dimethyl oxonium methylide.

\[
\text{CH}_2\text{OCH}_3, \text{CH}_3\text{OH} \xrightarrow{-\text{KOH}} (\text{CH}_3)_2\text{O}^+ \xrightarrow{\text{basic site}} (\text{CH}_3)_2\text{O}^+\text{CH}_2^-
\]

\[
\text{CH}_3\text{OCH}_3 \quad \text{or CH}_3\text{OH} \quad \text{Steven's Reaction}
\]

\[
\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{OCH}_3 \xrightarrow{\text{z}^+} (\text{CH}_3)_2\text{O}^+\text{CH}_2\text{CH}_3 \quad \text{CH}_3\text{CH}_2\text{OCH}_3
\]

Figure 5.4: The trimethyloxonium ion mechanism for methanol conversion.

This question has been tackled by Hunter and Hutchings (ref. 61 of [177]) who used chemical modelling techniques to discover whether the Al-0 moiety of the zeolite is nucleophilic or basic in its action towards TM0. Reaction of TM0\textsuperscript{+}SbCl\textsubscript{5} with LiAl(O\textsuperscript{4}Pr\textsubscript{4}) (a model for the zeolite conjugate base), gave results consistent with either methylation of the isopropoxide or nucleophilic chloride attack. No products resulting from ylide formation were observed.

A range of methylating agents were also used including the known ylide precursor (CH\textsubscript{3})\textsubscript{3}S\textsuperscript{+}. No reaction with LiAl(O\textsuperscript{4}Pr\textsubscript{4}) was observed. This was thought to indicate that the zeolitic Al-0 moiety would be unlikely to form an ylide intermediate.

Hutchings et al. [192] have demonstrated that (CH\textsubscript{3})\textsubscript{2}S is less reactive over H-ZSM-5 than (CH\textsubscript{3})\textsubscript{2}O under comparable conditions, the same trend observed for CH\textsubscript{3}SH and CH\textsubscript{3}OH [176]. This was seen as evidence against the mechanism in Figure 5.4 since if deprotonation of TM0 is assumed to be rate determining, the sulphur analogue should be more reactive owing to d-orbital participation and polarisability effects.

Further evidence against this mechanism was provided yet again by Hunter and Hutchings (ref. 62 and 63 of [177]). They demonstrated that different methylating agents, CH\textsubscript{3}OH, CH\textsubscript{3}I and (CH\textsubscript{3})\textsubscript{2}SO\textsubscript{4}, reacted over ZSM-5 to give similar product distributions. This observation was thought to imply a common reaction path with the reagents acting as methylating agents. They considered the reaction of (CH\textsubscript{3})\textsubscript{2}SO\textsubscript{4} as particularly significant. In acidic conditions it displayed a similar reactivity to methanol, even though
the oxygens of \((\text{CH}_3)_2\text{SO}_4\) are expected to be less nucleophilic than those of \(\text{CH}_3\text{OH}\) under these conditions. It was thought unlikely that \((\text{CH}_3)_2\text{SO}_4\) and \(\text{CH}_3\text{OH}\) would generate similar levels of oxonium ions as required by the TMO mechanism to account for the relative reactivities. In basic conditions, \((\text{CH}_3)_2\text{SO}_4\) proved several orders of magnitude more reactive than \(\text{CH}_3\text{OH}\). Formation of an oxonium ion from \((\text{CH}_3)_2\text{SO}_4\) in basic conditions was thought to be highly unlikely suggesting that reaction does not proceed via a TMO central intermediate. Hunter and Hutchings concluded that if TMO was formed in the zeolite lattice, it was likely to act as a methylating agent, not an ylide precursor. This conclusion was supported by the NMR study of Chang [193], who synthesised TMO-ZSM-5 and monitored its decomposition at room temperature. The sample slowly decomposed to methylated ZSM-5 and physisorbed dimethyl ether. Methylated ZSM-5, or equivalently, ZSM-5 with surface methoxy species have now been observed during the reaction of methanol over H-ZSM-5 before the onset of hydrocarbon formation (see Section 5.2.2.4).

The formation of TMO has recently been observed using solid-state NMR spectroscopy by Munson and Haw [77] and Munson et al. [76] from dimethyl ether over H-ZSM-5. Similarly, ethyl dimethyl oxonium ion formation from ethyl methyl ether has been observed [76]. However, Munson et al. [76] found it difficult to reconcile their results with the mechanism in Figure 5.4 since,

1. oxonium ions were not observed in their experiments on methanol conversion, i.e., when methanol was present in quantities corresponding to 50-100% of the maximum adsorption capacity of the catalyst,
2. no spectroscopic signals suggestive of oxonium ylides were observed,
3. neither ethyl dimethyl oxonium or methyl ethyl ether formation has been observed from TMO,
4. the concentration of TMO (derived from dimethyl ether) decreases below detection limits at 400K, well before the onset of hydrocarbon formation at 473K.
Munson et al. [78] have also studied the stability of trialkyloxonium, trialkysulphonium and trialkylselenium ions in zeolites H-ZSM-5 and H-Y. The onium ions were formed by adsorption of the corresponding dimethyl chalcogenides. They found that at low coverage, dimethyl ether was physisorbed, protonation occurring as the temperature was raised (not observed over Na-ZSM-5). At higher coverage of dimethyl ether, TMO was observed, but only at temperatures below the onset of hydrocarbon formation. Further, they found that formation of the more stable sulphonium and selenonium ions resulted in quantitative titration of strong Brönsted sites and that the resulting onium ions did not form hydrocarbons even after prolonged heating at 523K. Trialkylonium ions did not form over γ-alumina, i.e., in the absence of strong Brönsted sites. In addition, partial loading of the zeolite with the stable onium species (<1 equivalent) permitted methanol conversion to proceed at a reduced rate. However the trimethylonium species were not consumed. Trialkyloxonium ions were not observed in the presence of excess methanol, unlike the trialkysulphonium and selenonium ions. This last result was explained on the basis of soft-hard acid-base theory. Briefly, methanol and dimethyl ether are hard bases (high electronegativity, low polarisability) whereas dimethyl sulphide and dimethyl selenide are soft bases (polarisable with possible d-orbital participation). Since \( \text{H}^+ \) is a harder acid than \( \text{CH}_3^+ \), hard-soft acid-base theory predicts that dimethyl ether should be preferably protonated and that dimethyl sulphide and dimethyl selenide should be preferably methylated. Protonated methanol is not a strong alkylating agent and thus although it will methylate dimethyl sulphide and selenide (both soft acid/bases), it will not readily methylate dimethyl ether. Therefore, trialkysulphonium and trialkylselenium but not trialkyloxonium ions are observed on reaction of the dimethyl chalcogenides with methanol.

Finally, Luk'yanov [194, 195] reported work in favour of the TMO mechanism. He studied the effect of \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio on the activity of H-ZSM-5 zeolites in different steps of the MTG process. He reported the formation of new catalytic sites in the presence of water vapour over relatively high aluminium content zeolites (\( \text{Si}/\text{Al} \approx 34 \)). These sites could also be generated by mild steaming. The sites were shown to display remarkably high
activity in the steps of alkene aromatisation and low activity in the steps of alkene formation from oxygenates. Luk’yanov further suggested that these enhanced activity sites could be very acidic hydroxyl groups formed from a bridging hydroxyl and a non-framework aluminium center acting as a strong electron acceptor. With this assumption about the nature of the enhanced activity sites, it appears that an increase in the hydroxyls acidity leads to a decrease in its ability to catalyse formation of the initial C–C bond. This is in agreement with the TM0 mechanism in which the critical step is ylide formation from TM0, the rate of which should increase with the basicity of the active center. The conjugate base of the enhanced activity hydroxyls appears to be so weak that C–C bond formation stops altogether. Note however that this argument could equally apply to any mechanism for which deprotonation is the rate determining step, e.g., the surface methyl oxonium ylide pathway, Section 5.2.2.4.

5.2.2.3 Free radical mechanism.

It has been known for some time that at elevated temperatures, dimethyl ether decomposes to form methyl radicals. This naturally raises the question of the possibility of a radical mechanism for the MTG process. Clark et al.[86] have reported the clearest evidence supporting involvement of radicals in methanol conversion. Using a spin trapping reagent they detected radicals by electron spin resonance during the reaction of dimethyl ether over H-ZSM-5. The use of spin trapping reagents made identification of the actual radical impossible. Clarke et al. suggested that the radical could be \( \cdot \text{CH}_2\text{OCH}_3 \) fragments formed from dimethyl ether at solid state defects. Clarke et al. further suggested three possible free radical pathways for formation of C–C bonds. See Figure 5.5.

Whether this was intended or not, Clarke et al.’s proposals have been interpreted in the literature as involving non-surface bonded species. Thus, path iii. of Figure 5.5 can be discounted on the basis of the \( \text{H}_2 \) co-feeding experiments Hunter and Hutchings used to discount the free carbene mechanism (see Section 5.2.2.1 and [186]). Further experiments by Hunter et al.[196] demonstrated that reaction of dimethyl ether over a known radical initi-
Figure 5.5: Free radical mechanisms for C-C bond formation [86].

ator (pre-dried dibenzoyl peroxide supported on celite) and over Na-ZSM-5 gave dimethoxyethane as product. Since no ethanol was observed, this was considered as evidence that path i. of Figure 5.5 was unlikely even though the CH₂OCH₃ species must have been formed. Reaction of dimethoxyethane over H-ZSM-5 was found to produce a different product spectrum from reaction of either dimethyl ether or methanol over this catalyst. This was interpreted as an indication that dimethoxyethane was unlikely to be an important intermediate in methanol conversion.

The most convincing reports refuting a radical mechanism have been supplied by Hunter et al. (see ref. 29 and 52 of [177]) in the form of O₂ and NO co-feeding experiments. Both diatomics are stable π-radicals, free O₂ being a diradical while free NO is a monoradical. It was thought that if MTG chemistry proceeded via a radical pathway then NO would scavenge these radicals leading to deactivation. Reaction of a radical species with O₂ on the other hand would not change the number of radicals present and thus cause no deactivation. It was observed that co-feeding O₂ with methanol or dimethyl ether resulted in rapid and irreversible deactivation of the zeolite whilst co-feeding with NO had no effect over the timescale of their experiment. In addition, if O₂ were reacting as a radical scavenger, deactivation should have been at least partially reversible. On the basis of these results, Hunter et al. concluded that direct involvement of radicals in the methanol conversion was unlikely and that it was more probable that an intermediate was susceptible to molecular oxygen.

Later NO co-feeding experiments by Chang et al. (see ref. 73 of [177])
noted that NO does in fact cause deactivation of the MTG process over H-ZSM-5 after an induction period dependent on the partial pressure of NO and the Al content of the zeolite. A deactivation pathway involving surface methoxy species was subsequently proposed (see pages 294-297 of [177]). Hutchings and Hunter [197] then showed that radical defects in the zeolite were not important in the initial steps of the MTG reaction by preloading H-ZSM-5 with NO.

5.2.2.4 The surface methyl oxonium mechanism.

As previously mentioned, surface methyl-oxonium species has been observed repeatedly by both FTIR [178, 56, 198, 199] and solid state NMR [76, 200, 201, 202, 203] during experiments on methanol conversion and trimethyl oxonium ion decomposition. Forester and Howe [56], Anderson et al. [201] and Salehirad and Anderson [202] actually observed the formation of surface methyl-oxonium species prior to the onset of hydrocarbon formation. Surface methyl-oxonium ions have also been implicated in the MTG process [192, 190, 204] who found the same product distribution when different methylating agents were passed over H-ZSM-5.

This experimental evidence points to the formation of a surface bound intermediate, a methyl-oxonium ion, as an initial reaction step. However, Hutchings et al. [192] argue that a single intermediate cannot explain the observed product distributions and their change with conversion and reaction time. Evidence for a second intermediate was provided by Mole [205, 205] in a study of the reaction of CH$_3$OH/D$_2$O over H-ZSM-5. His results indicate that hydrogen exchange in the methyl-oxonium intermediate must occur, note, however, that other works [206] have shown extensive label scrambling in H-ZSM-5). Hutchings et al.[207] repeated Mole's work at lower temperatures (240°C-290°C) and methanol conversions, aiming to show that Mole's results were applicable to the analysis of initial reaction events. Reaction of CH$_3$OD/H-ZSM-5 showed that as the temperature is increased, methanol conversion to hydrocarbons occurs at the expense of conversion to dimethyl ether. At very low conversions no incorporation of deuterium into dimethyl ether was observed. As the temperature (and therefore conversion) was
Figure 5.6: Surface methyl-oxonium ion mechanism [177].

raised, the level of deuterium found in all primary reaction products (dimethyl ether, ethene, methane) increased. $\text{CH}_3\text{OCH}_3/\text{CD}_3\text{OCD}_3$ were also reacted in equal proportions over pre-deuterated ZSM-5 at 220°C and 249°C. Very rapid exchange of CD$_3$ units to form CD$_3$OCH$_3$ was observed even at 220°C (9% dimethyl ether conversion). However, the level of deuterated ethene and methane present was lower than expected on the basis of the overall level of deuterium. The result was thought to indicate that ethene is more readily derived from a C$_1$ intermediate containing hydrogen rather than deuterium — a primary isotope effect. Hutchings et al. also suggested that the C$_1$ intermediate leading to ethene must be different from that lead-
ing to dimethyl ether on the basis that if there was only one intermediate, similar isotope distributions would be expected.

These results were used by Hunter, Hutchings and coworkers [192, 190] to suggest a two step mechanism in which deprotonation of the surface methyl-oxonium species results in formation of a surface bound methylide intermediate, iso-electronic with a surface associated carbene. This was thought to be the crucial intermediate in initial C–C bond formation. The primary isotope effect mentioned above was considered to be consistent with slow formation of this surface methylide species by loss of $\text{H}^+$. See Figure 5.6.

Indirect evidence for the surface bound methylide comes from the dioxygen co-feeding experiments mentioned in the section from page 88. Rapid irreversible deactivation was observed on co-feeding $\text{O}_2/\text{CH}_3\text{OH}$ or $\text{O}_2/\text{CH}_3\text{OCH}_3$ [190]. Reaction of the surface oxonium methylide with $\text{O}_2$ is expected to form formaldehyde which is known to cause rapid deactivation.

The surface methyl-oxonium ion mechanism is the only one proposed that accounts for production of methane explicitly. A similar proposal for methane production alone was also suggested by Munson et al. [76] who showed (using in-situ solid state NMR) that methane was not produced from cracking processes at 523K or from radical decomposition of dimethyl ether. However, they suggest that hydride abstraction from hydrocarbons, not methanol, as in Figure 5.6 accounts for methane production. Methane was only observed from reaction of methanol.

More recently, Salehirad and Anderson have reported a detailed study of the MTG process over the less acidic H–SAP0–34 catalyst using $^{13}\text{C}$ NMR spectroscopy. Use of this catalyst, rather than the more reactive H–ZSM–5, was considered to be more appropriate to the study of initial events. Their work clearly points to the importance of surface methyl-oxonium ion intermediates which were unambiguously characterised in a sample loaded with a 1:1 methanol to Brönsted acid site ratio at temperatures as low as 473K. In all experiments methane, ethene and dimethyl ether were formed as primary products. Their results also suggest, in contrast to other reports [208, 209], that ethene forms in a similar way to that shown in Figure 5.6 and that higher hydrocarbons form from stepwise alkene methylation via surface methyl-oxonium groups. The observation of isobutane as the highest con-
centration hydrocarbon product in all of their experiments is then explained on the basis of carbenium ion stability. Formation of methane as a primary product was considered as being consistent with the methyl-oxonium ion pathway.

More details concerning this mechanism are described in reference [177].

5.2.2.5 The CO catalysed mechanism.

In 1990 Jackson and Bertsch [210] proposed a mechanism for formation of the first C–C bond during methanol conversion over H-ZSM-5. They based their proposal on the homogeneous MTG reaction involving polyphosphoric acid (PPA) which occurs at the mild temperature of 200°C. They made the assumption that MTG chemistry in PPA and over H-ZSM-5 are mechanistically similar. Jackson and Bertsch argued that past proposals for the mechanism of methanol conversion involved some unlikely looking exotic species. They particularly disliked the idea of deprotonating methyloxonium ions to form methylide species, a feature of all the non-radical mechanisms discussed so far. They argued that no direct evidence of the methylide species has been reported and that model chemical studies indicate that extremely strong base, for example, sodium hydride are required for their formation. Jackson and Bertsch considered as significant the in-situ solid-state NMR observations of Anderson and Klinowski [75, 166] who observed CO as one of the first formed species during methanol conversion and who suggested that it may actually be the active catalyst. Carbon monoxide however has not been observed in all studies and it may be that catalyst preparation, feed rate, conversion etc. are important in this respect.

Jackson and Bertsch carried out an NMR study of the homogeneous PPA-methanol system. Central to their report was an observation that CD₃OD/PPA did not generate products in which ¹H was substituted into the methyl groups attached to oxygen. This is markedly different to the work of Mole [205, 211] and Hutchings et al. [207] whose results for H-ZSM-5 led to the surface methyl-oxonium mechanism shown in Figure 5.6. Jackson and Bertsch proposed a scheme in which CO is the active catalyst and in which ketene, O=C=CH₂, is a transient intermediate. See Figure 5.7.
Jackson and Bertsch accompanied their NMR work with an *ab-initio* study using a MP2/6-31G/*//HF//6-31G/* level of theory and including vibrational and thermal corrections. The acid site was not included explicitly in their calculations as they considered that it should be treated as a source of medium to strong Brønsted acidity with no special properties. The CO pathway was found to be energetically reasonable for a process at 200°C whilst the methylxonium pathway (active site not represented) was found to be extremely endothermic.

Other experimental work supporting CO as an active catalyst comes from Derouane et al. (ref. 9 of [210]) who studied the effect of adding CO to the methanol/H-ZSM-5 system. They found that CO reduces or eliminates the induction period before hydrocarbon production.

Despite this, Hutchings et al. [207] concluded in a recent report that CO plays no significant mechanistic role in the formation of the primary products of methanol conversion, either as an intermediate or as a catalyst. They demonstrated that CO added to the feed stream during MTG chemistry over zeolite H-Y had little effect on the induction period; they demonstrated that for a variety of methylating agents under a variety of conditions, ketene

$$
\text{CH}_3\text{CH}_3 \xrightleftharpoons{\text{base}} [\text{CH}_3\text{O}]^+ + \text{CH}_3 \xrightarrow{\text{base}} \text{CH}_3\text{CH}_3
$$

Figure 5.7: CO catalysed mechanism via ketene [210].
never produced products consistent with its methylation, an important step in Figure 5.7; they showed that $^{13}$CO is not incorporated into MTG products, and they carried out the labelling experiments discussed earlier (page 90) to show that isotope exchange of methyl protons occurs in the initial stages of methanol conversion over H-ZSM-5.

5.3 Theoretical literature studies

Theoretical studies on the methanol to gasoline process are far less numerous than their experimental counterparts. The greatest obstacle to progress in this respect has been the computational expense of performing high quality ab-initio or first-principles calculations on solid-adsorbate systems [17, 19]. This difficulty has severely limited the scope to which quantum chemical techniques can usefully contribute to the problem of methanol reactivity inside the pores of zeolites. However, advances and availability of computer technology together with the continuing development of efficient computer codes has enabled the computational chemistry community to begin to make an impact on this field.

The following sections will outline the more recent theoretical work pertaining to the mechanism of the MTG process.

5.3.1 General Observations

The local structure of alumino-silicate Brønsted acid sites is now widely believed to consist of the bridging hydroxyl unit [A10(H)Si]. It has been extensively studied with a range of quantum chemical techniques [17, 19, 212, 213, 214, 215, 100] and forcefield methods, e.g., [216], and will not be discussed further except to note that the calculated proton affinity of the bridging hydroxyl, a property dependent on the ability of the system to stabilise charge, is extremely sensitive to the size of the molecular fragment being used to model it [215], i.e., the energy of the negative conjugate base is sensitive to long range polarisation effects which converge slowly with cluster size. Indeed, the calculated values of the proton affinity have been reported to oscillate markedly on addition of extra shells to small cluster models[215]. Fortuitously however, even small 3T clusters reproduce the proton affinity
of alumino-silicate Brönsted acid sites within experimental bounds. Periodic DFT [217, 218] and combined quantum-chemical/analytical-potential models (QM/MM) [140, 219, 141] have made substantial contribution to this type of problem.

Given knowledge of the active site, the initial step in any reaction study is the characterisation of the reactant–active site complex. In the present case this is the methanol adsorbed at the acid site. The primary question is then whether the methanol preferentially forms a physisorbed (\(\text{CH}_3\text{OH}...\text{HOZ}\)) or a chemisorbed (\(\text{CH}_3\text{OH}^+...\text{HOZ}\)) complex (Z represents the zeolite or alumino-silicate bulk). This particular problem will be discussed more extensively in the next section. At this stage it is worth commenting on the difficulty of describing proton transfer processes quantum chemically. Allavena et al. [100] have summarised studies of proton transfer processes in zeolites (within the cluster approximation). An illuminating example of the difficulties associated with a quantum mechanical analysis of such problems is highlighted by calculations of ammonia adsorption. Figures 5.8 shows the HF//HF/6-31G* and MP2//HF/6-31G* (see Section 3.2.2, Chapter 3, for a description of the notation) calculated reaction coordinates for proton transfer from 2T and 3T alumino-silicate acid sites to adsorbed \(\text{NH}_3\). Two features are immediately apparent. The first is that choice of a representative fragment of the alumino-silicate acid site is crucial due, in this case, to the importance of hydrogen bonding to multiple lattice oxygens. The second is that inclusion of electron correlation (here at the MP2 level) is critical in order to get potential energy surfaces that are even qualitatively correct.

On a different note, application of quantum chemical techniques to reactions in condensed matter suffers from having little or no direct experimental results with which to compare. It is thus difficult to judge the quality of the calculations. Two experimental techniques that have been used extensively for this purpose are infra-red/Raman vibrational spectroscopy (we refer to Section 2.3, Chapter 2) and solid state NMR spectroscopy (see Section 2.4, Chapter 2) of the reacting species in-situ. However, it is now commonly believed that these techniques (particularly the former) give spectra that cannot, for example, differentiate between chemisorbed and physisorbed methanol [41, 220, 200]. For a more complete discussion of the methodological
Figure 5.8: Calculated reaction coordinates for proton transfer from a 2T (top) and 3T (bottom) Brönsted acid site model to adsorbed NH$_3$[100]. ZOH represents the acid site, B represents NH$_3$.

problems involved in quantum mechanical calculations of alumino-silicate systems, see Section 3.3, Chapter 3.

Despite these problems there has been some successful applications of quantum chemical techniques to simple reactions in zeolites. A recent example is the H/D isotope exchange of methane [221, 222] at zeolitic Brönsted acid sites. Kramer et al. [222] rationalised the different rates of this reaction in faujasite and MFI type zeolites by showing that oxygens of the acid site had different proton affinities depending on their specific location i.e., on the zeolite structure. Differences in proton affinity of these oxygens were shown to be responsible for the observed variation in rates.
The following sections now review first the work on methanol adsorption at Brönsted acid sites and secondly the small, but rapidly increasing, number of studies of reactivity at Brönsted acid sites.

5.3.2 Methanol adsorption at Brönsted acid sites

Initial methanol adsorption at Brönsted acid sites has important implications for methanol conversion in alumino-silicates. Proton transfer to form bound methoxonium ions (CH$_3$OH$_2^+$) would obviously activate the methyl carbons towards nucleophilic attack (either by polarising the carbon centre or by improving the stability of the leaving group). Initial adsorption also represents the simplest problem that can be tackled by quantum chemical techniques. Bates and Dwyer [223] studied methanol adsorption using a 3T model cluster to represent the Brönsted acid site. At the HF/6-31G* level and imposing $C_2$ symmetry, they reported a proton transfer energy of 5.7 kJmol$^{-1}$ (see Table 5.1). Similar work by Sauer et al. [224], also imposing $C_2$ symmetry, reported a favourable heat of reaction for proton transfer of -6 kJmol$^{-1}$. They observed distinct minima corresponding to both physisorbed and chemisorbed species.

Gale et al. [220] reported a similar study using BP86/DZVP density functional theory techniques and found only one minimum energy structure corresponding to the physisorbed species. No symmetry contraints were used. They considered the chemisorbed structure reported previously to be a transition state for proton transfer between two framework oxygens, indicating that use of symmetry constraints, rather than an inadequacy in the method, was responsible for the different results. These conclusions have now been reported by a number of authors [124, 62, 173, 225, 226, 41]. Gale et al. [220] also analysed the Mulliken charge distributions of the physisorbed complex but found no significant perturbation of the methyl group's charge distribution on adsorption. They concluded that adsorption does not activate the methanol carbons to nucleophilic attack and any increased susceptibility to attack must therefore be due to changes in the leaving group.

More recently Gale [41] has extended the work on methanol (as well as water and ammonia) adsorption using a BLYP/DZVP2 DFT method. He
compared the results of calculations using the BP86 and BLYP functionals to the MP2 results of Haase and Sauer[62]. Differences in hydrogen bond lengths of 0.08 angstroms arising from use of BP86 and BLYP functionals were observed, the BP86 results being in better agreement with the MP2 results; note that this is in contrast to the studies reported in Chapter 4. Given the uncertainties in the model, basis set and functionals, Gale was unable to determine which was the more appropriate method. Rationalisation of the experimental infra-red spectrum based on calculated vibrational frequencies of the 3T cluster models was not possible by direct comparison. Further, Gale [41] calculated the energy of adsorption of a second methanol molecule on a 4T model but proton transfer to the adsorbate was not seen in any calculation. Haase and Sauer [227] carried out similar calculations on two methanol adsorption over a model 5T acid site. No heats of formation were quoted although they did report formation of a stable methoxonium ion when a second adsorbed methanol molecule was present.

Figure 5.9: 11T faujasite model for CH$_3$OH physisorption at a Brönsted site. HF/SVP optimised structure [62].
One of the most extensive cluster calculations on methanol adsorption at zeolitic Brønsted acid sites using cluster models has been reported by Haase and Sauer [62]. Using MP2/DZP(TZP on O) methods, zeolite fragments of up to 5T sites were used to model the acid site. Under no circumstances was the ion-pair complex found to be stable and they were able to demonstrate that this structure was in fact a transition state. In addition Haase and Sauer studied methanol physisorption on an acid site formed from a 11T fragment of faujasite at a HF/SVP (split valence, polarisation function on heavy atoms) level of theory. The optimised structure is shown in Figure 5.9. For the faujasite model Haase and Sauer estimated an adsorption energy of $-83 \pm 20$ kJmol$^{-1}$ with little or no barrier to proton transfer after addition of estimated corrections for zero-point vibrational energy and basis set superposition error. They concluded that the potential energy surface for adsorption of methanol is a broad shallow potential well which accommodates two symmetry related equivalent neutral complexes with the Brønsted proton attached to different oxygen sites and with the ion-pair complex connecting them. See Figure 5.10. The vibrational spectrum of the physisorbed complex calculated at the MP2/DZP(TZP) level and corrected for basis set superposition error (BSSE) was found to partly rationalise the OH stretching and bending regions observed in the experimental infra-red spectrum. The calculated $^1$H NMR shifts of this complex were also shown to be in agreement with experiments on zeolite H-rho for which results at a loading of one methanol per acid site were available. The vibrational spectrum of the chemisorbed (transition state) complex was not in agreement with experiment. Haase and Sauer [62] conclude that although it is conceivable that a larger model or more extensive basis set may result in a stable ion-pair complex, comparison of the calculated properties with experiment suggests that methanol is predominantly physisorbed in alumino-silicate solid acids.

Attempts to improve the finite cluster model by embedding the quantum mechanical fragment in a point charge array have been attempted for many years; but, despite this effort, problems with the technique are still numerous [17, 19]. A particularly difficult task is the choice of the position and magnitude of the point charges in order to describe the Madelung field correctly.
<table>
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<tr>
<th>Complex</th>
<th>Method</th>
<th>$E_{HF}$</th>
<th>$E_{DFT}$</th>
<th>$E_{MP2}$</th>
<th>$\Delta E_{ZPE}^a$</th>
<th>$\Delta E_{BSSE}^b$</th>
<th>$E_{TOTAL}$</th>
<th>Reference</th>
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$^a$ Correction for zero-point vibrational energy. $^b$ Correction for basis set superposition error. $^c$ Cluster embedded in a point charge array.
Greatbanks [226] published work in which the point charges were fitted to reproduce the electrostatic potential derived from periodic Hartree-Fock calculations of the perfect crystal structure. Application of this method to the study of methanol adsorption on a 3T alumino-silicate fragment at the HF/6-31G* level (correlation estimated using the BLYP functional) gave the structure shown in Figure 5.11, i.e., with one strong hydrogen bond to the acid site and one weak hydrogen bond to a more distant oxygen. Proton transfer from the zeolitic acid site to form the ion-pair structure was not observed.

Periodic studies using embedded QM/MM procedures have not, as yet, been applied to the problem of methanol adsorption in alumino-silicate molecular sieves. However, a number of first-principles periodic DFT studies on small unit cell zeolites and SAPOs have been reported. Shah et al.[61, 228, 217] have carried out static, periodic, plane-wave DFT calculations using the BP91 gradient corrected functional on the microporous materials chabazite and sodalite, the former being active for methanol conversion. With one alumino-silicate Brönsted acid site and one methanol molecule per unit cell their study revealed that in sodalite only physisorbed methanol was present but that in chabazite both physisorbed and methoxonium ions could exist, the latter only when methanol was positioned within
the electrostatic field of an 8-ring window. The calculated adsorption energy for methanol was 82 kJmol$^{-1}$ and 73 kJmol$^{-1}$ for the methoxonium ion in chabazite and the physisorbed species in sodalite, a surprisingly small difference. Shah et al. argue that the observed vibrational spectrum of adsorbed methanol can be rationalised on the basis of the fundamental frequencies of the physisorbed and chemisorbed species. Nusterer et al.[229] have reported similar studies using periodic molecular-dynamics DFT techniques (BP86 functional). Their dynamics study of methanol adsorbed in sodalite (one methanol per unit cell) concurred with the results of Shah et al., i.e., methanol is physisorbed in sodalite, the dominant structure being similar to that shown in Figure 5.11. No adsorption energies were quoted; however the calculated vibrational spectrum derived from their 11ps trajectory at 400K was found to rationalise all aspects of the O-H and C-H stretching region of the observed spectrum. Following these studies, Haase et al.[64] published a periodic DFT (PW91) molecular dynamics simulation of one methanol molecule inside the pores of chabazite containing only one Brønsted acid site. In a similar manner to Shah et al.[61, 228, 217], they discovered a stable methoxonium ion within the 8-ring channels but were able to show that the probability of forming this structure was relatively small; they observed a

Figure 5.11: 3T model for CH$_3$OH physisorption at a Brønsted site. HF/6-31G* optimised cluster embedded in a point charge array [226].
physisorbed structure -18 kJmol\(^{-1}\) more stable than the chemisorbed one. Finally, Nusterer et al.[230] have continued their periodic dynamics study by adsorbing two methanol molecules inside the sodalite cage. They found an equilibrium between physisorbed and proton transferred methanol with the equilibrium shifted in favour of the methoxonium ion clearly showing the load dependance of initial adsorption.

The various adsorption energies reported in the references discussed above are compiled in Table 5.1. It is clear that correlation, BSSE and zero point energies and environment significantly contribute to the calculated energies. However even corrected the calculated adsorption energies from cluster calculations are generally close to the lower bound of the experimental values of -110 to -120 kJmol\(^{-1}\) (see [41, 62] and references therein). One experimentalist has reported a methanol adsorption energy of -63 kJmol\(^{-1}\) [231]. Gale [41] and Haase and Sauer [62] conclude that this underestimation of binding energies is due to neglect of long range electrostatic and dispersion interactions. This effect is clearly seen on comparison of cluster and periodic calculation of the adsorption energy. It is concluded therefore that at low coverages methanol is more likely to exist in a physisorbed state within the pores of acidic molecular sieves but at higher coverages or in specific environments, proton transfer can occur.

5.3.3 Methanol reactivity at Brönsted acid sites

Given the difficulties encountered in understanding the nature of methanol adsorption at Brönsted acid sites it is hardly suprising that even fewer computational studies of methanol reactivity in zeolites have been reported. Those studies that have been reported are mostly concerned with aspects of the methyl-oxonium ylide mechanism discussed in Section 5.2.2.4.

Blaszkowski and van Santen [173] used DFT (BP86/DZVP) techniques to model dehydration of a single methanol molecule at an alumino-silicate Brönsted acid site (alternatively this process could be described as methyl- ation of surface oxygen sites). The resulting reaction coordinate is shown in Figure 5.12. The energetic barrier for the reaction (from the ‘end-on’ adsorption complex) was found to be 215 kJmol\(^{-1}\). The transition state has a
'penta-coordinate' carbon center typical of $S_N2$ reactions (substitution, nucleophilic, bimolecular) although it is clear that the O-C-O angle is not 180°, the optimum angle for orbital overlap in this type of process. Blaszkowski and van Santen [173] also performed a detailed equilibrium and reaction rate study based on a statistical thermodynamics approach coupled with transition state theory.

Zicovich-Wilson et al. [225] pursued the problem of strain in the transition state in their work on the surface methylation process. They studied the reaction involving one methanol molecule on a 3T site using MP2 single point energy calculations with large mixed basis sets at HF/3-21G optimised geometries (various symmetry constraints were also applied). For the process shown in Figure 5.12 they estimated an activation barrier about 30 kJmol$^{-1}$ higher than Blaszkowski and van Santen's result. Their transition state was analogous to the one in Figure 5.12 with an O-C-O angle of 124°, significantly different from the 180° ideal. In an effort to remove this strain from the transition state they studied methylation of a lattice oxygen site that was not directly bonded to Al. Using a 2T site model, they were able

![Diagram](image_url)

Figure 5.12: BP86/DZVP calculated reaction path for formation of surface methyl-oxonium ion from a single methanol molecule at an alumino-silicate Brønsted acid site [173].
to show that methylation of an oxygen site in the third coordination shell of Al was more favourable than methylation of a bridging oxygen in the first coordination shell as the transition state for the former was more relaxed with an O-C-O angle of 168°, close to the S_N2 optimum. They also showed that methylation of oxygen in the third coordination shell of Al resulted in a much less stable system than methylation of an oxygen site in the first coordination shell and was thus more likely to play an active role in further reactions.

Błaszkowski and van Santen [143] went on to study formation of surface methyl-oxonium ions (Z0CH_3) when two methanol molecules were adsorbed at the acid site. Again they employed the BP86/DZVP recipe and a 3T cluster. A simple S_N2 pathway led to an activation barrier of 168 kJmol\(^{-1}\) from a side-on adsorption complex, a reduction of 47 kJmol\(^{-1}\) with respect to the case of a single methanol molecule. This comparison highlights the importance of solvation in the transition state as well as the ability of the reactants to form the optimum O-C-O angle for S_N2 processes.
Formation of dimethyl ether from ZnCH₃ and adsorbed methanol, and directly from two adsorbed methanol molecules was subsequently reported [143]. The activation energy for the former was found to be 160 kJmol⁻¹ at the BP86/DZVP level over 3T clusters which dropped to 98 kJmol⁻¹ (1T clusters) in the presence of water. The barrier for the latter, direct condensation of two adsorbed methanol molecules, was found to be 89 kJmol⁻¹ (3T clusters), see Figure 5.13. They concluded that the formation of dimethyl ether will proceed much more rapidly from condensation of multiple adsorbed methanols. Shah et al. [232] reported similar results, based on periodic DFT (PW91) calculations, of relative energies of intermediates along both of the pathways discussed above for dimethyl ether formation in chabazite. As noted in Section 3.3, Chapter 3, periodic DFT methods have not, as yet, had analytical second derivatives implemented and therefore optimising transition states is still prohibitively expensive.

Finally, Blaszkowski and van Santen [174] have studied a number of pathways for formation of the first C-C bond over 1T clusters using a BP86/DZVP//LDA/DZVP recipe. They concluded that ethanol and ethyl

![Figure 5.14: BP86/DZVP calculated reaction path for formation of ethanol from two adsorbed methanols at a model Bronsted acid site via a surface methyl-oxonium ion [174].](image)
methyl-ether are the first formed species with a C-C bond. They did not study hydrocarbon formation directly from dimethyl ether or methanol on the basis that this would involve generation of carbene like species which they considered to be energetically prohibitive. One of their calculated pathways for formation of ethanol is shown in Figure 5.14, (involving ZOCH₃ and additional adsorbed water). A pathway for formation of ethanol from direct reaction of two adsorbed methanol molecules was also found to proceed with a similar activation barrier, see Figure 5.15. The lowest activation barriers for formation of the first C-C bond were calculated to be ~300 kJmol⁻¹ relative to the adsorption complex of two methanol molecules for all reaction profiles studied.

Blaszkowski and van Santen [174] have noted the reduction in activation barriers for a number of reactions when water is present and shown (using 1T clusters and BP86/DZVP//LDA/DZVP calculations) that although
trimethyl-oxonium ions can form at alumino-silicate Brönsted acid sites, they are unlikely to be important in initial C-C bond formation. The latter is in agreement with solid-state NMR experiments [77, 78] (see Section 5.2.2.2). Hydrocarbon formation from ethanol and dimethyl ether was also studied in detail [174].

Chuvylkin et al.[233] have studied a solid-state acid catalysed reaction of methanol using an INDO semi-empirical quantum mechanical technique and a 2T alumino-silicate model (terminated by pseudo-ions). Starting from a methylated surface oxygen, they studied initial C-C bond formation through interaction of the methylated surface with methanol, see Figure 5.16. Note the connection with the last stage of the surface methyl-oxonium mechanism described in Section 5.2.2.4 and illustrated in Figure 5.6. Chuvylkin et al. showed that the proposed mechanism for C-C bond formation in which concerted deprotonation of the surface bound methyl group and protonation of the lattice oxygen site (mediated by methanol) was more favourable than a process in which deprotonation of the surface bound methyl group led to a protonated methanol species, the latter acting as a methyllating agent to form an ethylated surface and water. Deprotonation of the methylated surface was shown to be the most energetically unfavourable step.

Computational results directly related to the involvement of carbene (CH2) species in the methanol to gasoline process have been reported by Drenth et al.[187]. They showed, using HF/STO-3G methods and a simple
model for a Brønsted acid site that a carbene could be stabilised within the framework of zeolitic materials.

Vetrivel et al. [234] combined lattice simulation calculations of methanol in H-ZSM-5 and Hartree-Fock calculations using STO-3G and 3-21G basis sets. Adsorption configurations for methanol in ZSM-5 were obtained by lattice simulation within the Born potential model. From these configurations, 3T models were generated and optimised quantum mechanically. The fragments were embedded in an array of point charges in order to simulate the extended zeolite structure. Suprisingly Vetrivel et al. obtained the structure shown in Figure 5.17 for methanol adsorbed at an alumino-silicate Brønsted acid site. This corresponds to the unactivated dissociation of a methyl C-H bond on adsorption. Gale et al. [142] later showed that this result was due to the embedding scheme employed in which an ‘ionic’ cluster was embedded in a point charge array of ‘non-formal’ charges, leading to an overall negative system. Gale et al. [142] repeated the work of Vetrivel et al. using semi-empirical methods and concluded that strong association through hydrogen bonds of the acid site with methanol was the dominant initial process. In contradiction to the density functional theory work of Gale et al. [220] (see Section 5.3.2), significant increase of the carbon atom charge on association was observed indicating an increase in susceptibility to nucleophilic attack.

Jackson and Bertsch [210] reported a unique \textit{ab-initio} study into the methanol conversion reaction by considering carbon monoxide to be the
active catalytic species, see Figure 5.7 and Section 5.2.2.5. They believed that the solid acid acted only as a source of acidic protons and therefore neglected the actual acid site in their calculations. Within this approximation they were able to show that at the MP2//HF/6-31G* level the CO catalysed reaction was much more energetically favourable than the more popular surface bound methyl group pathway for the methanol to gasoline process. Experimental evidence supporting the CO catalysed process has now been largely refuted (see Section 5.2.2.5).

5.3.4 Summary

Experimental and theoretical literature concerning the mechanism of methanol conversion to hydrocarbons over acidic alumino-silicate molecular sieves has been presented. Experimentally, there is still a good deal of confusion concerning the conversion mechanism although the importance of the surface methyl-oxonium ion is apparent. Further, of all the hypothetical mechanisms discussed, the surface methyl-oxonium ion pathway appears to be the most appealing. This route does, however, still involve deprotonation of a -CH₃ group, a point that has been the subject of heated debate. It is aspects of this mechanism that will be reported in the following Chapters.

Computational studies of the methanol to gasoline process at an atomistic level are clearly lagging behind experimental work, although the work of Błaszkowski and van Santen, carried out at the same time as the work reported in this thesis, has gone some way to rectifying this situation. Initial methanol adsorption at alumino-silicate Brønsted acid sites is still in debate although it appears likely that an equilibrium between physisorbed and chemisorbed methanol exists, the equilibrium position lying in favour of the physisorbed structure. The theoretical contribution to methanol reactivity (from cluster calculations) currently indicates two probable pathways,

1. the methyl-oxonium ion pathway in which ethanol and ethyloxymethylether are the first formed products with a C–C bond, and

2. direct reaction of multiple adsorbed species in which the acid site acts merely as a proton source.
We continue with the results of cluster calculations on the formation of surface methyl-oxonium ions by a number of routes and then proceed with a discussion of the possibility of forming C–C bond via surface stabilised carbenes.
Chapter 6

MTG : Formation of surface methyl-oxonium ion

As shown in the last Chapter, the surface methyl-oxonium ion mechanism for methanol to gasoline (MTG) conversion over Brønsted acidic molecular sieves provides better rationalisation of experimental facts than any other. We have therefore chosen this mechanism as the basis for our computational study and this Chapter will discuss calculations concerning the initial step, i.e., formation of surface methyl-oxonium ions, ZOCH₃. Four different pathways for formation of ZOCH₃ have been studied over 3T and 4T aluminosilicate clusters;

1. from one methanol molecule (Sn₁-like mechanism),
2. from two methanol molecules (Sn₂ mechanism),
3. from dimethyl ether (Sn₂ mechanism),
4. from dimethyl ether and water (Sn₂ mechanism),

Each will now be discussed in turn.

6.1 Methodological Details

We have used the BLYP/DZVP, BLYP/TZVP and MP2/6-31G**//HF/6-31G** methods (DGauss3.0 and Gaussian-94 respectively) and the cluster
approximation to study the methylation problem, specific details being given in Table 6.1. Given the discussion in Chapter 4, we will not consider the methodological shortcomings further. The reader is reminded, however, that the BLYP/DZVP and MP2/6-31G**//HF/6-31G** methods lead to activation barriers that are underestimated and overestimated by up to 30% respectively, that bond lengths from the BLYP and HF methods are too long (~0.01Å) and too short (~0.02Å) respectively and that BLYP/DZVP, and BLYP/TZVP methods lead to calculated vibrational frequencies that are too low, (by about the anharmonic contribution) but that are often in good agreement with experiment (especially BLYP/TZVP). In all calculations, except those involving the 4T cluster, all degrees of freedom were optimised without symmetry constraints. The 4T cluster was generated from a forcefield optimised unit cell of H-ZSM-5 [235]. Terminal Si and two dihedral angles (O-Al-O-Si and Al-O-Si-O) were then fixed at their initial positions in order to prevent unrealistic relaxation of the cluster. This cluster also has the bond terminating hydrogens attached directly to Al. Although this termination is quite severe, it has been shown to give adequate results, at least in the system studied [173]. All minimum energy structures have zero negative Hessian eigenvalues and all transition states structures have a single dominant Hessian eigenvalue. In some cases the transition state structures had small negative eigenvalues in addition to the one corresponding to the reaction coordinate of interest. These were invariable due to rotation of the terminal SiH₃ groups which were found to contribute little, if anything, to the activation barriers or optimised geometries. In general therefore, no attempt was made to optimise these structures further. The Cartesian coordinates of all of the structures displayed in the Figures are tabulated in Appendix A. Calculation of NMR chemical shifts were carried out using BLYP/TZ2P//BLYP/TZVP methodologies with the GIAO algorithm as described in Section 4.1, Chapter 4.

We emphasize that all energies are internal energies resulting from static electronic structure calculations at stationary points on the adiabatic potential energy surface. Thus, as with all such calculations, thermal and entropic effects are neglected.
6.2 Methanol Adsorption

Before we discuss the various pathways for formation of surface methyl-oxonium ions, the present calculations present the opportunity to discuss the long-debated subject of the nature of methanol adsorption at aluminosilicate Brönsted acid sites in the low coverage limit.

The BLYP/TZVP structure of one methanol molecule adsorbed at a Brönsted acid site (3T cluster), with two strong hydrogen bonds between methanol and the acidic hydroxyl, is shown in Figure 6.1. The calculated adsorption energies of -71 (BLYP/DZVP) and -70 (BLYP/TZVP) kJmol\(^{-1}\) or -62 kJmol\(^{-1}\) (BLYP/DZVP and BLYP/TZVP) after correction for zero-point vibrational energies are comparable to previous cluster calculations, see Table 5.1, Chapter 5, and form a lower bound to the experimental values of -63 kJmol\(^{-1}\) [231] to -115 kJmol\(^{-1}\), (referenced in [62]). Table 6.2 shows the BLYP/DZVP and BLYP/TZVP calculated (harmonic) vibrational spectrum of the bare acid site and methanol–acid site complex compared to other studies and experiment (note the marked basis set dependance).
Figure 6.1: BLYP/TZVP optimised structure of CH$_3$OH physisorbed via two strong hydrogen bonds to a 3T cluster model of an alumino-silicate Brønsted acid site. The hydrogen bonds are 1.55Å (methanol O to acidic H) and 1.85Å (lattice O to methanol H).

6.2.1 Vibrational Spectrum of the Physisorbed Methanol

The BLYP/TZVP calculated frequencies of the bare acid site (ZOH), whilst in good agreement with HF/DZP[62] and BLYP/DZVP2[41] results, give $\nu_{OH}$(ZOH) a little too high with respect to the experimental value. The DZVP frequencies for the ZOH structure are in worse agreement with the other theoretical values, $\nu_{OH}$(ZOH) being too low with respect to experiment. The results for the physisorbed complex, ZOH...CH$_3$OH, are broadly in agreement with experiment provided that Fermi-resonance is invoked in order to explain the A-B-C pattern (three broad, intense peaks) of the experimental spectrum [46, 62, 52, 65]; see Section 2.3, Chapter 2. The results of Mirth et al.[58] for 10$^{-3}$ torr of methanol adsorbed in H-ZSM-5 show Evans windows at ~2700 cm$^{-1}$ and ~2000 cm$^{-1}$, and A-B-C peaks at 2900, 2440 and 1687 cm$^{-1}$ leading to estimates of $\nu_{OH}$, $\delta_{OH}$ and $\gamma_{OH}$ of 2400-2600 cm$^{-1}$, 1350 and 1000 cm$^{-1}$ respectively (see Table 6.2). Note that Mirth et al.[58] originally assigned the 1687 cm$^{-1}$ band to a hydroxyl bend of protonated methanol. For $\nu_{OH}$, $\delta_{OH}$, $\gamma_{OH}$ and $\nu_{CH_3}$, the TZVP frequencies are in reasonable agreement.
with experiment and the other theoretical results listed whereas the DZVP frequencies show unsystematic deviations with respect to the TZVP results. The experimental assignment of $\nu_{\text{OH}}(\text{ZOH})$ leads to a shift on adsorption of -1000 to -1200 cm$^{-1}$, in excellent agreement with the TZVP, PAW[63] and MP2[62] results, but not with the DZVP or HF[62] calculated frequencies.

The TZVP assignment for $\nu_{\text{OH}}(\text{CH}_3\text{OH})$ in the adsorbed complex of 3268 cm$^{-1}$, whilst lower than the experimental value of around 3500 cm$^{-1}$ is in agreement with the MP2 results tabulated. Although Haase and Sauer [62] showed that correction for BSSE can lead to a blue-shift (increase) in the calculated frequency of this vibration, it seems more likely that the vibration arises from methanol that is only weakly hydrogen bonded, either to the surface or to other methanol molecules; we note, for example, that $\nu_{\text{OH}}(\text{CH}_3\text{OH})$ in the methanol dimer appears around 3500-3600 cm$^{-1}$ (see Table 4.2, Chapter 4).

As noted above, if the Fermi-resonance hypothesis is used to analyse experimental IR spectra of sorbed methanol, then both the current work (BLYP/TZVP) and the MP2 cluster calculations of Haase and Sauer [62] agree that the physisorbed complex can fully rationalise the experimental spectrum with the exception of the peak observed at $\sim$3500 cm$^{-1}$, assigned to $\nu_{\text{OH}}(\text{CH}_3\text{OH})$. Nusterer et al.[229], however, were able to rationalise the entire spectrum from results of their first-principles molecular dynamics study of CH$_3$OH in sodalite (although their calculated spectrum did not clearly show the ABC pattern in the OH stretching region; a combination band of the lattice at $\sim$2000 cm$^{-1}$ was believed to be responsible for this effect). Nusterer et al.[229] found only weak binding of the methanol hydroxyl to framework oxygens such that during their simulation at 400K, this hydroxyl formed hydrogen bonds to various lattice oxygens. Shah et al.[61, 228], on the other hand, rationalised the observed spectrum without involving the Fermi-resonance model by assigning fundamental vibrational modes from static, periodic DFT calculations of protonated methanol in chabazite and physisorbed methanol in sodalite to all of the observed peaks, i.e., taking the ABC peaks as separate fundamentals. In their analysis, the 3500 cm$^{-1}$ peak was also assigned to $\nu_{\text{OH}}(\text{CH}_3\text{OH})$ of physisorbed methanol.

Thus, it appears that physisorbed methanol probably dominates the ob-
A correspondence to other studies and experiments. Frequencies are in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>structure</th>
<th>vibrational mode</th>
<th>DZVP (BLYP)</th>
<th>TZVP (BLYP)</th>
<th>DZP (BLYP)</th>
<th>DZVP2 (BLYP)</th>
<th>DZVP (BP86)</th>
<th>PAW (^a) (BP86)</th>
<th>DZP (0.95 scaled)</th>
<th>observed [^c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZOH</td>
<td>(\nu_{\text{OH}})</td>
<td>3583</td>
<td>3672</td>
<td>3688</td>
<td>3666</td>
<td>-</td>
<td>3570</td>
<td>-</td>
<td>3610</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{OH}})</td>
<td>1124</td>
<td>1042</td>
<td>1045</td>
<td>1037</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(\gamma_{\text{OH}}) (^b)</td>
<td>396</td>
<td>247-335</td>
<td>299</td>
<td>398-508</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZOH...CH(_3)OH</td>
<td>(\nu_{\text{OH}}(\text{ZOH}))</td>
<td>2731</td>
<td>2451</td>
<td>3188</td>
<td>2675</td>
<td>2398</td>
<td>2250</td>
<td>2300-2600</td>
<td>2400-2600 (^c)</td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{CH}_3})</td>
<td>3336</td>
<td>3268</td>
<td>3653</td>
<td>3292</td>
<td>3237</td>
<td>3500</td>
<td>3260-3360</td>
<td>3545</td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{CH}_3})</td>
<td>3069</td>
<td>3035</td>
<td>-</td>
<td>3070</td>
<td>3086</td>
<td>3100</td>
<td>3066</td>
<td>2993</td>
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<tr>
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<td>3030</td>
<td>3000</td>
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<td>3029</td>
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<td>3037</td>
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</tr>
<tr>
<td></td>
<td>(\delta_{\text{OH}(\text{CH}_3\text{OH})}) (^b)</td>
<td>2954</td>
<td>2942</td>
<td>-</td>
<td>2964</td>
<td>2972</td>
<td>2800</td>
<td>2940</td>
<td>2856</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{OH}(\text{ZOH})}) (^b)</td>
<td>1462-1344</td>
<td>1491-1387</td>
<td>1350</td>
<td>1458</td>
<td>1496</td>
<td>-</td>
<td>1421</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(\delta_{\text{OH}(\text{ZOH})}) (^b)</td>
<td>1344</td>
<td>1491</td>
<td>1250</td>
<td>1432, 1341</td>
<td>1372</td>
<td>-</td>
<td>1353</td>
<td>1350 (^c)</td>
</tr>
<tr>
<td></td>
<td>(\gamma_{\text{OH}(\text{ZOH})}) (^b)</td>
<td>889</td>
<td>981</td>
<td>784</td>
<td>967</td>
<td>1055</td>
<td>-</td>
<td>1015</td>
<td>1000 (^c)</td>
</tr>
<tr>
<td></td>
<td>(\tau_{\text{C-O}})</td>
<td>194</td>
<td>171</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{C}=\text{O}})</td>
<td>960-977</td>
<td>924</td>
<td>-</td>
<td>995</td>
<td>-</td>
<td>1027</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(\Delta\nu_{\text{OH}(\text{ZOH})})</td>
<td>-852</td>
<td>-1221</td>
<td>-500</td>
<td>-991</td>
<td>-</td>
<td>-1320</td>
<td>&gt; 1000</td>
<td>-1000 to -1200 (^c)</td>
</tr>
<tr>
<td></td>
<td>(\Delta\nu_{\text{OH}(\text{CH}_3\text{OH})})</td>
<td>-315</td>
<td>-399</td>
<td>-78</td>
<td>-399</td>
<td>-</td>
<td>-</td>
<td>-417</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\): Projector augmented-wave periodic DFT calculation in sodalite \[^{229}\].

\(^b\): Strongly coupled with other normal modes.

\(^c\): Frequencies based on the Fermi-resonance interpretation of the observed spectrum in reference \[^{58}\].
served IR spectrum of methanol adsorbed in Brönsted acidic zeolites. A number of factors argue against the need for a proton transferred species to fully rationalise the spectrum. The first and probably most convincing is the experimental spectrum itself. The ABC pattern of the observed hydroxyl region has peaks that are not simple combinations of Gaussian/Lorentzian curves as would be expected from purefundamentals. However, a number of slightly different adsorption geometries are likely to be present, and the spectrum is probably a combination of a number of overlapping fundamentals and hence is not expected to be simple. Other important features of the experimental spectrum are the red-shifts and subsequent broadening of fundamental band widths on hydrogen-bond formation with the bond primarily responsible for the fundamental. It is known that the magnitude of the shifts and the peak broadening are proportional to the strength of the interaction[52]. The interpretation of the spectrum in terms of Fermi-resonance is consistent with this knowledge. However, if each of the ABC peaks are taken to be fundamentals then the observed band broadening on hydrogen bond formation is small.

One can also argue against observation of the chemisorbed species in the IR spectrum on the basis of the likely concentration of each species. The calculations of Shah et al.[217] on chabazite show that proton transfer will only occur if methanol is positioned inside an 8-ring channel. They suggest that a similar phenomenon would probably occur in 10-ring systems. However, they also found that the adsorption energy of the physisorbed species in sodalite was not much smaller than that of the chemisorbed species in chabazite (with a difference of ~10 kJmol⁻¹). Given that there are many more adsorption sites outside 8 or 10-rings in most zeolites, and that adsorption of methanol inside an 8 or 10-ring will incur an entropic penalty, and that the energetic difference of the two adsorption types is quite small, it is likely that at normal temperatures the physisorbed species will greatly dominate in concentration. This conclusion has now been confirmed by periodic DFT dynamics studies of methanol in chabazite [64].

On balance, it seems probable therefore that the observed IR spectrum is due to a physisorbed species with a single strong hydrogen bond between the methanol oxygen and the acidic hydroxyl and a much weaker (or even
absent) hydrogen bond between the methanol hydroxyl and lattice oxygens or other adsorbates. This result emphasises the problem of isolated cluster methodologies which favour strong interaction of the methanol hydroxyl with a neighbouring oxygen of the Brönsted site.

6.2.2 $^{13}$C NMR Spectrum of Physisorbed Methanol

In order to corroborate the above discussion, the $^{13}$C NMR isotropic chemical shift for physisorbed methanol has been calculated; $\delta_{\text{TMS}}$ was found to be 47.0 ppm. This calculated shift is a few ppm lower than the experimentally reported value of 50 ppm. The difference could be due to a variety of reasons, the most likely of which is that the experimental spectra do not correspond to the case of exactly one methanol molecule per acid site. Even if the experimental conditions corresponded to one methanol molecule for every acid site, clustering is still likely to occur, since the energy of adsorption of the first and second molecules are quite similar [41]. It is clear from the results of the methanol dimer study that even weakly interacting species can have a marked effect on the $^{13}$C shift. The disagreement between experiment and theory could also be due to effects induced by the specific environment of the adsorption site. The specific environment can lead to perturbations of the chemical shielding tensor as suggested, for example, by Bronnimann and Maciel [236] who reported that a CH$_3$O$^-$ species trapped in the $\beta$ cages of zeolite HY was probably responsible for a peak at 56 ppm whilst liquid-like methanol and a second immobile CH$_3$O$^-$ species in the supercages of zeolite HY resonate at 50 ppm. The disagreement could also be due to weaknesses in the cluster methodology which was used to obtain the geometry of the adsorption complex used to calculate the NMR spectrum. This methodology neglects long range electrostatic and dispersion effects resulting in an underestimation of the degree of proton transfer to methanol, an effect which would deshield carbon and give a down-field shift in $\sigma_{\text{iso}}$, i.e., a larger value of $\delta_{\text{TMS}}$. It is also almost certainly true that the observed shift is a population-weighted average arising from many different adsorption species (both physisorbed and chemisorbed) being in thermal equilibrium. Haase and Sauer [62] have argued against this population-
weighted average hypothesis on the basis of calculations of the $^1$H NMR shifts of the physisorbed and chemisorbed species in the cluster approximation. The proton transferred complex, a transition state on the cluster potential energy surface, was used to estimate the properties of the hypothetical chemisorbed species. They concluded that only the physisorbed structure was required in order to rationalise the experimental spectrum and that the proton-transferred complex led to shifts which were much larger than experimentally observed. However, if the physisorbed structure was dominant and/or there was rapid interconversion of the physisorbed and chemisorbed species in a limited number of environments (e.g., 8 and 10 rings of the lattice) as suggested by Shah et al.\[61, 228\], then, as in the case of the IR spectrum, the shift of the physisorbed species would dominate the observed spectrum and little could be said about the presence (or lack) of the chemisorbed structure. Finally, if we assume, as in the analysis of the IR spectrum, that the dominant physisorbed species is one in which the methanol hydroxyl is either weakly bound to the surface, to another adsorbate or is free, then its observed $^{13}$C shift should show similarities to the acceptor molecule in the methanol dimer (see Table 4.3, Chapter 4). The shift of 49.1 ppm for this species is much closer to the observed value of 50 ppm for methanol adsorbed in zeolites and supports our earlier conclusion concerning the nature of the dominant species.

6.3 Surface Methylation:

Calculated Reaction Profiles

6.3.1 One and Two Methanol Molecules

Figure 6.2 shows the BLYP calculated reaction paths for formation of surface methyl-oxonium ions (Z0CH$_3$) over model Brönsted acid sites (Z0H) involving one and two methanol molecules. The reaction profiles for the one methanol case calculated using TZVP and DZVP basis sets were very similar with energies varying by only a few kJmol$^{-1}$. Indeed, only for the weak intermolecular degrees of freedom was there any difference in geometries.

In the one methanol case, the process involves breaking the C=O bond
Figure 6.2: BLYP/TZVP (top) and BLYP/DZVP (bottom) optimised structures along the reaction path for formation of surface methyl-oxonium ions (ZOMe) over 3T model Brønsted acid sites (ZOH). The top diagram shows the $S_{n}1$-like process involving a single methanol molecule whilst the lower diagram shown the $S_{n}2$ process involving two methanol molecules. In the top diagram the lower energy profile is of the equivalent $S_{n}2$ process reported by Blaszkowski and van Santen [173]. All energy changes are corrected for zero-point vibrational energy and are in kJmol$^{-1}$.
of methanol and forming a new C-O bond between the methanol's -CH₃ and a lattice oxygen; distances in the transition state being 2.29 Å (C₉H₈O₇-O₉H₈O₇), 2.30 Å (C₉H₈O₇-O₉H₈O₇) and 1.02 Å (O₉H₈O₇-H₉O₇). The calculated process is a concerted one in which proton transfer to methanol and C-O bond breaking/formation occurs simultaneously. Indeed, proton transfer occurs early on in the reaction and it is the C-O bond cleavage which dominates the activation barrier. For this reaction then, the question of protonation or not in the initial adsorption complex is not important. We have chosen to label this process 'Sn1-like' since it involves breaking the C-O bond in 'protonated' methanol followed by attachment of the -CH₃ moiety to a lattice oxygen, the former being more advanced in the transition state than the latter. Unlike the Sn1 mechanism, however, the current pathway does not involve a stable charged carbenium ion intermediate, but proceeds, instead, via a first order transition state. It is possible that the 'Sn1' character of the pathway would increase on incorporation of the electrostatic environment of the molecular sieve into the calculation, but the present work makes no attempt to do so. For comparison, the energetic profile of a similar reaction proceeding via an Sn2 mechanism [173] is included in Figure 6.2.

The second pathway, methylation, involving two methanol molecules, is a classical Sn2 pathway with an O-C-O angle in the transition state of 169° and a trigonal planar CH₃. As above, the mechanism is a concerted one with proton transfer and C-O bond breakage and formation occurring simultaneously. Unlike the case above, however, fracture and formation of the C-O bonds is equally developed in the transition state; distances in the transition state structure being 2.12 Å (C₉H₈O₇-O₉H₈O₇), 1.94 Å (C₉H₈O₇-O₉H₈O₇) and 1.03 Å (O₉H₈O₇-H₉O₇). The second molecule in this reaction merely acts as a proton donor enabling the reacting methanol to be activated by the Brønsted proton as well as allowing it to form the optimum geometrical position for the process. Thus, any species that can mediate proton transfer, e.g. water, would be able to replace the 'by-stander' methanol molecule with a minimal effect on the reaction energetics. The second methanol molecule also plays the rôle of solvent. We note that the physisorbed structure shown in Figure 6.2 is not the lowest energy structure for adsorption of two methanol molecules [143]. The low-
est energy configuration, involving an 8-member hydrogen-bonded ring is \( \sim 55 \text{ kJmol}^{-1} \) more stable. This would therefore give an overall activation barrier of \( \sim 180 \text{ kJmol}^{-1} \). This is in comparison to the barrier reported by Blaskowski and van Santen [143] of \( \sim 160 \text{ kJmol}^{-1} \) at the BP86/DZVP level. This type of discrepancy was apparent from the study reported in Chapter 4 and is almost certainly due to difference in the gradient-corrected density functional.

It is clear then that the calculated internal energy changes suggest that the formation of surface methyl-oxonium ions proceeds more readily via reaction of two methanol molecules (or one methanol molecule and a suitable proton transfer agent) than via the reaction of only one. The second pathway is, however, likely to have a more unfavourable entropic contribution at finite temperatures than the first one, although this term has not been calculated.

### 6.3.2 One dimethyl ether and one dimethyl ether and water

In Chapter 5, Sections 5.2.1 and 5.3.3 and Figure 5.13, we discussed the fact that dimethyl ether can form readily from methanol inside the pores of acidic zeolites. The possibility that dimethyl ether, not methanol, could be the primary methylating agent operating to form surface methyl-oxonium ions cannot, therefore, be ignored. Figure 6.3 shows the calculated reaction coordinates for formation of \( \text{ZOCH}_3 \) from dimethyl ether with and without the involvement of water. The latter was obtained using MP2/6-31G**//HF/6-31G** methods whilst the former used BLYP/DZVP.

Following the work of Zicovich-Wilson et al. [225] concerning the importance of a linear 'bond forming - bond breaking' angle in the transition state of Sn2 reactions, the methylation of a lattice oxygen in the third coordination shell of Al has been studied, which is the reason for employing a 4T cluster and indeed, an O-C-O angle of 172° in the transition state is observed. Methylation of this third shell oxygen does, however, lead to charge separation in the system with negative charge localised around the Al centre and positive charge localised around the CH3. The product is therefore a high energy configuration and is likely to be more reactive. As in the case of the methanol reaction above, proton transfer occurs early in the reaction.
Figure 6.3: MP2/6-31G**//HF/6-31G** (top) and BLYP/DZVP (bottom) optimised structures along the reaction path for formation of surface methyl-oxonium ions (ZOMe) over 4T and 3T model Brønsted acid sites (ZOH). The top diagram shows the $S_22$ process involving a single dimethyl ether molecule whilst the lower diagram shows the $S_22$ process involving dimethyl ether and water. Energy changes are in kJmol$^{-1}$.

and it is the change of local bonding between the two oxygens and the carbon centre that contributes most to the activation barrier. The CH$_3$ in the
transition state is trigonal planar, the two C-O distances being 1.95Å (C-O_{\text{lattice}}) and 2.12Å (C-O_{\text{dme}}).

The second dimethyl ether pathway, shown at the bottom of Figure 6.3, is similar in nature to that of the two methanol case. It is a classical SN2 pathway with a trigonal planar CH$_3$ moiety in the transition state, an O-C-O angle of 170° and two C-O distances of 2.11Å (C-O_{\text{lattice}}) and 1.94Å (C-O_{\text{dme}}). Proton transfer is almost complete by the time the transition state is reached and similar to the two methanol case the second molecule, here water, is an effective bystander, assisting proton transfer in order to facilitate formation of the optimum reactive geometry and helping to solvate the system. Unlike the two methanol case, a much more stable adsorption configuration is unlikely and the energetic profile shown in Figure 6.3 needs no additional comment.

As above, the calculated internal energy changes suggest that formation of surface methyl-oxonium ions proceeds more readily via reaction of two species than via reaction of only one.

6.3.3 Formation of Surface Methyl-oxonium ions -
Summary and Discussion of Calculated Results

Adsorption of methanol at an alumino-silicate Brönsted acid site in a 1:1 ratio has been extensively discussed. We concluded that, even if proton transfer does occur, the protonated methanol is unlikely to be important due to its low concentration. Certainly, the observed IR and $^{13}$C NMR spectra are more easily rationalised on the basis of physisorbed methanol, including the long debated 3500 cm$^{-1}$ band which merely highlights a weakness in cluster methodologies. It is likely therefore that the dominant adsorbed species is a physisorbed one with one strong hydrogen bond between the methanol's oxygen and the acidic hydrogen and one weak, or absent, hydrogen bond between the methanol's hydroxyl and a lattice oxygen.

Subsequently, four possible reaction pathways for formation of surface stabilised methyl-oxonium ions were presented. Recalling the benchmark calculation reported in Chapter 4, we noted that BLYP/DZVP calculations could lead to activation barriers ($\Delta E_{\text{act}}$) that are up to 30% too low and vice
versa for MP2/6-31G**//HF/6-31G** methods. Accounting for these errors, estimates of the absolute activation barriers and the relative activation barriers, i.e., with respect to gas phase reactants, are shown in Table 6.3.

Table 6.3: Formation of Surface Methyl-oxonium ions: Summary of calculated activation barriers and of changes in cluster's dipole moment on activation, $\mu_{act}$; ↑ that the dipole moment increases on going from reactant to transition state and vice-versa.

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Method</th>
<th>True $\Delta E_{act}$</th>
<th>Relative $\Delta E_{act}$</th>
<th>$\mu_{act}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>One methanol (S$_n$1-like)</td>
<td>BLYP/TZVP</td>
<td>244-317</td>
<td>174-247</td>
<td>↑</td>
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<tr>
<td>One methanol (S$_n$2)[173]</td>
<td>BP86/DZVP</td>
<td>210-273</td>
<td>140-203</td>
<td>–</td>
</tr>
<tr>
<td>Two methanols (S$_n$2)</td>
<td>BLYP/DZVP</td>
<td>182-237</td>
<td>52-107</td>
<td>↓</td>
</tr>
<tr>
<td>One dimethyl ether (S$_n$2)</td>
<td>MP2/6-31G**//HF/6-31G**</td>
<td>132-180</td>
<td>60-116</td>
<td>↑</td>
</tr>
<tr>
<td>One dimethyl ether and water (S$_n$2)</td>
<td>BLYP/DZVP</td>
<td>125-163</td>
<td>52-90</td>
<td>↑</td>
</tr>
</tbody>
</table>

A number of conclusions are apparent:

1. Two species will react more readily than one (two methanols, dimethyl and water and probably mixtures of these), which is due to more favourable geometries in the transition state and to solvation effects.

2. On the basis of the calculated activation energies, dimethyl ether is likely to be the methylating agent responsible for formation of surface methyl-oxonium ions during the MTG process.

3. If only one species is available to react, it will methyleate a lattice oxygen not bonded to A1, highlighting the importance of achieving the optimum geometry in the transition state.
4. The fact that proton transfer occurs early in the reaction coordinate implies that the largest contribution to the activation barriers come from changes in C-O bonding and that the question of initial protonation of the reacting adsorbate is not important here.

In addition, we can attempt to rationalise the effect of the electrostatic environment of the molecular sieve on the size of the activation barriers, by studying the change in the cluster's dipole moment ($\mu$) as progress is made along the reaction coordinate. The change in $\mu$ on going from the adsorption complexes to the transition states is shown in Table 6.3. An increase in $\mu_{\text{act}}$ indicates that the degree of charge separation on activation of the reactants increases and a polar environment should, therefore, stabilise the transition states more than the reactants. Since molecular sieves are generally accepted to be polar solids, all of the activation barriers, with the exception of the two methanol case, are probably overestimated.

Comparison of the calculated activation barriers with experiment is difficult for this process as interpretation of experimental data in terms of this pathway has not been reported. Jayamurthy and Vasudevan [182] analysed their temperature programmed reaction study of MTG conversion over H-ZSM-5 in terms of formation of dimethyl ether and subsequent formation of hydrocarbons from dimethyl ether. They reported activation barriers of 108 and 195 kJmol$^{-1}$ respectively. The current calculated activation barriers for the energetically easiest routes are within these experimental bounds.

Thus, the initial stages of the surface methyl-oxonium ion mechanism for the MTG process appears to be,

$$[\text{ZOH} + 2\text{CH}_3\text{OH}]_{\text{ads}} \rightarrow [\text{ZOH} + \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}]_{\text{ads}} \rightarrow [\text{ZOCCH}_3 + \text{CH}_3\text{OH} + \text{H}_2\text{O}]_{\text{ads}}.$$ 

The next Chapter will present results concerning the transformation of surface methyl-oxonium ions.
Chapter 7

MTG : Reaction of Surface Methyl-oxonium Ions

Different mechanisms for MTG conversion over Brönsted acidic molecular sieves were discussed at length in Chapter 5. However, even the most plausible pathway, the methyl-oxonium ion mechanism, [177] (see Section 5.2.2.4, Chapter 5) requires that surface stabilised carbenes or methylide species are formed as a result of \(-\text{CH}_3\) deprotonation. Deprotonation of methyl groups has been the subject of heated debate and it is this problem which concerns the current Chapter.

Chapter 6 reported studies of the formation of surface methyl-oxonium ions. This Chapter reports computational studies of their deprotonation in the absence of any other adsorbates and in the presence of an addition molecule of methanol, the latter leading to formation of a \(\text{C}\text{-C}\) bond in surface ethyl-oxonium ions, \(\text{CH}_2\text{CH}_2\).

7.1 Methodological Details

All calculation in the present Chapter employ the cluster approximation and BLYP/DZVP and MP2/6-31G**//HF/6-31G** quantum chemical methods (DGauss 3.0 and Gaussian-94 respectively). Unless stated otherwise, all degrees of freedom of the clusters were fully optimised and characterised by their harmonic vibrational spectra. Small residual imaginary frequencies
(excluding the imaginary frequency corresponding to the reaction path at the transition state) with negligible intensities remained at some optimised geometries. These were always due to rotation of the cluster terminating groups, SiH₃, and were found to contribute little to the absolute or relative energies. We emphasize that all energies are internal energies resulting from static electronic structure calculations at stationary points on the adiabatic potential energy surface. Thus, as with all such calculations, thermal and entropic effects are neglected.

7.2 Surface Methyl-oxonium ion deprotonation

This initial study of the ability of zeolites to deprotonate surface methyl-oxonium ions, employs the simplest possible basic site, i.e., a neighbouring lattice oxygen of the methylated acid site. Figure 7.1 shows the BLYP/DZVP optimised reaction path for formation and deprotonation of a model surface methyl-oxonium ion. The first step, formation of ZOCH₃ from two methanol molecules, is identical to that shown in Figure 6.2, Chapter 6, and is included here only for completeness.

Figure 7.1 shows the deprotonation reaction occurring on a model cluster in which all geometrical degrees of freedom were unconstrained throughout the optimisations. In order to probe the effect of different zeolite structures on the deprotonation step, this part of the reaction has also been studied on clusters in which the Si-Si distances were constrained to be 5.55, 5.98 and 6.51 Å. The constrained structures are qualitatively similar to those in Figure 7.1 and are not shown; specific details of each are given in Tables 7.1 and 7.2.

Figure 7.1 and Tables 7.1 and 7.2 indicate that allowing the cluster complete freedom during the geometry searches leads to an unrealistic expansion of the active site as a result of ZOCH₃ deprotonation: a Si-Si distance of 6.2Å in the reactant, ZOCH₃, results in a product (pr-II) Si-Si distance of 7.2Å. Constraining this distance during deprotonation leads to a more reasonable distortion of the active site and, surprisingly, has little effect on the activation barrier for deprotonation, i.e., the process is expected to occur with a similar activation barrier at Brönsted acid sites in different topological
Figure 7.1: BLYP/DZVP optimised reaction path for the formation and deprotonation of a model surface methyl-oxonium ion, ZOCH$_3$ over a 3T cluster. The $\Delta E$s are energy changes for the deprotonation step and are tabulated in Table 7.1. The structures shown were optimised without geometry constraints. The deprotonation reaction was also studied on clusters with fixed Si-Si distances (see text). These structures are qualitatively similar to those above and are not shown. Further details can be found in Tables 7.1 and 7.2.
Table 7.1: BLPY/DZVP calculated energy changes for the deprotonation step of the reactions shown in Figure 7.1. The energies in parentheses have been scaled by 1.3 to account for the error of up to 30% observed for pure DFT activation barriers observed in Chapter 4. The labels refer to those in Figure 7.1. The entire process $\text{ZOH} + 2\text{CH}_3\text{OH}(g) \rightarrow \text{ZOH} + \text{CH}_2(g) + \text{CH}_3\text{OH}(g)$ was modelled only on the zeolite fragment with no geometry constraints. $\text{ZOCH}_3$ deprotonation was studied with all models. $\Delta E(2)$ is the activation barrier for $\text{ZOCH}_3$ deprotonation. All energies are in kJmol$^{-1}$ and are corrected for zero-point energies within the harmonic approximation.

Positions within a given zeolite framework provided that other effects, e.g., steric effects are not significant. In all cases, deprotonation of $\text{ZOCH}_3$ leads to the ‘carbene’ product being partially inserted into the cluster framework with generation of a neighbouring Brønsted acid site.

<table>
<thead>
<tr>
<th>Constraint</th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\Delta E_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non</td>
<td>221</td>
<td>-55</td>
<td>234</td>
</tr>
<tr>
<td></td>
<td>(287)</td>
<td>(-72)</td>
<td></td>
</tr>
<tr>
<td>$r(\text{Si-Si}) = 6.51$</td>
<td>215</td>
<td>-41</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(280)</td>
<td>(-53)</td>
<td></td>
</tr>
<tr>
<td>$r(\text{Si-Si}) = 5.98$</td>
<td>222</td>
<td>-55</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(289)</td>
<td>(-72)</td>
<td></td>
</tr>
<tr>
<td>$r(\text{Si-Si}) = 5.55$</td>
<td>232</td>
<td>-57</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>(301)</td>
<td>(-74)</td>
<td></td>
</tr>
</tbody>
</table>
The information on effective atomic charges in Table 7.2 indicates that the product (pr-II) should probably be thought of as a surface stabilised carbene with an effective net charge of about zero. The reactive nature of the product (pr-II) is illustrated by the overall energy change for its formation from ZOCH\textsubscript{3} of 165-175 kJmol\textsuperscript{-1}. Figure 7.1 and Table 7.2 also show that desorption of the carbene (singlet) is energetically expensive, i.e., of similar magnitude to formation of the carbene itself. Thus, gas phase carbene production is unlikely, given the energetic cost of formation and desorption, and it is therefore probable that these species play little role in the MTG process. This result is in accord with the experimental work of Hunter and Hutchings [177], especially when it is recalled that the BLYP/DZVP method can lead to activation barriers that are up to 30\% underestimated, and clearly indicates that formation of ethene via carbene polymerisation is unlikely.

It is interesting to note that as the Si-Si distance decreases, the transition state for deprotonation (ts-II) becomes more product-like with the [C...H] distance of the fragmenting bond increasing from 1.72 to 1.81Å. This mechanistic change is also evident in the values of the Mulliken charges of the CH\textsubscript{2} and H fragments shown in Table 7.2. These values, together with the character of the normal modes corresponding to the imaginary frequency at the transition states (not shown), indicate that the barrier for deprotonation is dominated by movement of the positively charged methyl proton to give a negatively charged CH\textsubscript{2} fragment in the transition state. Presumably, relaxation of the system to give a neutral CH\textsubscript{2} fragment occurs as the reaction coordinate proceeds towards the product. It is clear that the ‘degree of deprotonation’ in the transition state increases with decreasing Si-Si distance, i.e., q(CH\textsubscript{2}) becomes more negative and it might be expected therefore that a better description of the environment would be more important as the Si-Si distance decreases.

The deprotonation activation barriers for the different models vary by only 17 kJmol\textsuperscript{-1}. This variation reflects the different stabilities of the ZOCH\textsubscript{3}, which change unsystematically, and the energies of the transition states (ts-II), which increases with decreasing Si-Si distance. The energies shown in Table 7.1, however, lack any contribution from the environment of the extended alumino-silicate. This contribution can be qualitatively assessed,
<table>
<thead>
<tr>
<th>Constraint</th>
<th>Property</th>
<th>Reactant ZOCH₃</th>
<th>Transition State (ts-II)</th>
<th>Product (pr-II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non</td>
<td>μ</td>
<td>4.07</td>
<td>1.71</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td>q(CH₃)</td>
<td>0.32</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>q(CH₂)</td>
<td>-</td>
<td>-0.14</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>q(H)</td>
<td>-</td>
<td>0.43</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>r(Si-Si)</td>
<td>6.15</td>
<td>6.52</td>
<td>7.17</td>
</tr>
<tr>
<td>r(Si-Si) = 6.51</td>
<td>μ</td>
<td>3.39</td>
<td>1.61</td>
<td>3.85</td>
</tr>
<tr>
<td></td>
<td>q(CH₃)</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>q(CH₂)</td>
<td>-</td>
<td>-0.14</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>q(H)</td>
<td>-</td>
<td>0.44</td>
<td>0.46</td>
</tr>
<tr>
<td>r(Si-Si) = 5.98</td>
<td>μ</td>
<td>3.73</td>
<td>2.91</td>
<td>4.57</td>
</tr>
<tr>
<td></td>
<td>q(CH₃)</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>q(CH₂)</td>
<td>-</td>
<td>-0.17</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>q(H)</td>
<td>-</td>
<td>0.44</td>
<td>0.48</td>
</tr>
<tr>
<td>r(Si-Si) = 5.55</td>
<td>μ</td>
<td>4.39</td>
<td>2.90</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>q(CH₃)</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>q(CH₂)</td>
<td>-</td>
<td>-0.21</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>q(H)</td>
<td>-</td>
<td>0.44</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Table 7.2: BLYP/DZVP calculated properties of the optimised structures along the reaction coordinate for ZOCH₃ deprotonation shown in Figure 7.1. Dipole moments (μ) are in Debye, distances (r) are in Å, and Mulliken net atomic charges (q) are in au.
as in Chapter 6, by using the dipole moments, $\mu$, as a measure of the degree of charge separation in the active site. Table 7.2 indicates that in proceeding along the reaction coordinate from ZOCH$_3$ to the transition state (ts-II), there is always a decrease in $\mu$, i.e., a polar environment would stabilise ZOCH$_3$ more than the transition states (ts-II) and the activation barriers for deprotonation shown in Table 7.1 should be taken as lower bounds. Still, given the approximate nature of the current models, the range of estimated activation barriers, 215-301 kJmol$^{-1}$ (accounting for up to 30% error), is reasonable for a process occurring between 500-600K, and it is concluded that surface stabilised carbenes can be generated over Brönsted acidic zeolites.

7.3 Surface Methyl-oxonium Ion Reaction:

Formation of a Surface Ethyl-oxonium Ion

The last Section indicated that Brönsted acidic zeolites contain sites (lattice oxygens) that are basic enough to deprotonate surface stabilised carbenes. However, it has been suggested that it would be more favourable for deprotonation to occur at the same time as the resulting CH$_2$ fragment inserts into a C-H or C-O bond of an additional adsorbate to form the first C-C bond. This section reports calculations of the latter process resulting in formation of surface ethyl-oxonium ions, ZOCH$_2$CH$_3$. It is noted that Blaszkowski and van Santen [174], see Section 5.3.3, Chapter 5, studied formation of a C-C bond via deprotonation of an adsorbate rather than a surface species.

The processes shown in Figures 7.2 and 7.3 are complicated and will be discussed in detail. Note however that the concerted process, Figure 7.3, is identical to that employed in Section 4.2, Chapter 4 (using 1T clusters) to discuss methodological difficulties in describing activated processes. Both stepwise and concerted pathways start from methanol adsorbed at a methylated Brönsted acid site, pre-I (C-O$_{\text{lattice}}$ 1.44 Å) and pre-IV of Figures 7.2 and 7.3 respectively. The long C$_{\text{ZOMe}}$...O$_{\text{methanol}}$ distance of 2.33Å indicates that methanol adsorption occurs mainly through interaction with the lattice oxygens, H$_{\text{methanol}}$...O$_{\text{lattice}}$ is 2.08Å. The stepwise reaction then proceed through a barrier of 231 kJmol$^{-1}$ involving deprotonation of the methyl-
Figure 7.2: MP2/6-31G**//HF/6-31G** optimised reaction path for the formation of adsorbed CH₂CH₂ (prod-III) from a surface methyl-oxonium ion and methanol (pre-I) over a 5T cluster. The reaction proceed via a surface ethyl-oxonium ion (pre-III) in a step wise manner which involves formation of a surface stabilised carbene (int-I). Terminal H have been removed for clarity. Energies are in kJmol⁻¹.
oxonium ion and protonation of the lattice Al-O, aided by methanol (ts-I, Figure 7.2). This is reminiscent of the mechanism for formation of methyl-oxonium ions when two adsorbates are present (see Section 6.3, Chapter 6) in which the second adsorbate molecule helps in proton transfer, enables the optimum reaction geometry to be achieved and helps solvate the transition state. Relaxation of ts-I leads to the formation of a surface stabilised carbene, CH₂, and regeneration of the acid site (int-I). For this part of the calculation, the terminal Hs were fixed at the geometry of the pre-I complex in order to prevent unrealistic relaxation of the cluster on CH₂ generation. It was shown in Section 7.2, however, that this has little effect on the activation barriers. The surface stabilised carbene then attacks the adsorbed methanol in a S² process (C₉O(C₂H₅)₆methanol distance of 2.52 Å C₉methanol-0methanol 1.71 distance of Å) with an activation barrier of 224 kJmol⁻¹ to give the surface ethyl-oxonium ion (C₂OCH₂lattice of 1.46 Å) and water (prod-III). Note that in this last step, transfer of the acidic proton to methanol, thereby improving the leaving group, i.e., water, again occurs early in the reaction coordinate.

The surface ethyl-oxonium ion (pre-III) then dehydrogenates (ts-III) to form adsorbed ethene (prod-III) with an activation barrier of 206 kJmol⁻¹. This can be compared to the barrier calculated by Blaszkowski and van Santen [174], for a similar process at the BP86/DZVP//LDA/DZVP level of 123 kJmol⁻¹. The reverse reaction, ZOCH₃ formation from adsorbed ethene, has been studied previously, the best estimate of the barrier being 100 kJmol⁻¹ [221] from MP2/6-31G* calculations on a 1T cluster. The present MP2/6-31G**//HF/6-31G** 1T cluster result of 126 kJmol⁻¹ together with the BLYP/DZVP 1T cluster result of 88 kJmol⁻¹ (see Section 4.2, Chapter 4) and the BP86/DZVP//LDA/DZVP estimate of 66 kJmol⁻¹ confirms our earlier estimate of errors of up to ±30% for pure DFT and MP2 corrected HF calculated activation barriers respectively.

The concerted reaction, Figure 7.3 differs from the stepwise pathway only in the mechanism of formation of the surface ethyl-oxonium ion. The concerted pathway proceeds through a barrier of 465 kJmol⁻¹ with simultaneous deprotonated of the surface methyl group and transfer of methanol C's bonding from its O to the C of the surface methyl-oxonium ion. Note that
Figure 7.3: MP2/6-31G**//HF/6-31G** optimised reaction path for the formation of adsorbed \( \text{CH}_2\text{CH}_2 \) (prod-V) from a surface methyl-oxonium ion, \( \text{ZOCH}_3 \), and methanol (pre-IV) over a 5T cluster. The reaction proceeds via a surface ethyl-oxonium ion (pre-V) in a concerted manner through a single transition state (ts-IV). Note that the second half of the reaction is identical to that shown in Figure 7.2. Terminal \( \text{H} \) have been removed for clarity. Energies are in kJmol\(^{-1}\).
the proton removed from the methyl-oxonium ion is transferred to the methanol's \( \text{OH} \), resulting in water being formed as a byproduct. The relevant distances in the transition state are \( C_{\text{methyl}} - C_{\text{methanol}} \) of 2.58 Å, \( C_{\text{methyl}} - H_{\text{methyl}} \) of 2.06 Å, \( C_{\text{methyl}} - O_{\text{methanol}} \) of 2.16 Å, and \( O_{\text{methanol}} - O_{\text{lattice}} \) of 1.98 Å. Relaxation of the transition state ts-IV then leads to an ethyl-oxonium ion and adsorbed water (prod-IV). Structures prod-IV, pre-V, ts-V and prod-V of Figure 7.3 correspond exactly to prod-II, pre-III, ts-III and prod-IV of Figure 7.2.

### 7.4 Deprotonation and Reaction of Surface Methyl-oxonium Ions: Summary and Discussion of Calculated Results

Given the results discussed above concerning the transformation of methyl-oxonium ions, it now seems appropriate to discuss the rôle, or lack, of \( \text{ZOC\textsubscript{2}}\text{CH\textsubscript{3}} \) species in hydrocarbon formation. Jayamurty and Vasudevan [182], as a result of a temperature programmed surface reaction study, concluded that the MTG process is made up of two distinct steps; dehydration of methanol to form dimethyl ether and conversion of dimethyl ether to form hydrocarbons. Further, as a result of pre and post adsorption of methanol and co-feeding of methanol and dimethyl ether during the reaction, they concluded that methanol was not involved in the second step of the process. They reported activation barriers of 108 and 195 kJmol\(^{-1}\) for methanol dehydration and dimethyl ether conversion respectively. Jayamurty's and Vasudevan's experimental activation barrier for dimethyl ether formation was based on the observation of water evolution during the TPSR run as it was shown that desorption, not activation, was the rate determining factor for the observation of dimethyl ether. Their analysis did not however include the possibility that observation of water could be due to the formation of \( \text{ZOC\textsubscript{2}}\text{CH\textsubscript{3}} \) (see for example Chapter 6) as well as due to the formation of dimethyl ether.

The current calculations give an activation barrier for the formation of \( \text{ZOC\textsubscript{2}}\text{CH\textsubscript{3}} \) from gas phase reactants (\( \text{ZOH} + 2\text{CH\textsubscript{3}}\text{OH} \)) of 306 kJmol\(^{-1}\) and 364 kJmol\(^{-1}\) for the stepwise and concerted reactions respectively (using the
BLYP/DZVP energetics from the two methanol pathway and an adsorption energy of -130 kJmol\(^{-1}\), see Section 6.3.1, Chapter 6). With respect to the two methanol adsorption complex, the energetic barriers are 436 kJmol\(^{-1}\) and 494 kJmol\(^{-1}\) respectively; with respect to the dimethyl ether and water adsorption complex, they are 445 kJmol\(^{-1}\) and 503 kJmol\(^{-1}\) respectively. Scaling of the activation energies only by ±30% gives rise to barriers of 326 and 363 kJmol\(^{-1}\) (relative to the two methanol adsorption complex) and 332 and 372 kJmol\(^{-1}\) (relative to the dimethyl ether and water complex) for the stepwise and concerted pathways respectively. This compares to the barriers of around 300 kJmol\(^{-1}\) at the BP86/DZVP level reported by Blaskowski and van Santen for formation of the first C-C bond in ethanol and ethyl methyl ether, which, after applying our +30% correction for activation barriers calculated by such methods, brings their estimates to around 350-400 kJmol\(^{-1}\). Formation of the first C-C bond within a surface ethyl-oxonium ion is thus shown to be at least as likely as its formation in an adsorbate. Further, taking the values literally, it appears that the methyl-oxonium ion pathway suggested by Hunter and Hutchings via a surface stabilised carbene is the most likely route to hydrocarbon formation. However, it is our opinion that the errors in the methods and models are too large to distinguish one route from another on the basis of differences in energies of 10-20% of the total barrier. It must also be noted that the theoretical estimates for the rate determining steps, i.e., C-C bond formation, are still substantially higher than the experimental estimate of 195 kJmol\(^{-1}\) [182] for hydrocarbon formation from dimethyl ether. This discrepancy could indicate that the pathways studies theoretically are not operative during MTG conversion, but it is more likely that errors in the theoretical method and models, as well as difficulties in experimental interpretation of thermodynamic studies [237], are the cause of the problem. Further work with larger clusters, embedded clusters or periodic systems with more accurate quantum chemical techniques will be needed in order, unambiguously, to resolve this problem.

Recall, the experimental work that originally led to the suggestion of the methyl-oxonium ion pathway, discussed in Section 5.2.2.4, Chapter 5. Hunter and Hutchings [177] interpreted results of isotope labelling experiments as indicating that the C\(_1\) moieties leading to ethene production must
Figure 7.4: Schematic representation of a probable mechanism for the MTG process based on the combined results of the current theoretical work, those of Blaskowski and van Santen [143, 174] and experiment. See text for more details.

be different from those leading to dimethyl ether on the basis that if they were the same, similar isotope distributions would be expected. In the context of the current calculations and those of Blaskowski and van Santen [], this observation is satisfied if dimethyl ether is produced by reaction of two adsorbed methanol molecules, see Figure 5.13, Chapter 5, and ethene, or the primary product containing a C-C bond is formed from a methyl-oxonium ion. Unfortunately, little more can be said about the mechanism
from experimental works and we must conclude that any, or all, of the theoretically suggested pathways involving methyl-oxonium ions presented here and by Blaskoski and van Santen [174], could be in operation during methanol conversion.

We thus conclude that methyl-oxonium ions play a crucial rôle in the MTG process, although exactly how the first C–C bond is formed, and what the primary species containing such a bond is, is a too delicate a problem to elucidate from the current levels of method and model. Figure 7.4 does, however, indicate a probable pathway for C–C bond formation from methanol over a Brønsted acidic zeolite, consistent with the current calculations, those of Blaszkowski and van Santen and with experimental results.
Part III

Ti(IV) Partial Oxidation Catalysis
Part III Abstract

The final Part of this thesis reports extensive Density Functional Theory calculations on the nature, state of hydration and hydrolysis, reactivity towards hydrogen peroxide and ethene, and deactivation of Ti^IV active sites in titanosilicate catalysts. The discussion begins with a review of the literature concerning the nature and reactivity of active sites in these materials.

Chapter 9 presents results of cluster calculations which suggest that in dehydrated conditions, 4-coordinated (-OSi)$_4$Ti, (-OSi)$_3$TiOH, and (-OSi)$_2$Ti(OH)$_2$ species can all exist depending on the synthesis method used to prepare the catalyst. In the presence of water, hydration of all of the Ti$^IV$ species to form 6-coordinated complexes is observed, in agreement with experiment. In addition, a single molecule of water is shown to promote titanyl, Ti=O, formation from silica embedded titanium (IV) hydroxides. Calculations modelling the grafting of Cl$_2$Ti($\eta^5$-C$_5$H$_5$)$_2$ to the surface silanols of MCM-41 mesoporous silicas are also reported.

Chapter 10 continues with a study of the mechanism of alkene epoxidation in the presence of hydrogen peroxide (H$_2$O$_2$). The proposed mechanism based on these calculations and work in the open literature is shown in Scheme 2, below. The overall activation barrier for epoxidation of ethene with hydrogen peroxide was calculated to be 62–92 and 70–103 kJmol$^{-1}$ relative to initial adsorption complexes for the reaction via a titanium hydroxide and titanyl species respectively. These values compare favourably with available experimental estimates. Our proposed mechanism, Scheme 2, can explain the observed solvent dependence, effect of adding base or acid, the acidic behaviour of titanosilicate H$_2$O$_2$ couples, deactivation of the catalyst by Ti($\eta^2$-O$_2$) formation, and the observed dependence on activity of the peroxide structure and the Ti-OR group in organic derivatives of the Ti$^IV$-site. Suggestions for the improvement of the catalytic process are discussed.
Scheme 2: The proposed mechanism for alkene epoxidation at Ti-OR sites based on the current work and that in the open literature. R represents either =SiO-, H or an organic function. The calculations do not indicate a strong preference for either pathway 1 or 2 for formation of the active oxygen donating species, Ti$^{IV}$($\eta_2$-OOH), although we note that path 2 is likely to be more strongly dependent on solvent. Formation of the active oxygen donating species will also depend upon the concentration of hydroperoxide at the Ti$^{IV}$ site and on competitive adsorption with solvent or base for two coordination sites. Steps 3 give rise to acidity in the presence of hydrogen, but not alkylhydroperoxides. Steps 4 and 5 describe alkene epoxidation and catalyst deactivation respectively. These two processes are likely to compete, but since the activation barrier for Step 5 is less than that for Step 4, deactivation will only be significant when the concentration of alkene becomes smaller than that of the active oxygen donating species. Finally, Step 6, self-repair of the catalyst and diffusion of the products closes the catalytic cycle; initial results suggest that catalyst self-repair could be rate limiting.
Chapter 8

$\text{Ti}^{IV}$ Oxidation Catalysts: Literature Review

The success of zeolites in numerous industrial catalytic processes [13] has stimulated the search for catalysts containing elements other than $\text{Al}^{3+}$ embedded in a silica framework; $\text{Ti}^{IV}$ is one important example. $\text{Ti}^{IV}$ partial oxidation catalysts have played a major rôle for many years in the production of organic feedstocks, e.g., propylene oxide, hydroquinone, cyclohexanone oxime, but it was not until 1983 and the discovery of titanosilicate-1 [238] that the field was transformed. These crystalline, framework substituted $\text{Ti}^{IV}$-silicas are active for many oxidation processes under mild conditions ($< 373K$), are highly efficient, show high selectivities and when used with $\text{H}_2\text{O}_2$ or $\text{ROOH}$ as the sacrificial oxidant are environmentally friendly [5, 9]. The numerous reviews that have appeared in recent years is testimony to the importance of these catalysts [239, 5, 9].

The Density Functional Theory cluster calculations presented in the forthcoming Chapters study the nature of $\text{Ti}^{IV}$ active sites in siliceous molecular sieves, their reaction with sacrificial oxidant $\text{H}_2\text{O}_2$ and the formation of ethene oxide from ethene. It is these topics that dominate the literature survey reported below.
8.1 General Observations

Introducing Ti$^{IV}$ into SiO$_2$ glasses, i.e., by forming TiO$_2$-SiO$_2$ mixed oxides, led to the first Ti$^{IV}$ catalyst of its type to be exploited industrially, e.g., Shell Oil have been producing propylene oxide with a TiO$_2$-SiO$_2$ catalysts since the early 1970s [240]. Attempts to introduce Ti$^{IV}$ into crystalline zeolites was reported as early as 1967 [241], but unequivocal evidence for framework substitution was not presented. It was not until 1983 that Taramasso et al. [238] and the EniChem company reported the crystalline structure of TS-1, Ti-silicate-1 (MFI structure) with Ti$^{IV}$ isomorphously substituted into the silica framework. The evidence for framework substitution will be discussed below. However, since the discovery of TS-1, numerous molecular sieves claiming Ti$^{IV}$ substitution have been reported, e.g., ZSM-12 [242], zeolite β [243], ALPO-5 [244], MCM-41 [245, 246].

The catalytic properties of TS-1 and other Ti$^{IV}$-molecular sieves are unique; oxidation (with aqueous H$_2$O$_2$) of many organic compounds is efficient and selective; oxidation products can be obtained in high yield under mild conditions and very little H$_2$O$_2$ decomposition is observed. However, difficulties in reproducing the materials in different laboratories, as well as the traditional belief that Ti$^{IV}$ prefers octahedral, rather than tetrahedral, coordination led to widespread scepticism concerning the isomorphous replacement of Si$^{IV}$ [247]. In addition, Pauling's rules of coordination based on the ratio of the ionic radii of the cation and anion suggests that isomorphous substitution is unlikely. The production of 100,000 ton/year of catechol and hydroquinone by the selective oxidation of phenol with H$_2$O$_2$ over TS-1 [248], together with reports of technology for the production of cyclohexanone oxime from cyclohexanone, NH$_3$ and H$_2$O$_2$ [249] has, however, led to widespread interest in Ti$^{IV}$-molecular sieves.

Today, there is no doubt concerning the tetrahedral coordination of Ti$^{IV}$ in the frameworks of Ti-molecular sieves provided that caution is taken during synthesis and preparation. Our present interest is in the oxidative character of framework substituted Ti-silicas on which the next few sections will concentrate. However, it should be recognised that there are many aspects of these materials that merit notice, e.g., the fact that TiO$_2$-SiO$_2$ mixed
oxides display acidity [250], that only a limited amount of Ti\textsuperscript{IV} (a few wt%) can be incorporated into the lattice, that in the presence of extra-framework Ti\textsuperscript{IV} the efficiency of the catalyst is drastically reduced, that the catalytic process is solvent dependent, that shape selectivity often plays an important role in the observed reactivity trends and product distributions, and that the material's hydrophobicity is an important factor in explaining their behaviour. Some of these observations will be discussed below. However, for more information the reader is referred to the reviews of Arends \textit{et al.}[9] and Notari [5].

The discussion of the local structure of Ti\textsuperscript{IV} defects in silica hosts will begin with a brief overview of the properties of Ti\textsubscript{2}0\textsubscript{2}-Si\textsubscript{2}0\textsubscript{2} mixed oxides since much of the understanding of the behaviour of analogous molecular sieves is based on these materials. Brief mention of molecular analogues, the Ti\textsuperscript{IV}-silasequioxanes, will then be followed by a discussion of results pertaining to the mechanism of partial oxidation catalysis over these solids.

8.2 The Nature of Ti\textsuperscript{IV}

8.2.1 Ti\textsubscript{2}0\textsubscript{2}-Si\textsubscript{2}0\textsubscript{2} mixed oxides

Ti\textsubscript{2}0\textsubscript{2}-Si\textsubscript{2}0\textsubscript{2} mixed oxides have been recognised for some time as active and selective catalysts for olefin epoxidation [240] and as noted above, form the basis of the Shell Oil process (91-95% selectivity with respect to propene, 96-97% peroxide conversion).

The composition of the samples range from pure Ti\textsubscript{2}0\textsubscript{2} to pure Si\textsubscript{2}0\textsubscript{2}, the ratio having a major influence on catalytic properties [5]. There are also a number of different synthesis routes and, for example, the pH at which the synthesis occurs is known to affect strongly the properties of the resultant mixed oxides [251, 252, 253]. However, methods now exist to maximise the degree of Ti\textsuperscript{IV} dispersion and the number of Si-O-Ti bonds, the latter being widely considered as the most important species in olefin epoxidation with H\textsubscript{2}O\textsubscript{2} [254, 255, 256, 257] (much lower activity is observed with Ti\textsubscript{2}0\textsubscript{2} supported on other oxides, \textit{e.g.}, Al\textsubscript{2}O\textsubscript{3}, MgO, or in mechanical mixtures [248]). A property of Ti\textsuperscript{IV} highly dispersed on silica is its enhanced

148
Reducibility to Ti$^{III}$ and indeed, this property has been used to indicate tetrahedral coordination. Another indicator for the presence of dispersed Si-O-Ti moieties is the 950-960 cm$^{-1}$ frequency band in the IR spectrum of the sample. This indicator has been used extensively and its nature will be discussed in more detail in Section 8.2.2.

Numerous cases exist, however, in which there is evidence for surface nanophases of TiO$_x$ or crystalline anatase. For example, in the samples studied by Srinavasan et al. [258], containing 2 wt% of TiO$_2$ deposited on preformed fumed Cabosil, both nanophases and crystalline anatase were detected, but with great difficulty. TiO$_x$ nanoparticles can drastically effect the catalytic efficiency of TiO$_2$-SiO$_2$ mixed oxides by catalysing the decomposition of H$_2$O into H$_2$O and O$_2$ [248]. In certain forms, however, TiO$_2$ can be mildly active for alkene epoxidation [256].

Mixed oxides formed from the hydrolysis of Ti and Si precursors at neutral pH (Ti:Si ratio of 1:8) and analysed by XANES indicates that Ti$^{IV}$ is present in 5, or a mixture of 4, 5 and 6 coordination; evidence for purely octahedral coordination, as in anatase, was not observed [252, 253]. They derived Ti-O distances of 1.82 Å which compare to those in anatase and rutile of 1.94 Å, the former being typical for Ti$^{IV}$ in tetrahedral coordination. TiO$_2$ particles sizes could only be estimated at <10Å implying that most of the Ti$^{IV}$ in these domains occupy Ti-O-Si positions. The Ti$^{IV}$ coordination was observed, with XANES and UV-vis spectroscopy, to expand reversibly on H$_2$O exposure.

The general picture from these studies is that in the mixed oxides, at low TiO$_2$ concentration, with a preparation that allows sufficient interaction of the metal oxides, TiO$_2$ is present as very small domains in which the tetrahedral coordination of Ti$^{IV}$ differs from its octahedral coordination in anatase and rutile. Further, in the presence of adsorbable compounds, Ti$^{IV}$ reversibly increases its coordination number up to 6. There is significant chemical difference between the labile, 6 coordinated, hydrated, highly dispersed Ti$^{IV}$ in silica and the stable octahedral system in anatase or rutile, as shown, for example, in the fact that Ti$^{IV}$ in a state of high dispersion is more readily reduced to Ti$^{III}$. The acidity in these samples, particularly in the TiO$_2$ rich region is considered to be due to domain boundary defects [5].
Lastly, by analogy with other metal oxides, titanyl groups, Ti=O, have been suggested as possible species that are responsible for the unique reactivity of Ti^IV^-silicas. The species shown in Figure 8.1, considered to be formed during calcination, was suggested on the basis of comparisons with other transition metal oxide systems and is thought to stabilise the tetrahedral coordination of Ti^IV, increase the oxygen's electrophilicity, prevent solubilisation of Ti^IV, and to prevent polymerisation of the Ti=O functionality [255, 256, 257, 27, 259, 260]. Although this species is known to give rise to an IR band at around 950 cm$^{-1}$, consistent with the observed spectrum, its UV-vis absorption band has not been observed in TiO$_2$-SiO$_2$ mixed oxides and its existence is still uncertain.

### 8.2.2 Crystalline Ti$^IV$-silicates

By far the largest contribution to the literature has concerned the microporous titanosilicate TS-1 as this material has been developed for industrial application and has been available for the longest period. It was also the first material to make strong claims on the tetrahedral nature of Ti$^IV$ in a silica framework.

The X-ray patterns of silicalite-I and TS-1 show a change in structure from monoclinic to orthorhombic on exchange of Si$^IV$ for Ti$^IV$ [238]. The data also indicate that Ti$^IV$ incorporation leads to an expansion of the unit cell volume ($V$). This expansion has been shown to be consistent with an increase in the size of a TO$_4$ tetrahedron when Si is replaced by Ti, leading to
Figure 8.2: Schematic representation of Ti$^{IV}$ hydrolysis in TS-1 [263]. This scheme applies equally well to other Ti-silicates.

A model in which TS-1 can be represented as silicalite with a few randomly located Ti$^{IV}$ species taking the place of Si$^{IV}$ [238, 5, 248, 261]. A similar study using accurate data from Rietveld analysis of X-ray powder patterns confirmed the relationship between the unit cell volume and Ti$^{IV}$ content [262]. Further, recent Hartree-Fock calculations on titanosilicate clusters have shown that the unit cell volume expansions are consistent with the local change in the Ti-O bond distance when the T atom is changed from Si$^{IV}$ to Ti$^{IV}$ [42]. On the basis of the unit cell expansion it appears that the maximum amount of Ti$^{IV}$ that can be incorporated into the TS-1 framework is around $x = 0.025$ [5].

The state of dispersion of Ti$^{IV}$ in TS-1 has been confirmed by X-ray photoemission spectroscopy [5], UV-vis spectroscopy [264, 44, 263] and atomistic simulation [37]. The diffuse reflectance UV-vis spectra of TS-1 shows a strong transition at 48,000-50,000 cm$^{-1}$ that is absent from silicalite and must therefore correspond to a charge transfer process localised on Ti$^{IV}$ [5, 264, 263]. The band in TiO$_2$ is at 30,000 cm$^{-1}$ whilst those from TiO$_2$ nanoparticles in TiO$_2$-SiO$_2$ mixed oxides lie between 30,500-40,000 cm$^{-1}$.
In addition, due to the fact that UV-vis absorption frequencies are a strong function of particle size for particles with diameters less than 10 Å, such experiments indicate that Ti^{IV} in TS-1 is more highly dispersed than in any other type of material. Similar results have now been reported for other solids, e.g. Ti-zeolite-β [266]. Ti^{IV} leaching under severe conditions to form species with Ti-O-Ti bonds has also been observed using UV-vis spectroscopy (the band is around 40,000 cm\(^{-1}\)) [267].

On addition of increasing amounts of \(H_2O\) the 48,000-50,000 cm\(^{-1}\) UV-vis band progressively shifts to 42,000 cm\(^{-1}\); the effect is reversible. The increase in coordination in the presence of adsorbable species could take place by simple addition of \(H_2O\) on Ti^{IV} or as a result of hydrolysis of Ti-O-Si bonds followed by addition of \(H_2O\) to the resulting TiOH groups [5, 44, 263]. TiO\(_2\) shows little tendency to form surface hydroxyls but the unusual environment of Ti^{IV} in the silica matrix as well as strain around the T centre when Si is replaced by Ti^{IV} (larger Ti-O distance) could force it to do so as shown in Figure 8.2. The strain around Ti^{IV} centres leading to distorted tetrahedra has been used to rationalise XANES and \(^{29}\)Si NMR spectra of Ti-MCM-41 samples [268].

Experimental evidence for the formation of TiOH species in TS-1 has been obtained from IR and NMR studies of TS-1 treated with labelled water. SiOH groups in silica have an absorption band at 985 cm\(^{-1}\) which is D-exchange sensitive; the 960 cm\(^{-1}\) band of TS-1 is not. It is, however, sensitive to \(H_2^{17}O\) and \(H_2^{18}O\) treatment with the band shifting from 960 to 952 and 937 cm\(^{-1}\) respectively, consistent with changes in the reduced mass of the Ti-O-Si harmonic oscillator [269]. A similar effect was seen in the \(^{17}\)O NMR spectra on \(H_2^{17}O\) treatment - a resonance at \(\delta = 360\) ppm, absent in treated silicalite-1, was observed [269]. These data are consistent with the reaction shown in Figure 8.3, involving hydrolysis of the Ti-O-Si bond to form TiOH groups. Attempts to observe \(\nu(Ti-O)\) stretching frequencies directly have so far been unsuccessful or ambiguous [5]. Bellussi et al.[269] consider that the labelling experiments are also consistent with the involvement of a titanyl species as shown in Figure 8.4, although it is noted that the lack of an UV-vis absorption band for the titanyl species in TS-1 and, indeed, any other Ti-silicate, has led to the conclusion that stable, long lived Ti=O
Figure 8.3: Schematic representation of the hydrolysis of Ti-O-Si bonds suggested on the basis of isotopic labeling experiments [269]

groups are not present in these systems [264]

The IR band at ~960 cm$^{-1}$ has been studied by many authors in an attempt to elucidate its origins and relate it to the catalytic properties of TS-1. The band is absent from silicalite and its intensity is linearly correlated with the amount of Ti$^{IV}$ incorporated into the framework [248]. The proposal that it is due to Ti=O groups [248] which show a stretching band in the same region (by reference to fresnoite [270] and JDFL-1[271]) has been dismissed due to the lack of UV-vis confirmation, as noted above. The assignment of the band to a local impurity mode of a SiO$_4$ unit bonded to Ti$^{IV}$, i.e., $O_3Si-O-Ti$, was suggested by Boccuti et al. [264]. This would explain its presence in TiO$_2$-SiO$_2$ mixed oxides, its sensitivity to $^{17}$O and $^{18}$O exchange and the fact that sensitivity to O exchange is not observed in pure silicalite. This band has also been the subject of extensive Hartree-Fock calculations on various cluster models of Ti-silicas [42]. The authors concluded that the band is due to the antisymmetric Ti-O-Si stretching mode of corner sharing tetrahedra and arises due to the fact that Ti-O bonds are typically 0.2Å longer than Si-O bonds. However, the 960 cm$^{-1}$ band has been observed in other silicas lacking Ti$^{IV}$, in zeolite-$\beta$ with only Al$^{3+}$ [272], in vanadium and in chromium silicates [273, 274, 275]. Given the theoretical results mentioned above it seems likely that the 960 cm$^{-1}$ band is best thought of as being due to [SiO$_4$] groups perturbed by the presence of T atom impurities, especially when the T-OSi bond length associated with the impurity is larger than Si-OSi bond lengths [44, 43]. Camblor et al.[276]
have also suggested that the band is better assigned to stretching vibrations of Si-O⁻ groups where the counterions can be H⁺, (CH₃)₄N⁺, Na⁺ or a neighbouring Ti atom impurity. Thus, the band should not, as is often the case, be used unambiguously to indicate Ti⁴⁺ incorporation or catalytic potential.

The 4-coordinate nature of Ti⁴⁺ in TS-1 can also be deduced on the basis of ESR spectra of CO reduced samples in comparison with those from Ti⁴⁺ exchanged ZSM-5 [277]. The ESR spectrum of both samples is consistent with the presence of only Ti⁴⁺. Reaction of the reduced TS-1 with O₂ produced a new signal, at the expense of the Ti⁴⁺ signal, assigned to superoxide ions. Addition of O₂ to Ti⁴⁺ exchanged ZSM-5 produced a superoxide signal with g-tensor values significantly different from those of the TS-1 sample. These results were interpreted as evidence for superoxide binding in very different environments. Further, the g-tensor values from the Ti⁴⁺ in the reduced TS-1 sample are consistent with a distorted tetrahedral environment providing strong evidence for the framework siting of the precursor Ti⁴⁺. The ease of reducibility of Ti⁴⁺ in TS-1 relative to the case in anatase or rutile, analogous to Ti⁴⁺ in the mixed oxides, has also been used as evidence for the 4-coordinate nature of Ti⁴⁺ in this material [278].

Lastly, X-ray absorption spectroscopy has been extensively applied to the problem of the nature of Ti⁴⁺ in silica molecular sieves [5, 266, 268, 154].
Figure 8.5: Schematic representation of extraframework edge-sharing [TiO\textsubscript{x}] units as suggested in reference [282].

279, 280, 281, 282, 283]. Initially Behrens et al. [284, 285] reported that much of the Ti\textsuperscript{IV} in TS-1 resides in octahedral sites which change to lower coordination upon dehydration. Trong On et al. [282] reported XANES and EXAFS results consistent with 4 coordinate Ti\textsuperscript{IV} in [TiO\textsubscript{x}] units sharing edges with [SiO\textsubscript{4}] tetrahedra in the framework, see Figure 8.5. These edge sharing [TiO\textsubscript{x}] units were not found in later experimental [279] or theoretical [42, 37] studies. Extensive studies of the effect of hydration has shown that the XANES spectrum changes position and intensity upon dehydration, as do the spectra of the mixed oxides, but unfortunately, XANES alone cannot differentiate between the Ti\textsuperscript{IV} in Ti\textsubscript{0.2}-Si\textsubscript{0.2} mixed oxides, in Ti\textsubscript{0.2} nanoparticles or in TS-1 samples. XANES and EXAFS analysis of pure samples of TS-1 has shown that the Ti\textsuperscript{IV} coordination number is around 4 and that the Ti-O distance is 1.80\textsubscript{Å}. A comparison of Ti-O distances in a range of different materials is shown in Table 8.1. It is clear that Ti\textsuperscript{IV} in states of 4, 5 and 6 coordination have Ti-O values in distinct ranges and that the \Delta R values for the 4 and 6 coordinate systems are sufficiently small that they do not overlap. This observation, combined with the fact that the short Ti=O distance in 5 coordinate fresnoite is easily differentiated by XAS, was considered to be conclusive evidence in favour of 4-coordinate Ti\textsuperscript{IV} [279, 286, 44].

The results discussed above have largely concerned TS-1. However, similar studies have been reported for Ti\textsuperscript{IV} incorporated into the framework of a number of other zeolites, ALPOs, SAPOs and more recently, mesoporous silicates, e.g. MCM-41 [268, 280, 281, 283]. As mentioned in Chapter 1, MCM-41 has long range structural order in only 2 dimensions with the channel walls being almost amorphous in nature (see Figure 1.3, Chapter 1). Ti-MCM-41 is thus intermediate in properties between Ti\textsubscript{0.2}-Si\textsubscript{0.2} mixed oxides and crys-
Table 8.1: Individual Ti–O distance (R), their averages, and the distributions within various Ti⁴⁺ containing compounds (ΔR) [279].

<table>
<thead>
<tr>
<th>Ti compound</th>
<th>Ti–O distance, R (Å)</th>
<th>average distance (Å)</th>
<th>ΔR (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>6-coordinate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ anatase</td>
<td>1.934 x 4, 1.980 x 2</td>
<td>1.957</td>
<td>0.046</td>
</tr>
<tr>
<td>TiO₂ rutile</td>
<td>1.949 x 4, 1.980 x 2</td>
<td>1.964</td>
<td>0.031</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>1.952 x 6</td>
<td>1.952</td>
<td>0.000</td>
</tr>
<tr>
<td>MgTiO₃</td>
<td>1.735 x 3, 1.956 x 2</td>
<td>1.846</td>
<td>0.221</td>
</tr>
<tr>
<td><strong>5-coordinate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba₂TiSi₂O₆ fresnoite</td>
<td>1.698, 1.970 x 4</td>
<td>1.916</td>
<td>0.270</td>
</tr>
<tr>
<td><strong>4-coordinate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba₂TiO₄</td>
<td>1.766, 1.812, 1.817, 1.836</td>
<td>1.808</td>
<td>0.070</td>
</tr>
<tr>
<td>Cs₂AlTiO₄</td>
<td>1.751, 1.757, 1.733 x 2</td>
<td>1.764</td>
<td>0.022</td>
</tr>
<tr>
<td>C₄₈H₆₈O₄Ti</td>
<td>1.780 x 2, 1.781 x 2</td>
<td>1.781</td>
<td>0.001</td>
</tr>
<tr>
<td>C₄₀H₅₂O₄Ti</td>
<td>1.778 x 4</td>
<td>1.778</td>
<td>0.000</td>
</tr>
<tr>
<td>C₈₈H₁₀₄O₈Ti₂ .₆C₇H₈</td>
<td>1.782, 1.797, 1.813, 1.845</td>
<td>1.809</td>
<td>0.063</td>
</tr>
<tr>
<td>TS-1</td>
<td>1.80 x 4</td>
<td>1.80</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>

talline Ti⁴⁺-silicas. The amorphous nature of the MCM-41 walls with a high degree of surface silanols does, however, lead to the possibility of grafting Ti⁴⁺ onto the channel walls rather than embedding it in the framework [281]. One such procedure using CP₂TiCl₂ as the Ti⁴⁺ precursor has been reported by Maschmeyer et al.[281]. In terms of the nature of Ti⁴⁺, XANES and EXAFS have suggested that after calcination, the dominant species is TiOH, tripodally bonded, through O, to Si [281, 287]. The results discussed above for TS-1 apply equally to this grafted Ti-MCM-41 with the distinction
that the major species is a titanium (IV) hydroxide and that because all of the Ti$^{IV}$ are in accessible positions, the material is a more active oxidation catalyst [288].

In summary then, a number of difficulties have been experienced in obtaining consistent results on the nature of Ti$^{IV}$ in crystalline silicas:

1. The difficulty of producing pure samples.
2. The difficulty of detecting small amounts of TiO$_2$ nanophases.
3. The change in coordination, from 4 to 6 upon adsorption of molecules from the gas phase.

However, after solution of these problems, the evidence is overwhelmingly in favour of Ti$^{IV}$ being in tetrahedral coordination within the framework of the silica host. Further, the unique chemical and catalytic properties of Ti$^{IV}$-silicas are likely to be due to the atomic, and probably random, dispersion of the Ti$^{IV}$ centres within these silicas.

### 8.2.3 Ti$^{IV}$-silasequioxanes

Recently, the use of soluble, molecular titanosilicates or Ti-silasequioxanes have been employed in order to model the active sites of heterogeneous Ti$^{IV}$-silica catalysts [287, 289, 290]. A schematic picture of one of these molecular systems is shown in Figure 8.6. It has been shown that, for Ti-silasequioxanes with different 'R' groups, the reactivity of these catalysts for cyclohexene oxidation with tetrabutyl-hydrogenperoxide (TBHP) decreases in the order $R = \text{MeO}^{-} > \text{ButO}^{-} > \text{Pr}^{i}O^{-}$ [287, 291]. They analysed these results as indicating that Ti-$R$ moieties in tripodally anchored materials, e.g. hydrolysed crystalline Ti-silicas or surface grafted Ti-MCM-41, are stable, under reaction conditions, towards hydrolysis. The authors also indicate that for catalytic activity, the chemical nature of the 'R' group is not important, although, from a steric point of view it can have a large effect on the properties of the catalyst. Abbenhuis et al.[289] studied the effect of hydrolysis of the Ti$^{IV}$ active site in Ti-silasequioxide gels during alkene epoxidation. They found significant leaching of Ti$^{IV}$ functions when only a single Ti-$\text{OSi}$ unit was present, suggesting that hydrolysis of these bonds
Figure 8.6: Schematic representation of a Ti\textsuperscript{IV}-octasilsequioxane showing only the tetrahedral T atoms. The T centres are connected through oxygen. These soluble systems are used to model the active sites in Ti\textsuperscript{IV}-silicas.

occurs during catalysis. They concluded that multiple Ti-OSi bonds, as in heterogeneous Ti-silicas, would make the catalyst more robust. A Ti\textsuperscript{IV}-silasequioxane catalyst, similar to that shown in Figure 8.6 with $R = C_5H_5$ was found to be an active catalysts that was stable to leaching and even reaction with aqueous HCl. Abbenhuis et al.[289] also saw no indication for loss of the R group.

Thus, it appears that for tripodally anchored TiR groups at least, the R group is stable towards hydrolysis whilst for catalytic oxidation to occur, a Ti-OSi bond must be cleaved.

8.2.4 The nature of Ti\textsuperscript{IV}: theoretical evidence

Only a small number of theoretical studies have been reported pertaining to the nature and local structure of Ti\textsuperscript{IV} in titanosilicates. Jentys and Catlow have used lattice simulation and Hartree-Fock quantum mechanical cluster calculations to show that in TS-1, the substitution energies of Ti\textsuperscript{IV} in different crystallographic positions were all within 10 kJmol\textsuperscript{-1}. They considered that this difference is small enough to allow random distribution, during synthesis, of Ti\textsuperscript{IV} over all of the T sites in the crystal. They also concluded that extra-framework, edge-sharing [TiO\textsubscript{x}] units as suggested by Trong-On
Figure 8.7: Schematic representation of the reactions studied by de Man and Sauer [42] to show that Ti$^{IV}$ substituted into a silica framework is more stable than in an edge-shared position (top) or in a 6 fold position as seen in ETS-10 (bottom).

et al.[282] and as shown in Figure 8.5, were unlikely. de Man and Sauer [42] have recently reported extensive calculations on the coordination, structural and vibrational properties of Ti$^{IV}$-silica clusters. They used Hartree-Fock techniques and clusters of up to 8T centres with Ti$^{IV}$ in sites of 4 to 6 fold coordination. Their calculations showed that it is favourable to substitute Ti$^{IV}$ into silica clusters and that Ti$^{IV}$ in corner sharing, tetrahedral coordination is more favourable than in edge sharing positions or than in six fold sites as in ETS-10. The later two processes are shown schematically in Figure 8.7. As mentioned above, their work has also provided detailed information concerning the nature of the 960 cm$^{-1}$ IR band observed in titanosilicates; the local nature of the perturbation arising from Ti$^{IV}$ incorporation was also demonstrated.

A number of authors have reported theoretical estimates for the local geometry of tetrahedral Ti$^{IV}$ sites in titanosilicates [292, 293]. The Ti-O Si bond lengths are predicted to be 1.803 Å HF/DZP, 1.798 Å BLYP/DNP [293], 1.81 Å BP86/DZVP [292], 1.79-1.82 Å HF/SVP [42], 1.79 Å HF/6-31G [294]. It is clear from comparison with Table 8.1 that current cluster models are
adequate in order to describe local Ti–O Si bonding in these materials.

8.3 Partial Oxidation Catalysis in TiIV-silicas: Mechanistic Detail

Although the study of the catalytic reactivity of TiIV-silicas has not matured as long as that of H-ZSM-5 with respect, in particular, to the MTG process discussed in Part II, a good deal of mechanistic studies on alkene epoxidation and alkane oxyfunctionalisation have been reported [9, 5, 248]. These two processes are thought to proceed via different pathways, the former via heterolytic, electrophilic oxygenation, the latter by a homolytic pathway. The difference is highlighted, for example, in the fact that epoxidations over TS-1 typically occur below 50°C, 1 atm pressure, whereas alkane oxidations typically require temperatures above 50°C [295]. It has been suggested that the threshold temperature is related to the temperature at which homolytic decomposition of H2O2 to H2O and O2 occurs [295]. We will begin our discussion with observations concerning the dependance of reactivity on solvent, peroxide and substrate structure. Lastly, a discussion of mechanisms suggested in the literature for both alkene epoxidation and alkane oxidation will be presented.

8.3.1 Effect of Solvent

It has been demonstrated a number of times that coordinating species, either solvent or reaction by-product, retard the rates and selectivities of epoxidations on metal oxide catalysts [260, 296]. In their study, Sheldon et al.[296] demonstrated that polychlorinated hydrocarbon solvents, i.e., polar species, with a low coordinating ability, were preferable.

Table 8.2 shows the effect of solvent on 1-octene oxidation over Ti-Al-β using H2O2 [9]. The presence of Al3+ in these samples, and thus Brönsted acidity, leads to acid catalysed reaction of the nascent epoxide and therefore the product selectivities have not been shown. Refering to Section 1.2, Chapter 1, we remind the reader that Ti-Al-β is hydrophilic, unlike TS-1; TiO2-SiO2 mixed oxides and Ti-MCM-41 are also hydrophilic in nature due
Table 8.2: Selected results showing the influence of solvent on the oxidation of 1-octene using $\text{H}_2\text{O}_2$ over Ti-Al-$\beta$ [9].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>Efficiency of $\text{H}_2\text{O}_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{OH}$</td>
<td>48</td>
<td>46</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{OH}$</td>
<td>47</td>
<td>39</td>
</tr>
<tr>
<td>$^3\text{PrOH}$</td>
<td>46</td>
<td>35</td>
</tr>
<tr>
<td>$^4\text{ButOH}$</td>
<td>36</td>
<td>31</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>9.1</td>
<td>1.5</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>57</td>
<td>30</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OHCH}_2\text{OH}$</td>
<td>7.7</td>
<td>0</td>
</tr>
<tr>
<td>CF$_3\text{CH}_2\text{OH}$</td>
<td>66</td>
<td>60</td>
</tr>
</tbody>
</table>

to the presence of surface silanols. The negative effect of $\text{H}_2\text{O}$, as well as the non-inhibiting effect of protic solvents, should be noted. Similar results have been observed for reactions over TS-1/$\text{H}_2\text{O}_2$. Clerici and Ingallina [297] reported that activity for 1-pentene epoxidation over TS-1 decreases in the order $\text{CH}_3\text{OH} > \text{CH}_3\text{CH}_2\text{OH} > ^4\text{ButOH}$. The yields and extent of side reactions increased in the same order. For example, in ethanol, selectivity to 1,2-epoxypentane was 71% whilst the remainder of the $\text{H}_2\text{O}_2$ was consumed by solvent oxidation. Khouw et al. [295] have reported a detailed study on the effect of $\text{H}_2\text{O}$ on the catalytic activity of TS-1 and TiO$_2$-SiO$_2$ coprecipitates using $\text{H}_2\text{O}_2$ in methyl-ethyl ketone; Table 8.3 summarises the results. It is clear that TS-1 is unaffected by the presence of $\text{H}_2\text{O}$ whilst it deactivates the coprecipitate with respect to both alkene and alkane oxidation. In contrast, Clerici et al. [298] have reported a retarding effect of $\text{H}_2\text{O}$ on the kinetics of propene epoxidation. These solvent effects have been explained on the basis of two hypotheses. Clerici and coworkers [269, 297, 298] have postulated that such strong solvent effects can only be explained by the direct involve-
ment of the solvent in an elementary reaction step. They suggest that in the presence of ROOH and a coordinating solvent, the reaction shown in Figure 8.8 occurs with formation of the active oxygen donating intermediate, Species I, i.e., hydrolysis of a SiO-Ti bond results in a titanium hydroper-oxo complex coordinated, in a five membered ring, to the solvent. This is in contrast to earlier work suggesting that TiIV(η2-O2) is the crucial intermediate [248, 299]. Clerici and Ingallina argue that TiIV(η2-O2) species cannot explain the observed solvent effects, the acidic properties of TS-1/H2O2 mixtures, and the behaviour towards additives (see below). The known inertness of TiIV(η2-O2) also weighs strongly against their involvement. Further, chemical modelling of TiIV oxidation catalysts with TiIV porphyrins found that TiIV(η2-O2) complexes were the poisoned form of active Ti=O catalysts [300].

Species I, Figure 8.8, is attractive in that it also explains the observed weak, solvent dependent, acidity of TS-1 and TiO2-SiO2 in the presence of H2O2 [298, 297, 295]. Khouw et al. [295] have studied the acid catalysed solvolysis of cis-2,3-epoxybutane to 2-methoxy-3-butanol in methanol

Table 8.3: Selected results showing the influence of H2O on the oxidation of 1-hexene and n-octane over TS-1 [295].

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>TiO2-SiO2 coprecipitates</th>
<th>TS-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conv. (%)</td>
<td>H2O2 eff. (%)</td>
</tr>
<tr>
<td>n-octane oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>anhydrous H2O2</td>
<td>2.71</td>
<td>4.37</td>
</tr>
<tr>
<td>aqueous H2O2</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>1-hexene epoxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>anhydrous H2O2</td>
<td>1.86</td>
<td>8.58</td>
</tr>
<tr>
<td>aqueous H2O2</td>
<td>0.24</td>
<td>0.53</td>
</tr>
</tbody>
</table>
at 30°C over TS-1 in the presence, and absence, of H₂O₂ or tetrabutyl hydrogenperoxide (TBHP). In agreement with earlier work [269, 297, 298] TS-1 without peroxide, as well as TS-1/TBHP mixtures show similar activity, whilst TS-1/H₂O₂ shows greatly increased activity. The same trend was observed on TiO₂-SiO₂ with H₂O₂ activating the surface for acid catalysed solvolysis whilst TBHP does not [295]. These observations are consistent with the acid-base equilibrium illustrated in Figure 8.8, active when R = H⁺ but not when R = alkyl. The results also show that silanol species formed on hydrolysis of Ti-OSi are not responsible for the acidity. Bellusi et al. [269] have previously shown that acid-catalysed solvolysis of oxirane rings occurs with inversion of configuration at the carbon centres.

Figure 8.8: Formation of solvated titanium peroxyo species (I). Clerici and coworkers [298, 301, 297, 269] have advocated this species as being crucial in explaining the behaviour of TiIV-silicas in oxidation catalysis.

Species I can also explain the observed retardation of epoxidation and
solvolysis kinetics in the presence of H$_2$O [269, 298]; the concentration of Species I is likely to be reduced by the poorer donor properties of the water ligand. On the basis of steric and electrophilic (pKa) arguments [9], the reduced activity when using ¹ButOH rather than CH$_3$OH has been explained on the basis of Species I [297, 295]. Further, Khouw et al. [295] have hypothesised that Species I can explain the observed activity for alkane oxidation shown by TS-1/H$_2$O$_2$ but not by TS-1/TBHP. They suggest that the acidity of the TS-1/H$_2$O$_2$ pair could be important for H-abstraction that is postulated to occur during alkane, but not alkene oxidation (see below). Species I is also consistent with the known tendency of Ti$^{IV}$ to expand its coordination shell above 4 and also has several organic analogues [269].

Unfortunately, no titanium hydroperoxo compounds have been prepared to date and no direct evidence for their presence has been recorded. It should also be noted that TS-1 is active for alkene epoxidation in the absence of solvents (although with reduced activity) [295] and Species I is therefore not necessary for this mode of reaction.

The second rational for the observed solvent effects is discussed in detail in reference [9]. They consider that the molecular sieve acts as a second solvent, extracting the substrate molecules from the bulk solvent. Which substrate molecules are selectively extracted is determined by the size and hydrophobicity of the pores of the molecular sieve (see Chapter 1, Part I) and the substrate. For example, a hydrophobic molecular sieve such as silicalite will selectively absorb apolar hydrocarbon substrates. The is especially important in hydrocarbon oxidations where the primary products are polar molecules which therefore rapidly diffuse out of the sieve rather than react further (they are more susceptible to oxidation than the reactants). Conversely, hydrophilic materials like Ti-Al-$\beta$, TiO$_2$-SiO$_2$, or Ti-MCM-41 will selectively absorb polar molecules. The latter explains why these materials are less active in aqueous media; the surface will preferentially adsorb water instead of an organic substrate. In hydrophobic materials like TS-1, the Ti$^{IV}$ sites are effectively screened from bulk water [295]. The rationale above is also consistent with recent work demonstrating that only alkenes with a hydrophilic group can be oxidised on TiO$_2$-SiO$_2$ mixed oxides using aqueous H$_2$O$_2$ as the sacrificial oxidant (see [295] and references therein).
On balance therefore it appears likely that both hypotheses are required in order to explain the combined acidity/solvent effects of reactions over Ti$^{IV}$-silicas; the use of non-coordinating solvents as well as solvent free systems for epoxidation reactions, however, highlights the redundancy of Species I in these cases.

8.3.2 Effect of Peroxide Structure

In a similar manner to variations in solvent discussed above, variation of the structure of the sacrificial peroxide in known to effect the results of catalytic oxidations over Ti$^{IV}$-silicas. In reference to Species I, Figure 8.8, we have already discussed the difference in acidic properties observed when using $^8$ButOOH (TBHP) and H$_2$O$_2$; the latter shows acidic properties, the former does not. Similarly, we have noted that TBHP is inactive for alkane oxidation but is active for alkene epoxidation over TiO$_2$-SiO$_2$ mixed oxides [295] (although it is active for both in Ti-MCM-41 [288]). TiO$_2$-SiO$_2$/H$_2$O$_2$ is active for both provided that anhydrous conditions are maintained over the coprecipitate as discussed above. Moreover, it has been demonstrated that anhydrous TBHP cannot be used as oxidant for alkane oxidation in TS-1 [301], and, in some cases, for alkene epoxidation [295]. In order to understand this effect in more detail, Khouw et al.[295] studied the adsorption capacities of organic molecules similar is size to TBHP in TS-1. In all cases, the molecules could diffuse into the intracrystalline pores, dispelling the possibility that the lack of reactivity could be due to diffusion limitations of the peroxide. In addition, they studied n-octane oxidation using $^9$ButOOH (NBHP), for which there should be no problems concerning reactant shape selectivity, but observed no activity. Lastly, alkane oxidation and alkene epoxidation were studied over an anhydrous TiO$_2$-SiO$_2$ coprecipitate for which microporous steric limitations should not be a constraint. TBHP and NBHP oxidised 1-hexene, but showed no activity towards alkanes. The authors concluded that two different mechanisms were needed to explain the phenomenon, both based on formation of Species I, Figure 8.8. The first, formation of Species I with $R = R' = \text{alkyl}$ in the zeolite pore was considered to prevent the reactants from approaching the activated titanium sites, retarding both
alkene and alkane activity. Thus, alkene epoxidation with TBHP over TiO$_2$-SiO$_2$ or Ti-MCM-41, for which there are less demanding steric limitations, is excellent [281, 283, 288]. The second involves the mechanism of alkane oxidation. Khouw et al. [295] hypothesised that the conjugate base of an acidic species (Species II with R=H in Figure 8.8) is required in order to abstract a hydrogen atom from a saturated hydrocarbon. However, use of a sacrificial alkyl hydroperoxide, i.e. with R = alkyl in Figure 8.8, will lead to an equilibrium for formation of Species II that lies well over towards Species I and activation of the C-H bond will therefore become more difficult. This hypothesis does not, of course, explain the activity of TBHP to alkane oxidation in Ti-MCM-41 [288].

Sheldon et al. [296] have demonstrated that the structure of the hydroperoxide, ROOH, can play an important rôle in determining the selectivities in TiO$_2$-SiO$_2$ mixed oxide catalysed epoxidation as shown in Table 8.4. The Table 8.4: Selected results showing the influence of peroxide structure on the oxidation of allyl chloride over a TiO$_2$-SiO$_2$ coprecipitate at 80°C [296].

<table>
<thead>
<tr>
<th>Hydroperoxide</th>
<th>Epichlorohydrin selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBHP</td>
<td>65</td>
</tr>
<tr>
<td>dichlorocumene</td>
<td>92</td>
</tr>
<tr>
<td>o-chlorocumene</td>
<td>69</td>
</tr>
<tr>
<td>cumene</td>
<td>6</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>46</td>
</tr>
<tr>
<td>tetralin</td>
<td>4</td>
</tr>
</tbody>
</table>

Low selectivities observed with cumene were considered to be due to heterolytic decomposition, a process known to be more facile for alkyl aromatic hydroperoxides than for alkyl hydroperoxides or hydrogen peroxide; this effect is, however, reduced when electron withdrawing groups are present. In addition, Sheldon et al. [296] considered that electron withdrawing substitu-
ents in the hydroperoxide are likely to increase the rate of epoxidation by enhancing the electrophilic nature of the Ti$^{IV}$-hydroperoxide complex, e.g., Species I, Figure 8.8. They demonstrated this effect by measuring the rates of allyl chloride epoxidation over a TiO$_2$-SiO$_2$ coprecipitate. For the hydroperoxides, cumene, o-chlorocumene and dichlorocumene, rates of 1:2.3:5 were reported. Sheldon and coworkers concluded that earlier data suggesting that the nature of the peroxide had little effect on the kinetics of oxidation did so due to the use of an alkene that was too reactive. Ledon and Varescon [300] have reported large variations in the regioselectivity of products formed during isoprene epoxidation over a Ti=0 porphyrin catalyst depending on the nature of the peroxide. They considered that these results indicated that the entire alkyl peroxide moiety exists in the active complex.

In conclusion therefore, alkyl hydroperoxides are not active for alkane oxidation over some (TS-1) but not all (Ti-MCM-41), Ti$^{IV}$-silica, whereas both hydrogen peroxide and alkyl hydroperoxides will epoxidise alkenes depending on steric and hydrophilicity constraints. The nature of the alkyl group in alkyl hydroperoxides can have a marked effect on the oxidation reaction provided that the effect is not masked by the use of reactive substrates.

### 8.3.3 Effect of Additives

In order to gain insight into the oxidation pathways over Ti$^{IV}$-silica catalysts, a number of authors have studied the effect of adding bases, acids, fluorides etc. to the reaction mixture [9, 295, 297].

Table 8.5 shows selected results of additive effects on the rate of epoxidation of 1-butene over TS-1 with H$_2$O$_2$ [297]. Small amounts of alkali-metal hydroxides or acetates improved yields up to almost quantitative results, and under the conditions studied, rates were not significantly reduced. Increased concentrations eventually inhibited TS-1 activity. Metal salts of strong acids, e.g., LiCl and NaNO$_3$, did not reduce the rate of 1-butene epoxidation at 0°C but the former, at least, inhibited allyl chloride epoxidation at 45°C. Addition of HCl improved rates whereas fluorides strongly reduced them. These effects were related to the properties of Species I, Figure 8.8 [297]. Small amounts of base improve the selectivity by reducing acidity (see
Table 8.5: Selected results showing the influence of additives on the epoxidation of 1-butene over TS-1 with H2O2 [297].

<table>
<thead>
<tr>
<th>Additive</th>
<th>H2O2 conv. (%)</th>
<th>H2O2 Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>LiCl(0.21 M)</td>
<td>91</td>
<td>84</td>
</tr>
<tr>
<td>NaN03(0.18 M)</td>
<td>92</td>
<td>85</td>
</tr>
<tr>
<td>HF(0.007 M)</td>
<td>10</td>
<td>95</td>
</tr>
<tr>
<td>NH4F(0.15 M)</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>CF3COOH(0.19 M)</td>
<td>95</td>
<td>64</td>
</tr>
<tr>
<td>CF3COOLi(0.18 M)</td>
<td>~0</td>
<td>-</td>
</tr>
</tbody>
</table>

a: solvolysis products 27%
b: effect can be reversed by addition of CF3COOH

Figure 8.8) and therefore secondary acid-catalysed reactions. At higher pH, however, formation of stable, charged peroxides, Species III, Figure 8.8, are thought to form which are inert towards alkenes due to electrostatic repulsion. Strong acids shift the equilibrium back towards Species I, re-establishing catalytic activity. Fluorides were considered to titrate available TiIV sites, preventing active TiIV-peroxide complexes from forming.

Khouw et al.[295] have studied the effect of NaOH loading on the catalytic activity of TS-1. Na-TS-1 was found to be inactive for both alkane and alkene oxidations. Unlike TS-1, Na-TS-1 does not change colour upon contact with H2O2(aq) suggesting that TiIV-OOH species do not form. Further, the 960 cm⁻¹ IR band observed in TS-1 was shifted to 985 cm⁻¹ in Na-TS-1. Following Camblor et al. [276], see Section 8.2.2, Khouw et al.[295] considered that their observations indicated the process shown in Figure 8.9.
The formation of $\eta_2$-peroxo complexes between H$_2$O$_2$ and Ti$^{IV}$-silicas is unquestionable; an UV-vis band at 26,000 cm$^{-1}$ (i.e., the sample turns yellow) is comparable to that from [TiF$_5$(O$_2$)]$^{3-}$, attributed to a O$_2^2- \rightarrow$ Ti$^{IV}$ charge transfer process [263]. These data do not, however, indicate that the peroxo species in Ti$^{IV}$ silicas is not a hydro- or alkyl-peroxide. Notari [5] has argued that Ti$^{IV}$-OOH formation (including bidentate binding of -OOR) would require less hydrolysis of the Ti$^{IV}$ site than formation of $\eta_2$-O$_2$ on the basis of the formal number of empty valence sites required. In agreement, Karlsen and Schöffel [293], using Density Functional Theory methods and small cluster models for the Ti$^{IV}$ site, found that formation of Ti$^{IV}$($\eta_2$-O$_2$) was endothermic by 90 kJmol$^{-1}$.

In the absence of additives, the thermal stability of $\eta_2$-O$_2$ complexes is limited to below 373 K [302, 303], but in the presence of base, the stability of the peroxo complex in TS-1 is markedly enhanced (up to 673K). Clerici et al. [297] suggested that this enhanced stability could explain the deactivation of the catalyst under these conditions (see Section 8.3.3.)

It has been observed that acid-catalysed hydrolysis reactions do not occur during the epoxidation reaction [5, 269]. This result was considered to indicate that the alkene was strongly coordinated to Ti$^{IV}$ in order to prevent formation of the complex responsible for acidity, i.e., in terms of the 5 membered ring Species I, the alkene blocks the coordination site required by the solvent. Oldroyd et al. [288] reported the deactivation of Ti-MCM-41 on TBHP or 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH) interaction in the absence of oxidisable alkene (their sample became yellow in colour). They
concluded that the alkene must preferentially bind to the Ti$^{IV}$ prior to peroxide interaction. Similarly, Ti=0 porphyrins form deactivated Ti$^{IV}$($\eta_2$-O$_2$) complexes during epoxidation with TBHP; after isolation, Ti$^{IV}$($\eta_2$-O$_2$) was found to be inactive for alkene epoxidation in the absence of additional TBHP. Their studies also suggest that a cis-hydroxo(alkylperoxo) complex, Figure 8.10, was likely to be involved during the reaction of the Ti=0 porphyrin and alkyl hydroperoxides. The observation that different peroxides led to variations on the regioselectivity of the epoxidation was also considered to indicate that the whole $\sim$OOR group was involved in the active oxygen donating species (see Section 8.3.2). In contrast, Khouw et al.[295] preloaded TS-1 with H$_2$O$_2$. After drying, the yellow catalyst was active, without additional oxidant for alkane oxidation at 80°C in methyl ethyl ketone (the colour yellow gradually faded). This implies that the peroxo complex is either the active oxygen donating species or is the precursor to it for alkane oxidation.

The apparent disagreement between reports of the activity of hydroperoxide preloaded materials is almost certainly due to the use of different materials, conditions, reactions times and the mechanism of reaction, e.g., for alkane and alkene oxidation. In addition, if Species I, Figure 8.8 and above, is important, there will be substantial difference in its properties when R = H and when R = $^t$Bu due to the stability of tertiary carbenium ions. Unfortunately, on the basis of UV-vis spectroscopy, it is unclear whether the peroxo species present is $\eta_2$-O$_2$, $\eta_2$-O$_2$ or bidentate $\sim$OOR and more work is required to solve this problem. In addition, it is unclear whether strong al-
kene binding is important prior to formation of the active oxygen donating species or whether catalyst deactivation to a $\eta_2$-$O_2$ complex, in the absence of oxidisable substrate, is merely a consequence of competing processes with the oxidation process being more rapid.

it is a case of competing reactions: in the absence of alkene, a less rapid deactivation pathway is followed.

8.4 The Mechanistic Proposals

From the preceding discussions it is clear that many factors contribute to oxidative activity of Ti$^{IV}$-silicas in the presence of a sacrificial oxidant and oxidisable substrate. Following Notari [5] the major properties leading to the unique chemical reactivity of Ti$^{IV}$-silicas in comparison to homogeneous systems can be summarised as follows:

- The resistance of the Ti$^{IV}$ centre to extensive hydrolysis.
- The thermal decomposition of Ti$^{IV}$ peroxo compounds leading to the possibility of different mechanisms occurring at low and high temperatures.
- Selective adsorption of reactants arising from host hydrophilicity/hydrophobicity properties.
- Shape selectivity including reactant diffusivity and transition state structural constraints.

Mechanistic proposals, to date, have been principally concerned with the donation of the activated $O$ from a Ti$^{IV}$ peroxo complex to the oxidisable substrate; radical and heterolytic mechanisms have been proposed.

Heterolytic mechanisms have been proposed on the basis of liquid phase analogues and are consistent with experimental observations that the reactions involve electrophilic attack of the peroxo compound on the organic substrate [27, 260, 297]. For example, Clerici and Ingallina [297] studied the reactivity of a number of alkenes in epoxidation reactions over TS-1 with $H_2O_2$. The rate of reaction was shown to be dependent on the nature of the alkene, e.g., the molecular weight, the presence of substituent groups,
the number, position and nature of the latter and the steric configuration of the alkene. The electrophilic behaviour of the epoxidising agent is highlighted by the reactivity trend of similarly hindered alkenes; allyl alcohol < allyl chloride < 1-butene and 3-methyl-1-butene < 2-methyl-1-butene < 2-methyl-2-butene for which reactivity correlates with the electron density of the double bond. However, in TS-1, shape selectivity with respect to reactants and transition states (see Figure 1.5, Chapter 1) often mask electronic effects. For example, cis/trans relative rates (16.2 for 2-butene [297]) probably results from restricted transition state shape selectivity, whilst the fact that 1-hexene reacts two orders of magnitude faster than cyclohexene highlights reactant selectivity. Thus, alkene reactivity is a complicated function of host properties and those intrinsic to the alkene; it is clear however that electrophilic transfer of oxygen takes place. In all cases, epoxidation of alkenes was found to be stereospecific [297, 295]

Oldroyd et al. [288] have recently published a study of alkene oxidation over Ti-MCM-41 using TBHP and 2-methyl-1-phenyl-2-propyl hydroperoxide, MPPh, as oxidant. The latter was employed as a radical trap, i.e., if homolytic cleavage of its peroxidic 0-0 bond takes place, rapid β-scission of the resulting alkoxyl radical (MPPO) precludes reaction with any substrate at concentrations of less than 1M,

\[
\text{PhCH}_2\text{CMe}_2\text{OOH} \rightarrow \text{PhCH}_2\text{CMe}_2\text{O} \rightarrow \text{PhCH}_2 \cdot + \text{Me}_2\text{CO}
\]

Thus, if radical processes take place when MPPh is used as oxidant, the main products are expected to be benzyl alcohol, benzaldehyde and dibenzyl rather than products arising from the substrate. In studies of cyclohexene oxidation over Ti-MCM-41, both TBHP and MPPh gave epoxide products indicating a non-radical pathway. Further, on oxidation of cis-stilbene over Ti-MCM-41 with either TBHP or MPPh, cis-stilbene oxide was the only oxidation product; reaction with \(^5\text{Bu}t\text{O} \cdot\) radicals gave substantial amounts of trans-stilbene oxide. This study, combined with the high yields of epoxides and the stereospecificity observed in epoxidation reactions [295, 297] has led to the widespread conclusion that Ti\(^{IV}\)-silicas catalyse the epoxidation of alkenes in the presence of a sacrificial oxidant in a non-radical manner.
8.5 Heterolytic Mechanisms

Notari [248] has suggested the mechanism shown in Figure 8.11 for alkene epoxidation via a TiIV(η2-O2) complex. It has already been noted, however, that TiIV(η2-O2) species cannot directly explain the observed acidity of titanosilicate/H2O2 mixtures or the effect of additives on activity; they are also known to be very stable (see Section 8.3.4 and references [5, 297]). In addition, Karlsen and Schöffel [293], using Density Functional Theory methods and small cluster models for the TiIV site, found that formation of TiIV(η2-O2) from Ti(OH)4 was endothermic by 90 kJmol⁻¹. TiIV(η2-O2) complexes have also been shown to be inactive for alkene epoxidation on the basis of studies with TiIV-porphyrins [300] and from the results of preloading of Ti-MCM-41 with hydrogenperoxides, see Section 8.3.4 and reference [288]. TiIV(η2-O2) complexes could, however, be the active species for alkane activation at higher temperatures [295]. Latour et al. [304] reported that on formation of TiIV(η2-O2) porphrin complexes from the Ti=0 form with H2O2, the peroxidic O-O bond remains intact. Further, Inamoto et al. [305] showed that its formation showed a first order dependence on [H⁺]. Ledon and Varescon [300] considered that these reports (together with the reactivity dependence on peroxide structure, see Section 8.3.2) were consistent with formation of a cis-hydroxo(alkylperoxo) or cis-hydroxo(hydrogenperoxo) complex, as shown in Figure 8.10, via proton assisted ring opening of the peroxo-ring.
Figure 8.12: Suggested pathway for epoxide formation from a Ti\textsuperscript{IV}-OOH...ROH complex as suggested by Clerici and coworkers [269, 298, 297].

(TPP is the porphyrin),

\[
O_2\text{Ti}(TPP) + H_3O^+ \rightarrow HOO - \text{Ti(OH)(TPP)}
\]

This hypothesis explains the rate retardation on addition of Na\textsubscript{2}HPO\textsubscript{4} (base) and is in line with the model suggested by Clerici and coworkers and shown in Figure 8.8, Section 8.3.1 [269, 298, 297], involving a solvent molecule coordinated to Ti\textsuperscript{IV} in a five membered ring.

Clerici and coworkers [269, 298, 297] suggested the alternative pathway for epoxide formation shown if Figure 8.12. This mechanism (with slight modification) has been studied in detail using theoretical methods by Neurock and Manzer [292]. Using Density Functional Theory (DFT) methods and 4\textsuperscript{T} clusters to model the Ti\textsuperscript{IV} site, they reported calculations on ethene epoxidation with methanol as the coordinating solvent. They found that ethene attacked the TiOOH complex at the oxygen attached to Ti\textsuperscript{IV}; interaction with the other oxygen was more repulsive. Clerici and Ingallina [297] argued that attack at the peroxide oxygen furthest away from Ti\textsuperscript{IV} was most likely on the basis of steric arguments. In agreement with the suggestions of Clerici and coworkers [269, 298, 297], the DFT studies show that hydrogen bonding in the 5 membered ring stabilises both the hydrogen-
peroxide complex and the transition state for epoxide formation. Neurock and Manzer also examined the effect of changing the substituents on the metal centre. They found that the effective charge on Ti$^{IV}$, and therefore on the peroxide oxygen attached to it, became more positive on increasing the electron withdrawing power of the ligand. This would, of course, reduce the initial repulsive peroxide-ethene interaction and would, additionally reduce the strength of binding of the product. They reported an overall reaction energy of -220 kJmol$^{-1}$, a value whose magnitude is expected to increase on increasing the electron withdrawing power of the ligands attached to Ti$^{IV}$. The calculated activation barrier for this process was found to be 210 kJmol$^{-1}$ [306]. Their reaction resulted in the direct generation of water and a TiOCH$_3$ complex. Whether the next step would be initial catalyst regeneration or whether catalysis proceeds at the tetrahedral TiOCH$_3$ site is unclear. Given the R dependence of TiOR active sites in silasequioxanes analogues reported in Section 8.2.3, this question is highly relevant.

Another mechanism based on that proposed for metal peroxo complexes involving the formation of a metallacycle intermediate is shown in Figure 8.13 [307, 308, 309]. This mechanism was suggested following obser-
vation of the inhibition of n-hexane oxidation on water/acetone mixtures over TS-1 when 1-octene was co-fed [309]. It was considered that this result indicated that the oxidisable substrate was strongly coordinated to the active TiIV oxygenating species and therefore that preferential coordination of 1-octene would retard alkane oxyfunctionalisation. The strong coordination of alkenes was also suggested by Oldroyd et al.[288] on the basis of catalyst deactivation observed when TBHP or MPPH were preloaded into Ti-MCM-41 (see Section 8.4). It could also be argued that for TS-1, but not Ti-MCM-41 or TiO2-SiO2 mixed oxides, the hydrophobic nature of the molecular sieve (see Section 1.2, Chapter 1) will lead to a high concentration of alkene within the pores of the host and therefore that alkenes are more likely to coordinate to TiIV prior to hydroperoxide interaction. However, Hutter et al. [256] have noted that TiO2-SiO2 mixed oxides, in the absence of alkenes, catalyse the decomposition of cumene hydroperoxide. On addition of cyclohexene, however, epoxidation competes very efficiently with decomposition. A similar effect could explain the deactivation of Ti-MCM-41 (and other materials [300, 295]) in the absence, but not presence, of an oxidisable substrate. Further, Clerici and Ingallina [297] could not reproduce the inhibition of alkane oxidation on introduction of an alkene, as observed by Huybrechts et al [309], and suggested that the effect could be due to admixtures of TiO2 in the sample used by Huybrechts et al.. TiO2 is known to decompose homolytically H2O2 and start radical chain processes. Furthermore, they argue that a two phase (liquid) water/acetone mixture could result in H2O2 preferentially dissolving in the acetone phase leading to formation of organic peroxides; decomposition under the relatively high temperatures used and in the presence of a TiIV compound, could then start a homolytic process. Clerici and Ingallina therefore consider that the competitive experiments of Huybrechts et al. [309] may have involved, at least partially, n-hexane oxidation by a radical chain mechanism that was inhibited by the presence of excess alkene. They also note that alkenes are unlikely to coordinate to the TiIV centre in the presence of oxygenated solvents such as water, alcohols, ketones etc.

Karlsen and Schöffel have reported a Density Functional Theory study of the oxidation of ethene via the pathway shown in Figure 8.14 [293]. Using small Ti(OH)4 clusters to model the TiIV site, they found that O1 in
the Ti$^{IV}$($\eta_2$-OOH) complex is highly activated with an O$_1$-O$_2$ bond distance of 1.521 Å relative to that in H$_2$O$_2$ of 1.49 Å. The $\eta_2$-OOH complex was found to be 33 kJ mol$^{-1}$ more stable than the $\eta_1$-OOH complex and formation of Ti$^{IV}$($\eta_2$-O$_2$) was found to be unfavourable by 90 kJ mol$^{-1}$. Karlsen and Schöffel [293] found that ethene approached O$_1$ in a spiro, rather than planar manner (preferred by 15 kJ mol$^{-1}$). The dominant orbital overlap in the spiro transition state was found to be between the HOMO of ethene and the LUMO of the $\eta_2$-OOH complex, reflecting the electrophilic nature of the reaction. A 0.22e charge transfer from the $\eta_2$-OOH complex to ethene in the transition state agrees with this analysis. They calculated an activation barrier of 96 kJ mol$^{-1}$ for the oxygen transfer step to ethene and an overall energy change of -105 kJ mol$^{-1}$ for epoxide formation (which should be compared with those of Neurock and Manzer of 210 kJ mol$^{-1}$ and -220 kJ mol$^{-1}$ respectively [306, 292]).

8.6 Homolytic Mechanisms

It has already been noted that, on the basis of the work reported by Oldroyd et al. [288] on the epoxidation of alkenes over Ti-MCM-41 with TBHP and MPPH (see Section 8.4), as well as on the high yields of epoxides and the stereospecificity observed in epoxidation reactions [295, 297], Ti$^{IV}$-silicas are thought to catalyse the epoxidation of alkenes in a non-radical manner. However, in their study of alkane oxyfunctionalisation, Khouw et al. [295] concluded, in agreement with others [297, 288], that alkane activation proceeds via a
radical mechanism but, unlike earlier work, they were able to show that the radicals formed have a very short lifetime or are restricted such that no rearrangements can take place. They used a 'radical clock' technique which utilises the rapid unimolecular rearrangements of radical intermediates. The production of rearranged products indicate that a radical intermediate with a longer lifetime than the time required for radical rearrangement is formed during reaction. This procedure is similar to that employed by Oldroyd et al.\cite{288} and discussed above. Khouw et al.\cite{295} studied the oxidation of ethylcyclopropane and iso-propylcyclopropane with $H_2O_2$ over TS-1 at 80°C. The ring opening reaction for radicals of these two species is very fast; however, no linear products were observed in the products, i.e. the alkanes did not rearrange. Stereoscrambling during oxidation strongly implies a radical mechanism and Khouw et al. concluded that the radicals formed within the molecular sieve do not behave like classical radicals in that they either have very short lifetimes or cannot rearrange due to restricted movement within the host pores.

Notari \cite{5} has suggested the radical mechanism shown in Figure 8.15 on the basis of Khouw et al.'s work and the evidence suggesting strong alkene
Figure 8.16: Suggested pathway for alkane oxidation on TS-1 as suggested by Khouw et al. [295].

binding to the Ti$^{IV}$ centre [309] (but see also reference [288]). The restricted radical lifetime/movement as suggested by Khouw et al. [295] would explain why classical radical behaviour has not been observed and is consistent with the ease of Ti$^{III}$ formation in highly dispersed Ti$^{IV}$-silicas (see Section 8.2). The pathway is also consistent with regioselectivities observed in alkane and alcohol oxidation [5]. The mechanism does not however account for the lack of activity of Ti$^{IV}$($\eta_2$-O$_2$) complexes in porphyrins and Ti$^{IV}$-silicas, the observed effect of additives such as acids and bases and the fact that oxygenated solvents are more likely to coordinate to Ti$^{IV}$ centres than alkenes, especially in hydrophilic systems such as Ti-MCM-41 and TiO$_2$-SiO$_2$ mixed oxides. If this mechanism were general, as hypothesised by Notari [5], it would also fail to explain the fact that in TS-1, H$_2$O$_2$ is active for both alkane and alkene oxidation whilst ROOH is only active for alkene activation (note however that Oldroyd et al. [288] have observed alkane activation using TBHP over Ti-MCM-41). In order to explain the dependence of alkane activity on peroxide, Khouw et al. [295] have proposed the mechanism shown in Figure 8.16. For more details see reference [295].
8.7 Partial oxidation of alkenes: summary

This Chapter has presented literature relevant to the understanding of the local nature of Ti$^{IV}$ in titanosilicates and to the partial oxidation of alkenes and other hydrocarbons over Ti$^{IV}$-silicas in the presence of a sacrificial oxidant. The importance of Ti–O–Si groups has been stressed, especially in light of recent silasequioxanes work, although the possibility of titanyl species being involved was noted. Of particular importance to mechanistic studies of alkene oxidation is the marked solvent effects, the behaviour in the presence of additives, the effect of varying the peroxide structure and the convincing arguments for non-radical, electrophilic reactivity of the active oxygen donating species. A number of important questions, however, still remain:

1. Is alkene binding to Ti$^{IV}$ an important requirement for oxidation?

2. What is the active oxygen donating species? It seems unlikely that it is a Ti$^{IV}(\eta_2-O_2)$ group. It also seems unlikely that it is a 5 membered solvent coordinated Ti$^{IV}$-OOR···O(H)R as suggested by Clerici [269, 298, 297] and coworkers due to the high activation barrier calculated by Neurock and Manzer [292]. However, considering the acidity of TS-1/H$_2$O$_2$ mixtures and the fact that alkene epoxidation can occur in the absence of solvent, the importance of this species is still unknown. Is the active oxygen donating species a Ti$^{IV}(\eta_2$-OOR) complex as suggested by Karlsen and Schöffel [293] or a cis-hydroxo(alkylperoxo) complex as suggested by Ledona and Varescon on the basis porphyrin studies?

3. What, if any, is the rôle of titanyl, Ti=O, species?

4. In organic derivatives of the Ti$^{IV}$ species, e.g., tripodally attached TiR groups, what is the rôle of the R group? Why do Ti–R bonds not hydrolyse during reaction and why does Ti$^{IV}$ not leach out of the system under normal operating conditions?

5. What is the rate determining step for substrate oxidation? Is it a transport step, a chemical transformation or an adsorption/desorption step? Theoretical work suggest that it is not adsorption or desorption.
[292, 293] and the majority of workers appear to consider that it is the oxygen transfer step.

The following Chapters report first-principles Density Functional Theory calculations in order to answer some of the questions posed above. Chapter 9 reports initial work on the nature and coordination of Ti$^{IV}$ in titanosilicate catalysts. Chapter 10 reports calculations on the interaction of the Ti$^{IV}$ site with ethene and hydrogen peroxide. The importance of Ti=0 is studied and a suggested mechanisms for alkene epoxidation is proposed.
Chapter 9

Ti^{IV}-silicas : The Ti^{IV} Site

The last Chapter reviewed the literature concerning Ti^{IV} embedded into, or grafted onto, a silica host. The resultant partial oxidation catalysts have been shown to be extremely active, giving high product selectivities and reactant conversions. However, a number of questions exist concerning both the nature of the dominant Ti^{IV} species and its behaviour towards H_{2}O.

This Chapter reports non-local density functional theory calculations within the cluster approximation on the hydrolysis and hydration of Ti^{IV} centres in titanosilicate catalysts. Results corroborate experimental observations concerning the nature and coordination of such sites in materials synthesised by different methods and studied under a variety of conditions. Also reported are calculations on the formation of Ti^{IV} active sites on silanolated surfaces such as the walls of mesoporous silicas by the reaction of terminal silanols with (\eta_5-C_8H_{12})_2TiCl_2. In line with experiment [281], the calculations predict that, after calcination, the dominant surface Ti^{IV} species is a (\equiv SiOl)_3TiOH complex. However, our results suggest that there could also be an appreciable concentration of the (\equiv SiOl)_2Ti(OH)_2 complex present. Formation of (\equiv SiOl)_2Ti = O species, studied in the presence, and absence, of a single molecule of H_{2}O is shown to be energetically feasible in the former case.
9.1 Methodological Details

We have used BP86/DZVP methods (DGauss3.0) and the cluster approximation (dangling bonds terminated by hydrogens) to study the formation and nature of Ti$^{IV}$ in titanosilicate materials. Given the discussion in Chapter 4, we will not consider methodological shortcomings further. The reader is reminded, however, that the BP86/DZVP method leads to activation barriers that are underestimated by up to 30% and that bond lengths are too long by ~0.01Å.

In all calculations, the geometry searches were carried out without symmetry constraints. In order to prevent non-physical relaxation of terminal SiH$_3$ groups during the geometry optimisation, the 4T, TiOH, and 5T, Ti(OSi)$_4$ clusters, see Figure 9.1 and Figure 9.2, were fully optimised; all other calculations had the Si coordinates fixed at these positions. Smaller clusters, e.g., the 3T, Ti(OH)$_2$ structure was built from the 4T, TiOH, fragment with the resulting Si coordinates fixed throughout. All other parameters were optimised. Thus, calculated energy differences are not reaction energies for the equilibrium geometries but reflect more accurately the constrained processes occurring at the surface sites.

All transition states structures have a single dominant Hessian eigenvalue. Due to the large number of species involved however, minimum energy structures were assumed to be true minima without confirmation from independent Hessian calculations. The ability of this type of calculation to predict accurate geometries of Ti$^{IV}$-silicas was reported in Section 8.2.4 (Chapter 8) and calculated geometries will not be discussed explicitly; however, the Cartesian coordinates of all of the structures displayed in the Figures are tabulated in Appendix A.

We emphasize that all energies are internal energies resulting from static electronic structure calculations at stationary points on the adiabatic potential energy surface. Thus, as with all such calculations, thermal and entropic effects are neglected.
9.2 Hydrolysis and hydration of Ti\textsuperscript{IV} sites in titanosilicates

The nature of Ti\textsuperscript{IV} sites in titanosilicates was discussed in detail in Section 8.2, Chapter 8. We recall that it has been reported that substitution of Ti\textsuperscript{IV} into a silica matrix results in strain around the substitution site which manifests itself in an expansion of the unit cell volume. Theoretical calculations have shown that the perturbation of the lattice is a very local effect extending essentially to the first coordination shell around Ti\textsuperscript{IV}. It has also been noted that well prepared titanosilicates contained tetrahedrally coordinated Ti\textsuperscript{IV} in highly dispersed, probably random locations, with Ti-OSi moieties being considered as crucial for oxidation activity in the presence of sacrificial oxidants. The characterisation of the nature and coordination state of Ti\textsuperscript{IV} sites has caused some debate and the importance, or not, of titanyl species, Ti=O and the significance of the various species reported in Figure 8.1 (Chapter 8), is still unclear. Ti-OSi are known to hydrolyse in the presence of water and/or hydrogenperoxides, although under normal conditions, Ti\textsuperscript{IV} remains anchored to the host; see Section 8.2, Chapter 8 for more details.

This section concentrates on describing the nature and coordination state of Ti\textsuperscript{IV} in Ti\textsuperscript{IV}-silicas, its hydrolysis and hydration, based on the following reactions for hydrolysis (see Figure 9.1),

\[
(\equiv \text{Si}0)^4\text{Ti} + \text{H}_2\text{O} \rightarrow (\equiv \text{Si}0)^3\text{TiOH} + \equiv \text{SiOH},
\]

\[
(\equiv \text{Si}0)^3\text{TiOH} + \text{H}_2\text{O} \rightarrow (\equiv \text{Si}0)^2\text{Ti(OH)}_2 + \equiv \text{SiOH},
\]

and the following reactions for hydration,

\[
(\equiv \text{Si}0)^4\text{Ti} + \text{H}_2\text{O} \rightarrow (\equiv \text{Si}0)^4\text{Ti.H}_2\text{O} + \text{H}_2\text{O} \rightarrow (\equiv \text{Si}0)^4\text{Ti.2H}_2\text{O}
\]

\[
(\equiv \text{Si}0)^3\text{TiOH} + \text{H}_2\text{O} \rightarrow (\equiv \text{Si}0)^3\text{TiOH.H}_2\text{O} + \text{H}_2\text{O} \rightarrow (\equiv \text{Si}0)^3\text{TiOH.2H}_2\text{O}
\]

\[
(\equiv \text{Si}0)^2\text{Ti(OH)}_2 + \text{H}_2\text{O} \rightarrow (\equiv \text{Si}0)^2\text{Ti(OH)}_2\text{.H}_2\text{O} + \text{H}_2\text{O} \rightarrow (\equiv \text{Si}0)^2\text{Ti(OH)}_2\text{.2H}_2\text{O}
\]

Figure 9.1 shows the BP86 optimised structures of the Ti(0Si)\textsubscript{4}, TiOH and Ti(OH)\textsubscript{2} complexes before and after hydration with one and two water molecules. It appears that the Ti(0Si)\textsubscript{4} complex is the most stable 4-coordinate form of Ti\textsuperscript{IV}, probably as a result of the larger number of T-O-T
Figure 9.1: BP86/DZVP optimised geometries of the surface Ti$^{IV}$ species before and after hydrolysis (across the top row) and hydration (down each column) with one and two H$_2$O molecules. The Ti(OSi)$_4$ complex is modelled by (H$_3$SiO)$_4$Ti, TiOH by (H$_3$SiO)$_2$TiOH, and Ti(OH)$_2$ by (H$_3$SiO)$_2$Ti(OH)$_2$. Energy changes are in kJmol$^{-1}$.

However, we note that the hydrolysis processes shown in Figure 9.1 (top row) have been modelled using isolated silanol species (H$_3$SiOH); in an actual molecular sieve, these silanols would probably be stabilised by hydrogen bonds. Assuming that in the real system each silanol is involved in only one hydrogen-bond, and using the estimate of the strength of this hydrogen-bond reported by Bleiber and Sauer of -27 kJmol$^{-1}$ (for two interacting H$_3$SiOH species in the gas phase)[149], we see that there is little energy...
difference between the three 4-coordinate Ti$^{IV}$ complexes. Thus, we predict that Ti$^{IV}$ substituted into a zeotype framework, as in TS-1, would readily hydrolyse to form TiOH and Ti(OH)$_2$ species with neighbouring silanol groups as suggested in reference [44, 263] as a means to relieve the strain imposed on the framework when Ti$^{IV}$ is substituted for Si. We note that there is unlikely to be a low energy pathway to form Ti(OSi)$_4$ from either the TiOH or Ti(OH)$_2$ species when Ti(OSi)$_4$ is grafted onto the surface since suitably positioned silanols would probably be unavailable.

Figure 9.1 also shows that in the presence of water the coordination shell around Ti$^{IV}$ expands (down each column). Little can be inferred from the relative binding energies of water in the different configurations as they are too similar, given the errors implicit in the model, e.g., the use of the cluster approximation. However, it is clear that only in the complete absence of water will pure 4-coordinate Ti$^{IV}$ be observed and only in the limit of a saturated system will 6-coordinate Ti$^{IV}$ be observed. Intermediate regimes of water partial pressures will lead to a mixture of Ti$^{IV}$ species with coordination numbers varying between 4 and 6. Conversion between the 4-coordinate Ti$^{IV}$ species and their subsequent hydrated structures could explain the previous uncertainty concerning the nature and coordination numbers of Ti$^{IV}$ centres in framework and grafted materials prepared in different ways and studied with different techniques and under different conditions [280, 279, 282, 44, 286, 284, 285, 43, 272, 266]; see Section 8.2, Chapter 8.

### 9.3 Grafting of a Ti$^{IV}$ precursor to surface silanols

We recall that the catalytic activity of Ti$^{IV}$ framework-substituted microporous materials, e.g., TS-1 and TS-2[238], is somewhat limited by the fact that only those reactants that are small enough to gain access to the Ti$^{IV}$ centres through the zeolitic channels can be converted. This prevents their use in the fine-chemical and pharmaceutical contexts where bulkier reactants dominate. The synthesis and use of Ti-MCM-41 with pore dimensions in the range of 25-100Å has made these titanosilicate catalysts more widely applicable. Maschmeyer et al.[281], have described a method of introducing Ti$^{IV}$ ions onto the framework of MCM-41 silicas using titanocene dichlor-
Figure 9.2: BP86/DZVP optimised geometries of the complexes relevant to Ti IV active-site formation via grafting. Cp represents $\eta_5$-C$_5$H$_5^-$. The TiCp complex is modelled by $(\text{H}_3\text{SiO})_3\text{TiCp}$, TiCp$_2$ by $(\text{H}_3\text{SiO})_2\text{TiCp}_2$, Ti(OH)$_2$ by $(\text{H}_3\text{SiO})_2\text{Ti(OH)}_2$, TiOH by $(\text{H}_3\text{SiO})_2\text{TiOH}$, and Ti=0 by $(\text{H}_3\text{SiO})_2\text{Ti}=0\ldots\text{O(}H\text{)SiH}_3$. Energy changes are in kJmol$^{-1}$.

The TiCp complex is modelled by $(\text{H}_3\text{SiO})_3\text{TiCp}$, TiCp$_2$ by $(\text{H}_3\text{SiO})_2\text{TiCp}_2$, Ti(OH)$_2$ by $(\text{H}_3\text{SiO})_2\text{Ti(OH)}_2$, TiOH by $(\text{H}_3\text{SiO})_2\text{TiOH}$, and Ti=0 by $(\text{H}_3\text{SiO})_2\text{Ti}=0\ldots\text{O(}H\text{)SiH}_3$. Energy changes are in kJmol$^{-1}$. After calcination, the Cp$_2\text{TiCl}_2$ (Cp = $\eta_5$-C$_5$H$_5$) treated MCM-41 silica becomes an active catalyst for selective oxidation of even bulky substrates. All intermediate materials produced in the catalyst preparation were examined by in-situ Ti K-edge X-ray adsorption spectroscopy (EXAFS and XANES)[280, 281].

This section describes calculations of the grafting pathway for formation of titanium containing species on the surface of MCM-41 or other silanolated surfaces. The grafting process was modelled using the following reactions.
for initial anchoring (see Figure 9.2),

\[
\text{Cp}_2\text{TiCl}_2 + 3(\equiv \text{SiOH}) \rightarrow (\equiv \text{SiO})_3\text{TiCp} + 2\text{HCl} + \text{CpH},
\]
\[
\text{Cp}_2\text{TiCl}_2 + 2(\equiv \text{SiOH}) \rightarrow (\equiv \text{SiO})_2\text{TiCp}_2 + 2\text{HCl},
\]

and with the following reactions for formation of the dehydrated TiOH active site, i.e., calcination,

\[
(\equiv \text{SiO})_3\text{TiCp} + \text{H}_2\text{O} \rightarrow (\equiv \text{SiO})_3\text{TiOH} + \text{CpH},
\]
\[
(\equiv \text{SiO})_2\text{TiCp}_2 + 2\text{H}_2\text{O} \rightarrow (\equiv \text{SiO})_2\text{Ti(0H)}_2 + 2\text{CpH}.
\]

We also report the relative stability of TiOH and Ti=O surface species from calculation of the energetics involved in the following reaction,

\[
(\equiv \text{SiO})_3\text{TiOH} \rightarrow (\equiv \text{SiO})_3(0=\text{Ti=O=Si} =)
\]

where the Ti=O complex has a dative covalent bond between the Ti centre and the 0 of an additional silanol; we note the absence of adsorbates.

Figure 9.2 shows immediately that if only local binding effects are important in the anchoring of \(\text{Cp}_2\text{TiCl}_2\) to surface silanols then there is an 89 kJmol\(^{-1}\) preference for formation of the TiCp complex over formation of the TiCp\(_2\) species. In the case of the latter structure, the second Cp ligand interacts with a silanol and is expelled as CpH. As above, the anchoring process shown in Figure 9.2 represents the reaction of \(\text{Cp}_2\text{TiCl}_2\) with isolated silanol species. Again assuming that in the real system, each surface silanol is involved in only one hydrogen-bond, that it must be broken before grafting, and that its strength is -27 kJmol\(^{-1}\)[149], then in order to form the TiCp complex by the process in Figure 9.2, an initial energy input of 81 kJmol\(^{-1}\) is required whilst in order to form the TiCp\(_2\) complex, an initial input of only 54 kJmol\(^{-1}\) is required. This reduces the energy difference between the two pathways to about 60 kJmol\(^{-1}\), formation of the TiCp complex still being the most favourable. The interpretation of the energy changes of the two anchoring pathways is complicated by the fact that the TiCp and TiCp\(_2\) complexes contain different numbers of Ti-0-Si bridges. The contribution to the energetics from the energy of condensation of hydroxyl species to form Ti-0-Si bridges will therefore be different in the two cases and it is possible that this effect leads to the different energy changes for the anchoring
pathways. However, it has been shown [310] that this condensation energy is of the order of only 0-20 kJmol\(^{-1}\), and it is thus likely that the reason for the differences in energies of formation of the two surface Cp complexes is primarily a steric one.

The calcination step of the reaction has been modelled by the formation of TiOH and Ti(OH)\(_2\) species from the TiCp and TiCp\(_2\) complexes respectively (see Figure 9.2). Formation of the Ti(OH)\(_2\) species from its precursor (TiCp\(_2\)) is much more favourable than formation of TiOH species from TiCp, presumably due to the relief of steric strain. Due to the large preference for the initial formation of the TiCp complex however, we predict that the TiOH species is the dominant one (it is more stable by 22 kJmol\(^{-1}\)). However, as noted above, 22 kJmol\(^{-1}\) is of a similar magnitude to the strength of silanol-silanol hydrogen bonds. If we account for the rupture of such a hydrogen bond before the Ti(OH) to Ti(OH)\(_2\) conversion can take place, then we predict that the two species probably coexist. The prediction of TiOH as a likely primary titanium-oxygen complex is in agreement with the EXAFS and XANES analysis [281]. We note however that EXAFS can not easily distinguish between the TiOH and Ti(OH)\(_2\) complexes. Additionally, Figure 9.2 shows that within the cluster approximation, and in the absence of adsorbates, there is a clear energetic preference for the TiOH and Ti(OH)\(_2\) species over the Ti=O complex, a species that was initially considered as a candidate for Ti\(^{IV}\) species in Ti\(^{IV}\)-silica [27, 260, 296, 259, 248]. The absence of a suitable absorption band in the UV-vis spectrum [264] strongly suggests that the species is not present in appreciable concentration, unlike the situation in the mineral fresnoite [270] and in the synthetic titanosilicate catalyst JDF-L1[271], in which Ti=O species have been unambiguously characterised. However, Ti=O have been implicated in oxidation catalysis over TiO\(_2\)-SiO\(_2\) mixed oxides as recently as 1995 [254, 255, 256, 257], and are able to explain IR and NMR responses to treatment with labeled water [269]. The formation of Ti=O species will be discussed in the next section.
9.4 Formation of Ti$^{IV}$=0 species

It has been noted that the calculations illustrated in Figure 9.2 indicate that formation of Ti=0 species is unlikely under normal operating conditions of the titanosilicate catalyst (typically less than 100°C, 1 atm pressure). However, those calculations represent a dehydrated system. In most oxidation reactions, H$_2$O or ROH molecules are present either as solvent or generated as by-products. This section therefore reports BP86/DZVP calculations that probe the possibility of forming Ti=0 species in the presence of a single molecule of water; Figure 9.3 illustrates the results.

![Figure 9.3: BP86/DZVP optimised reaction path for the formation of a titanyl group, modelled by (H$_3$SiO)$_2$Ti=O.HOSiH$_3$, from a silicate embedded titanium hydroxide, modelled by (H$_3$SiO)$_3$TiOH, in the presence of a single molecule of water. Energies changes are in kJmol$^{-1}$.

\[
\text{TiOH} + \text{water(g)} \rightarrow \text{TiOH} + \text{water(ads)} \rightarrow \text{Ti=O + water(ads) + silanol} \rightarrow \text{Ti=O + water(g) + silanol}
\]
Clearly the process shown in Figure 9.3 is essentially one of proton transfer from the titanium hydroxide to one of the other oxygens bound to Ti\textsuperscript{IV} and is thus dependant on one of the hydroxide forms of Ti\textsuperscript{IV} being present. It is also clear that, as shown above, unsolvated TiOH is much more stable than unsolvated Ti=O. In the presence of a single molecule of water however, Ti=O species can be formed with a true activation barrier of 67 kJmol\textsuperscript{-1} or an effective barrier of 40 kJmol\textsuperscript{-1} with respect to the original reactants (87 kJmol\textsuperscript{-1} and 67 kJmol\textsuperscript{-1} after +30\% scaling of the activation barrier, see Chapter 4). Furthermore, in the presence of a single water molecule, Ti=O is only 32 kJmol\textsuperscript{-1} less stable than the separated Ti\textsuperscript{IV} hydroxide, TiOH, and water, a change of 77 kJmol\textsuperscript{-1} with respect to the unsolvated case. Thus, small amounts of water, and/or protic solvents will enhancing the probability of forming titanyl species from any accesible Ti\textsuperscript{IV} hydroxide groups.

At present, no account of the environment of the Ti\textsuperscript{IV} site has been included within the calculations. However, if we examine the calculated change in the dipole moment (\(\mu\)) of the complexes leading to the transition state for formation of Ti=O, we note that activation results in an increase in \(\mu\) (3.23 Debye to 4.21 Debye). We also expect therefore that the environment provided by a partial ionic silicate framework would stabilise the transition state more than the solvated TiOH and that the estimated activation barrier of 67-87 kJmol\textsuperscript{-1} would therefore be an overestimate. In addition, formation of Ti=O by the pathway shown in Figure 9.3 involves rupture of a Ti-O-Si bond. The optimisation constraints employed in the current calculations (terminal Si fixed) will introduce an unknown error into the calculated energy changes due to structural strain. This strain is difficult to estimate without resorting to computationally prohibitive clusters, for example, 'closed' cubic silasesquioxanes. The error will, however, be system and site dependent, although it is likely that the constraints imposed in the current calculations will lead to the energy changes being upper bounds, the silanols formed during the reaction being unable to relax. Some attempt at estimating this strain energy is reported in the next Chapter.
9.5 Ti$^{IV}$-silicas: The Ti$^{IV}$ Site:

Summary and Discussion of Calculated Results

BP86/DZVP Density Functional Theory calculations have been reported which clarify some of the confusion concerning the nature and coordination of Ti$^{IV}$ sites in titanosilicates. Specifically, we have been able to show that partial hydrolysis of Ti–OSi bridges in framework substituted silicas is energetically feasible. Thus, in materials in which Ti$^{IV}$ is substituted into the framework, a mixture of Ti(OSi)$_4$, TiOH, and Ti(OH)$_2$ species are likely to exist when H$_2$O or other hydrolysing species are present. In the case of Ti$^{IV}$ grafted onto a silanolated surface, a mixture of only TiOH and Ti(OH)$_2$ species are likely. All of the Ti$^{IV}$ oxygenates studied were able expand their coordination shell in order to bind more water molecules, explaining, in part, previous uncertainties concerning the nature and coordination number of Ti$^{IV}$ centres incorporated into microporous and mesoporous silicas (see Section 8.2, Chapter 8 for more details). The results give no indication as to why some, but not all of the Ti–OSi bonds are hydrolysed during treatment with hydrogen peroxide and/or water and we suggest that steric constraints of the lattice could be important in this respect.

The importance of solvation of the Ti$^{IV}$ centre has been demonstrated in that titanyl groups are able to form with relative ease (with an absolute barrier of 67-87 kJmol$^{-1}$) from the hydroxide forms of 4-coordinate Ti$^{IV}$-silica in the presence, but not absence, of even a single molecule of water (and probably other protic solvents). However, given that the limiting case of aqueous TiO$^{2+}$ is known to be a very labile species (with oxygen exchange rate estimated at 16000±5000 s$^{-1}$ at 298 K) [311] and that no Ti=O UV-vis absorption has been measured in silicates, Ti=O species are probably very short lived species in dynamic equilibrium with TiOH and/or Ti(OH)$_2$. We suggest however, on the basis of the current calculations, that they could be present in sufficient concentration to provide a route to the active oxygen donating species for partial oxidation catalysis in hydroxide or pre-hydrolysed forms of Ti$^{IV}$-silicates. This last point will be discussed in more
detail in the next Chapter.
Chapter 10

$\text{Ti}^{IV}$-silicas : the epoxidation of alkenes

The preceding Chapter discussed the formation, via a grafting pathway, of $\text{Ti}^{IV}$ sites on the surface of silanolated surfaces such as MCM-41 or amorphous $\text{SiO}_2$. The nature of those sites, as well as of those in which $\text{Ti}^{IV}$ is embedded into the tetrahedral framework of a silica host, was also discussed in terms of the number of $\text{Ti}-\text{O}-\text{Si}$ bonds and their state of hydration. The formation of $\text{Ti}=\text{O}$ groups in the presence of $\text{ROH}$ species was reported.

This Chapter continues with a DFT study of the interaction of $\text{Ti}^{IV}$ model sites, i.e., \( (\text{SiO})_3\text{TiOH}, (\text{SiO})_2\text{Ti(OH)}_2, \) and \( (\text{SiO})_2\text{Ti}=\text{0} \), with ethene and hydrogen peroxide. Specifically, the nature and formation of the species that is active for oxygen donation during alkene epoxidation, as well as the oxygen donating step itself, have been probed. The possible involvement of the titanyl species, as well as a catalyst deactivation pathway is presented. Lastly, a mechanism for alkene epoxidation, based on the current calculations and on the literature reported in Chapter 8 is suggested.

10.1 Methodological Details

The calculations presented in this Chapter use the same BP86/DZVP cluster methodology as used in Chapter 9 and we refer the reader to that Chapter for more details. We stress, however, that +30% energy scaling of the ac-
tivation barriers will be included in all estimates of the activation barriers without further comment (see Section 4.2, Chapter 4). A spin-restricted approach has been used throughout, i.e., heterolytic, rather than homolytic, processes have been studied. All effective partial charges were calculated using the Natural Bond Analysis [312] module of Gaussian94[98]. The UV-Vis spectrum shown in Figure 10.12 was calculated using DMol, the Density Functional Theory code developed by MSI [313].

Due to the large number of species involved, confirmation of minima and transition state structures from independent Hessian calculations were not carried out. Instead, curvature information was gauged on the basis of the eigenvalues of the approximate Hessian matrix built up during the Quasi-Newton optimisation procedure (see Section 3.3, Chapter 3). All transition state structures have a single dominant, negative, (approximate) Hessian, eigenvalue, whilst all minimum energy structures have zero (approximate) Hessian eigenvalues. The ability of this type of calculation to predict accurately the local geometries of the Ti$^{IV}$ site in titanosilicate materials was reported in Section 8.2.4, Chapter 8, and calculated geometries will not be discussed explicitly; however, the Cartesian coordinates of all of the structures displayed in the Figures are tabulated in Appendix A.

We re-emphasize that all energies are internal energies resulting from static electronic structure calculations at stationary points on the adiabatic potential energy surface. Thus, as with all such calculations, thermal and entropic effects are neglected.

10.2 Interaction with Ethene

From the literature discussed above and our previous studies (see Chapter 8) it is clear that in materials in which Ti$^{IV}$ is embedded into the silica framework, at least 3 forms of dehydrated Ti$^{IV}$ sites are possible, (SiO)$_4$Ti, TiOH and Ti(OH)$_2$, see Figure 10.1. On a dehydrated Ti$^{IV}$-silica generated by a grafting procedure, only TiOH and Ti(OH)$_2$ sites are likely. Furthermore, in the presence of ROH adsorbates, Ti=O species are also energetically accessible (see Section 9.4, Chapter 9). We therefore need to consider the interaction of ethene with models representative of these species; we have chosen TiOH.
Figure 10.1: Schematic representation of the nature of dehydrated Ti\textsuperscript{IV} sites in titanosilicate catalysts. (SiO)\textsubscript{4}Ti represents Ti\textsuperscript{IV} isomorphously substituted into the silica framework. TiOH and Ti(OH)\textsubscript{2} represent hydrolysis products of (SiO)\textsubscript{4}Ti with the resulting silanol species not shown. TiOH and Ti(OH)\textsubscript{2} can also result from the grafting of a Ti\textsuperscript{IV} precursor onto the internal surface of a silicate host. In the latter case it is unlikely that a suitably placed silanol will be present in order to form (SiO)\textsubscript{4}Ti. Ti=0 represents a silica embedded titanyl species.

and Ti=0.

Figure 10.2 illustrates the interaction and reaction of a model TiOH species with ethene. A number of attempts were made to locate a stable minimum energy structure for the Ti\textsuperscript{IV}(\eta\textsubscript{2}-CH\textsubscript{2}CH\textsubscript{2}) complex; all resulted in the ethene substrate being expelled out of the Ti\textsuperscript{IV} coordination sphere. The configuration space search was not exhaustive but the result suggests that strong bidentate binding is unlikely. This result should be compared with the conclusion based on experimental observations that initial, strong alkene binding is required in order to explain tert-buty1 hydroperoxide (TBHP) preloading experiments in Ti-MCM-41\textsuperscript{[288]} and alkane/alkene competition kinetics in TS-1 \textsuperscript{[309]} (see Section 8.5, Chapter 8). We consider that the lack of \eta\textsubscript{2} binding probably reflects the energetic cost of distorting the Ti\textsuperscript{IV} site geometry relative to the energy gained on binding; we therefore expect similar results at (H\textsubscript{3}SiO)\textsubscript{4}Ti and Ti(OH)\textsubscript{2} sites. Binding of the substrate to TiOH via a single weak hydrogen bond (2 kJmol\textsuperscript{-1}) is followed, in this case, by activation of the alkene to form a surface SiOCH\textsubscript{2}CH\textsubscript{3} moiety, dative covalently bonded to a neighbouring Ti=0 species, as shown in Figure 10.2.

In the process shown in Figure 10.2, cleavage of a Ti-0-Si bond will
lead to a geometrical strain since the calculations were carried out with the Si positions fixed. In a real system, some relaxation can occur, even within the constraints imposed by a host lattice. This strain will be discussed in more detail below, where it is estimated to contribute around $-8 \text{kJmol}^{-1}$ to the activation barrier. With this in mind, the calculated absolute activation barrier for formation of Ti=O from TiOH in the presence of ethene is 114–148 kJmol$^{-1}$; comparison should be made with the calculated activation barrier for its formation in the presence of $H_2O$ of 59-77 kJmol$^{-1}$ after scaling and inclusion of the strain correction (see Section 9.4, Chapter 9). It is clear therefore, that $CH_2CH_2$ is effectively inert, under the mild reaction conditions experimentally employed, towards silica embedded titanium (IV) hydroxides.

Figure 10.3 shows the interaction of $CH_2CH_2$ with a Ti=O model. Adsorption of $CH_2CH_2$ with the site is two-fold; there is one hydrogen bond to
Figure 10.3: BP86/DZVP optimised geometries along the pathway for reaction of Ti=0 with ethene. The Ti=0 complex is modelled by (H₃SiO)₂Ti(=O)₂O(H)SiH₃. All Si positions were fixed throughout, see text. Energy changes are in kJ mol⁻¹; 'ts' indicates that the structure is a transition state.

The activation barrier of 43 kJ mol⁻¹ for alkene activation suggests that if Ti=0 species are present, either naturally or from the conversion of titanium hydroxides in the presence of ROH adsorbates, TiOR groups will probably form, depending on the substrate. It is known that the R group can affect the catalytic activity of TiOR species in Ti⁴⁺-silasesquioxanes [291, 287] (see Section 8.2.3, Chapter 8), and that at temperatures of 100°C, TS-1 is active for double bond isomerisation [314]; the
formation of TiOR is consistent with this observation. Exchange of R from R = H to R = CH$_2$CH$_3$ in TiOR derivatives of the TiOH cluster has the effect of increasing the strength of the Ti-OR bond as seen in the reduction in bond lengths from 1.82 to 1.81 Å. Natural Bond Analysis also predicts two natural Lewis-type localised bonds in the latter but not the former case. The formation of this 'double bond character' is accompanied by a lengthening of the siloxy Ti-0 bonds by about 0.01 Å; a similar phenomena is seen on formation of the Ti=0 species. In terms of effective partial charges, exchange of R from R = H to R = CH$_2$CH$_3$ reduces the negative charge on the alkoxy 0 centre from -0.967 to -0.776 electrons, reflecting a reduced nucleophilicity. Effective charges on titanium and the siloxy oxygens are changed very little. The results suggest, therefore, that 'electron donating' organic derivatives of TiOH will contain an alkoxy oxygen which is substantially less nucleophilic than that in the hydroxyl form, but will also have stronger Ti-OR and weaker Ti-0Si bonds. Although relevant data has not been published, it is expected that this effect should be observable using vibrational spectroscopy.

In conclusion, the most important result from this section, the lack of Ti$^{IV}$(η$_2$-CH$_2$CH$_2$) binding, sheds doubt on the epoxidation mechanism of Huybrechts et al.[309] and Mimoun [307, 308] shown in Figure 8.13, Chapter 8, as well as the radical mechanism suggested by Notari [5], shown in Figure 8.15, Chapter 8, all of which require a strong substrate interaction. It also implies that the hypothesis concerning initial alkene binding advanced by Oldroyd et al.[288] in order to rationalise the deactivation of Ti-MCM-41 in the presence of TBHP, but not TBHP and alkene, is probably incorrect; the effect is more likely to arise from competing processes, see Section 10.5 below. Derivitising titanium (IV) hydroxides with 'electron donating' organic groups (R) is seen to strengthen Ti-OR and weaken Ti-0Si bonds, agreeing well with the observation that the latter, rather than the former, are hydrolysed during epoxidation processes [287].

10.3 Interaction with H$_2$O$_2$

This section describes calculations on the interaction of our Ti$^{IV}$ model sites with H$_2$O$_2$. Figure 10.4 shows the reaction profile for formation of
Figure 10.4: BP86/DZVP optimised geometries along the pathway for hydrolysis of the hydroxy function of 'TiOH' with $\text{H}_2\text{O}_2$. The TiOH complex is modelled by $(\text{H}_5\text{SiO})_3\text{TiOH}$. All Si positions were fixed throughout, see text. The energy change marked with an asterix was estimated on the basis of the process using a Ti(OH)$_2$ model, see Figure 10.5. Energy changes are in kJmol$^{-1}$; 'ts' indicates that the structure is a transition state.

TiOH + HOOH(g) $\rightarrow$ TiOOH + HOH(g)

Figure 10.5 shows the same reaction involving a Ti(OH)$_2$ cluster. The pathway involves hydrolysis of a hydroxy function bonded to Ti$^{IV}$ and results in formation of a Ti($\eta_2$-OOH) complex and water. It is clear from the energetic profiles that there is little difference in reactivity between the TiOH and Ti(OH)$_2$ sites, the major
Figure 10.5: BP86/DZVP optimised geometries along the pathway for hydrolysis of the hydroxy function of ‘Ti(OH)₂’ with H₂O₂. The Ti(OH)₂ complex is modelled by (H₃SiO)₂Ti(OH)₂. All Si positions were fixed throughout, see text. Energy changes are in kJmol⁻¹; ‘ts’ indicates that the structure is a transition state.

difference being initial H₂O₂ binding. The similarity in reactivity is echoed in the effective charges on the O centres in the bond being hydrolysed; -0.97 electrons in both cases. The Ti(OH)(η₂-OOH) cis-hydroxo(hydroperoxide) complex formed on the Ti(0H)₂ site is similar to the one suggested by Ledon and Varescon[300] for the active oxygen donating species in Ti=O porphyrin catalysts (see Figure 8.10, Chapter 8); in the present work, the Ti(η₂-OOH) complexes arose naturally during geometry optimisation.

Given the fact that the η₂ complex has been calculated to be 33 kJmol⁻¹
more stable than the \( \eta_1 \) complex [293], and that the calculated activation barrier for epoxidation via a 5 membered, solvent-coordinated ring complex [269, 298, 297] as shown in Figure 8.8, is very high [306] (210 kJmol\(^{-1}\)), we have chosen to proceed, as did Karlsen and Schöffel [293] with the hypothesis that the \( \text{Ti}(\eta_2\text{-OOH}) \) complex is the active oxygen donating species. Karlsen and Schöffel noted in their calculations, that the \( \text{Ti}(\eta_2\text{-OOH}) \) complex is highly activated for oxygen donation, the 0-0 distance being 1.521Å. The current calculations predict a much smaller 0-0 bond distance of 1.48Å relative to the case in hydrogen peroxide of 1.49Å. The cause of the difference is unclear: Karlsen and Schöffel used a smaller \( \text{Ti} \) cluster to model the reaction path but we consider that this is unlikely to result in such a large discrepancy. The effective partial charges on the peroxidic oxygens of \(-0.488\) and \(-0.462\) electrons compared to those in \( \text{H}_2\text{O}_2 \) of \(-0.48\) does, however, indicate the electrophilic activation of one of those oxygens (the one directly bonded to titanium). The \( \text{Ti}(\eta_2\text{-OOH}) \) complex satisfies the experimental observation that use of \( \text{R'}\text{OOH} \) oxidants leads to reactivity that is dependent on the \( \text{R'} \) group, i.e., that \( \text{R'} \) is part of the active oxygen donating species; here \( \text{R'} = \text{H} \). And lastly, the hypothesis that an \( \eta_2 \), rather than an \( \eta_1 \), complex is the active oxygen donating species can explain the retarding effect of strongly coordinating solvents on the reaction - strongly coordinating solvents may block the extra coordination site required for \( \eta_2\text{-OOH} \) formation.

We have previously noted the \( \text{R} \) dependence on the activity of \( \text{TiOR} \) substituted octasilasesquioxanes [291, 287] (see Section 8.2.3, Chapter 8). Similarly, the fact that a \( \text{Ti-O} \) bond (which, in the experiment reported was a \( \text{Ti-OSi} \) bond) cleaves during epoxidation has been reported [289]. These two results imply that, in epoxidation reactions with \( \text{TiOR} \) derivatives, a \( \text{Ti-OSi} \) bond, rather than a \( \text{Ti-OR} \) bond, is being hydrolysed. In addition, Maschmeyer et al.[287] conclude that the \( \text{R} \) dependence indicates a steric rather than an electronic effect on activity and suggest that a similar effect could be operative for processes occuring at \( \text{TiOH} \), rather than \((\text{SiO})_4\text{Ti}\) sites, the latter being more sterically constrained. In order to test this hypothesis, we have calculated the reaction path shown in Figure 10.6 for formation of the active oxygen donating, \( \text{Ti}(\eta_2\text{-OOH}) \), species via hydrolysis of a \text{silox} function of the \( \text{TiOH} \) site. Unlike the previous case, hydrolysis
Figure 10.6: BP86/DZVP optimised geometries along the pathway for hydrolysis of the siloxy function of ‘TiOH’ with H$_2$O$_2$. The TiOH complex is modelled by (H$_3$SiO)$_3$TiOH. All Si positions were fixed throughout, see text. Energy changes are in kJ mol$^{-1}$; ‘ts’ indicates that the structure is a transition state.

Fixing a Ti-O Si bond leads to a SiOH group, dative covalently bonded to Ti$^{IV}$. Fixing the Si positions during geometry optimisation will therefore lead to structural strain, since the SiOH unit cannot relax. In order to estimate the magnitude of this effect whilst retaining some constraints to mimic those of the host lattice, the structures shown in Figure 10.7 were studied. All of the geometrical degrees of freedom in the reactant were optimised. One transition state was optimised with the Si fixed at the positions in the reactant whilst the other was optimised with the Si$^*$ centre shown in Figure 10.7 relaxed. The contribution of this strain to the activation barrier was thus
calculated to be -8 kJmol\(^{-1}\). We therefore estimate that Ti(\(\eta_2\)-OOH) formation at a TiOH or Ti(OH)\(_2\) site occurs with an absolute barrier of 48–73 kJmol\(^{-1}\) or 46–60 kJmol\(^{-1}\) for hydrolysis of the hydroxy or siloxy functions respectively, i.e., with little energetic preference for either pathway. Differences in the nature of the Ti\(^{IV}\) site, e.g., TiOH versus Ti(OH)\(_2\), and in its environment (resulting in changes in strain energy) appear to contribute only a small fraction to the barrier.

Lastly, Figure 10.8 shows the energetic profile for formation of Ti(\(\eta_2\)-OOH) from a Ti=O complex. It is clear that in the presence of H\(_2\)O\(_2\), Ti=O will rapidly convert to Ti(\(\eta_2\)-OOH). An absolute barrier of 35–46 kJmol\(^{-1}\) is about equal to the adsorption energy of H\(_2\)O\(_2\). The initial step of Figure 10.8 is merely adsorption of water, a pre-requisite for Ti=O formation (adsorption of a related ROH molecule would also probably suffice, see Section 9.4, Chapter 9).

In summary, formation of the active oxygen donating species, Ti(\(\eta_2\)-OOH), can proceed with an absolute activation barrier of 48–73 kJmol\(^{-1}\) by hydrolysis of a hydroxy function, or with a barrier of 46–60 kJmol\(^{-1}\) by hydrolysis of a siloxy function of a titanium (IV) hydroxide complex. Little preference was found for either pathway, in contrast to the suggestions made on the basis of chemical modeling experiments [287]. We have also shown that Ti=O species (formed in the presence of protic solvents or occurring naturally) are very reactive towards H\(_2\)O\(_2\); Ti(\(\eta_2\)-OOH) formation being dependent, essentially, on the availability of Ti=O species (the calculated barrier for their formation from TiOH complexes and water, including strain energy, is 59–77 kJmol\(^{-1}\), see also Section 9.4, Chapter 9).

### 10.4 Formation of Ethene Epoxide

For the hydrolysis processes described above, we have shown that the Ti(OH)\(_2\) model gives a reaction profile that is very similar to that from the TiOH model. We will therefore employ the computationally more efficient Ti(OH)\(_2\) cluster from this point forward.

Figure 10.9 shows the reaction of the active oxygen donating species with ethene. As noted by Neurock and Manzer [292], interaction of ethene
Figure 10.7: BP86/DZVP optimised geometries along the pathway for hydrolysis of the siloxy function of a modified ‘TiOH’ complex with H₂O₂. The model contains an extra Si-O-Si bridge in comparison with previous ‘TiOH’ models. The reactant structure was fully relaxed; the transition state structure shown at the top was optimised with all Si fixed at their position in the reactant and the transition state shown at the bottom was optimised with the highlighted Si centre relaxed. This procedures allows us to estimate the contribution of the strain to the activation barrier for hydrolysis of the Ti-O-Si bond when using the smaller 4T model where all Si positions are kept fixed; see Figure 10.6 and text. Energy changes are in kJmol⁻¹; ‘ts’ indicates that the structure is a transition state.

with a Ti(η₂-OOH) complex is repulsive. Our calculations are in agreement and although the [Ti(η₂-OOH)···ethene] complex is a converged minimum energy structure, the positive adsorption energy suggests that a very flat potential energy surface has led to failure of the optimisation algorithm. Also in agreement with Neurock and Manzer [292], the peroxidic oxygen centre attached to Ti⁴⁺ is more electrophilic than the other (less negative
Figure 10.8: BP86/DZVP optimised geometries along the pathway for formation of a Ti(\(\eta_2\)-OOH) complex from Ti=0 with H\(_2\)O\(_2\). The Ti=0 complex is modelled by \(\text{(H}_3\text{SiO)}_2\text{Ti}(=\text{O})\text{..O(H)SiH}_3\). All Si positions were fixed throughout, see text. Energy changes are in kJmol\(^{-1}\); ‘ts’ indicates that the structure is a transition state.

The effective partial charge), and it is this oxygen that is donated in the pathway shown. The mechanism is appealing in that the OH of the peroxide that is not donated to the alkene substrate is strongly coordinated to the Ti\(^{IV}\) centre prior to reaction (Ti...O distance of 2.25\(\text{Å}\)) and little atomic motion is required in order to ‘extract’ the active oxygen.

The activation barrier of 43-56 kJmol\(^{-1}\) is comparable to the barrier for formation of the Ti(\(\eta_2\)-OOH) complex itself. However, the barrier reported by Karlsen and Schöffel [293] for the same step over a Ti(\(\text{OH}\))\(_2\)(\(\eta_2\)-OOH) fragment of 96 kJmol\(^{-1}\) is substantially different. Given the difference in the peroxidic O=O distance between their work and the current calculations discussed in Section 10.3, we consider that their quantitative results should be treated
Figure 10.9: BP86/DZVP optimised geometries along the pathway for ethene oxide formation from Ti(OH)(\eta_2-OOH) and CH₂CH₂. The Ti complex is modelled by (H₃SiO)₂Ti(OH)OOH. All Si positions were fixed throughout, see text. Energy changes are in kJmol⁻¹; 'ts' indicates that the structure is a transition state.

with care. Using the value of 43-56 kJmol⁻¹ for the oxygen donation step, the overall barrier for the catalytic formation of ethene oxide by the reaction,

\[ \text{H}_2\text{O}_2 + \text{CH}_2\text{CH}_2 \xrightarrow{\text{cat}} \text{H}_2\text{O} + \text{CH}_2(\text{O})\text{CH}_2, \]

at a Ti(OH)₂ site calculated to be 66-77 kJmol⁻¹ relative to the [Ti(OH)₂···H₂O₂] adsorption complex and 28-39 kJmol⁻¹ relative to the separate reactants (the estimate is based on hydrolysis of a hydroxy function). Using our pre-
viously calculated reaction path for formation of Ti=0 species from TiOH groups in the presence of water (see Section 9.4, Chapter 9) and including the contribution of -8 kJmol\(^{-1}\) for strain energy in the transition state, we estimate that catalysis proceeding via a Ti=0 species involves an overall barrier of 70–103 kJmol\(^{-1}\) relative to a [TiOH···H\(_2\)O] adsorption complex and one of 43–76 kJmol\(^{-1}\) relative to separate reactants. We note, however, that initial formation of the titanyl species is expected to be strongly solvent dependent. Larger quantities and different protic solvents could result in a much larger rôle for this pathway. The overall energy of reaction is -204 to -262 kJmol\(^{-1}\) via a Ti(OH)\(_2\) site and -189 to -226 kJmol\(^{-1}\) via a Ti=0 site assuming that the reactivity of TiOH and Ti(OH)\(_2\) sites are similar.

In order to understand this step further, the diagram shown in Figure 10.10 was constructed from the Kohn-Sham molecular orbitals (K-S MOs) of the isolated fragments and the oxygen transfer transition state. Although the formal relationship between these single particle functions and the properties of the real, interacting system is unclear, they have been used by a number of authors to rationalise chemical phenomena [315] and we will proceed without further comment except to note that the K-S MOs are complicated in these unsymmetrical cases. Thus, for example, the fact that both ethene \(\pi\) to catalyst \(\sigma^*\) combinations are stabilised is simply due to mixing of these orbitals with others of the active site, i.e., the labels merely denote that the MO contains a large contribution from the idealised atomic valence combinations. Note also, that LUMO and HUMO are used in a frontier orbital sense, i.e., with respect to valence orbital combinations of the moiety orbital. In agreement with Karlsen and Schöffel [293], the results indicate that the ethene HOMO (\(\pi\)) to catalyst LUMO (\(\sigma^*\)) is the major interaction that leads to stabilisation of the transition state and therefore, to oxygen transfer; the catalyst HOMO (\(\pi^*\)) - ethene LUMO (\(\pi^*\)) separation is much larger (-6.03 eV compared to -5.07 eV). This result is consistent with the observed electrophilic nature of the epoxidation step. All other frontier orbitals combine in an approximately non-bonding manner. With this in mind, we have considered the effect of changing both alkene and active complex: the results are shown on the far right and left of Figure 10.10. Changing the active complex from Ti\(^{IV}\)(\(\eta_2\)-00H) to Ti\(^{IV}\)(\(\eta_2\)-00CH\(_2\)CH\(_3\)) raises
Figure 10.10: BP86/DZVP Kohn-Sham MO diagram describing the oxygen transfer step from a Ti\(^{IV}\)(\(\eta_2\)-00H) active site to ethene. Also included are the MO diagrams for the isolated Ti\(^{IV}\)(\(\eta_2\)-00CH\(_2\)CH\(_3\)) and allyl chloride fragments. See text for more details.

the K-S MO energies by 0.3 - 0.4 eV. Since the dominant interaction leading to oxygen transfer and transition state stabilisation involves the catalyst \(\sigma^*\) orbital, it is expected that interaction of Ti\(^{IV}\)(\(\eta_2\)-00CH\(_2\)CH\(_3\)) will be less than with the Ti\(^{IV}\)(\(\eta_2\)-00H) complex. This conclusion is supported by the effective charges on the oxygen being donated of –0.462 and –0.474 electrons, respectively, for the Ti\(^{IV}\)(\(\eta_2\)-00H) and Ti\(^{IV}\)(\(\eta_2\)-00CH\(_2\)CH\(_3\)) complexes. However, oxygen donation also involves formation of a new Ti–OH bond. The formally non-bonded Ti···O distance in Ti\(^{IV}\)(\(\eta_2\)-00H) is 2.21Å whereas that in the Ti\(^{IV}\)(\(\eta_2\)-00CH\(_2\)CH\(_3\)) complex is only 2.19Å and we expect that the latter
system will be the preferred one for the Ti–O bond forming component of this step. Changing the alkene from ethene to allyl chloride, the latter being less reactive for epoxidation, leads to a small stabilisation of the π-HOMO and a larger stabilisation of the π*-LUMO (ΔE = −0.73 eV). Although the small stabilisation of the HOMO will lead to a slightly smaller ethene π - catalyst σ* interaction, we consider that the magnitude of this change is unlikely, to have a marked effect on the stability of the transition state. However, the substantially more stable π*-LUMO results in very similar HOMO-LUMO, catalyst-alkene, and HOMO-LUMO, alkene-catalyst, gaps of 5.30 and 5.18 eV respectively, raising the possibility of a competing channel of reaction. Analysis of the form of the K-S MOs suggests that this alternative pathway could involve chlorination of the peroxidic part of the active site with formation of an allyl cation, CH₂CH₂CH⁺. It is clear that if this alternative channel were important, it would be observable in the product distribution resulting from oxidation of allyl chloride. However, we were able to find little experimental evidence indicative of such behaviour and the reduced reactivity of allyl chloride relative to unsubstituted alkenes probably derives from other sources; note, however, that Sheldon et al. [296] have observed the heterolytic decomposition of the sacrificial oxidant during allyl chloride epoxidation over TiO₂-SiO₂. It is clear, however, that the less reactive nature of allyl chloride is unlikely to be directly related to changes in the oxygen donation step.

In conclusion, the calculations suggest that epoxidation by a Ti⁴⁺(η₂-0OH) complex will proceed at the mild reaction temperatures experimentally employed. More encouraging is comparison with experimental activation barriers. Although we were unable to acquire data on epoxidation reactions, van der Pol et al. [316] have published a barrier of 71 kJmol⁻¹ for oxidation of straight chain alcohols. Assuming a similar pathway and noting that alcohols and alkenes have different intrinsic activities, agreement with our calculated barrier of 62–92 and 70–103 kJmol⁻¹ for reaction via a titanium hydroxide and titanyl species respectively, is favourable (the former range includes reaction at both model titanium (IV) hydroxides and via hydrolysis of either hydroxy or siloxy functions). On the basis of the lack of Ti⁴⁺(η₂-CH₂CH₂) binding reported above, the ability of the Ti(η₂-0OH) com-
plex to rationalise solvent effects on epoxidation, the effect of additives (see below), the fact that solvent is not required for activity, and the fact that the calculated activation barrier for the ‘Clerici mechanism’ (Figure 8.12, Chapter 8), reported by Neurock and Manzer [292, 306] is as high as 210 kJmol\(^{-1}\), the current mechanism in extremely appealing. We also stress that the current calculations indicate that titanyl groups are as likely to be involved in epoxidations over Ti\(^{IV}\)-silicas, as not, provided that protic solvents are present. Analysis of the molecular orbitals of the reactants and transitions state indicate that the major interaction leading to oxygen transfer is between the \(\pi\)-HOMO of the alkene and the \(\sigma^*\)-LUMO of the catalyst. ROOH oxidants, leading to Ti\(^{IV}\)(\(\eta_2\)-OOR) active sites will cause the activity for epoxidation to vary according to the nature of the R group; we expect that, because of opposing effects (electrophilicity of the active oxygen and degree of Ti\(\cdots\)OR formation in the transition state), a range of similarly hindered oxidants, with varying electron donating abilities, will give rise to a volcano-type curve for activity. Lastly, frontier orbital analysis suggests that allyl chloride could participate in a competing reaction during epoxidation processes. However, the less reactive nature of this alkene to oxidation is more likely to be due to other factors, e.g., electronic repulsion preventing initial approach of the substrate to the active site or formation of stable adsorption complexes of the reactant; it is unlikely to be directly related to changes in the oxygen donation step. We will discuss mechanistic implications in more detail below.

10.5 Catalyst Deactivation

It has been observed that catalyst deactivation occurs when the Ti\(^{IV}\)-silica host is preloaded with hydroperoxide [5, 288]. The catalyst changes colour from white to yellow and shows an UV-vis band at around 260,000 cm\(^{-1}\) assigned to formation of Ti(\(\eta_2\)-O\(_2\)) complexes [5].

Figure 10.11 shows the formation of such an \(\eta_2\)-O\(_2\) complex from Ti(\(\text{OH}\)) (\(\eta_2\)-O\(_2\)) by the transfer of hydrogen and the loss of water (note the similarity to the Clerici proposal Figure 8.8, Chapter 8). In agreement with Karlsen and Schöffel [293], formation of an isolated \(\eta_2\)-O\(_2\) complex is highly unfa...
Figure 10.11: BP86/DZVP optimised geometries along the pathway for deactivation of the active oxygen donating species, Ti(OH)(\eta_2-OOH), in the absence of an oxidisable substrate. The Ti complex is modelled by (H_3Si)_2Ti(OH)OOH. All Si positions were fixed throughout, see text. Energy changes are in kJmol\(^{-1}\); ‘ts’ indicates that the structure is a transition state.

The absolute activation barrier for formation of this \eta_2-O_2 function of 63-81 kJmol\(^{-1}\) is higher than that reported in the last section for the oxygen transfer step. This implies, of course, that in the presence of alkene, epoxidation occurs whilst in its absence, a slower, proton transfer process occurs which deactivates the catalyst. This rationale also explains the ef-
fect of base (it will aid deprotonation of the Ti(η2-OOH) complex) and the effect of acid (it will aid reformation of the Ti(η2-OOH) complex) on catalytic activity. Basic species, could, however, also deactivate the catalyst by competitive adsorption at TiIV. Lastly, since the deactivated catalyst has a distinct UV-vis absorption band, we have calculated the optical spectra of the [Ti(η2-OOH)···H2O]ads and Ti(OH)(η2-O2) complexes for comparison. We have used a simplistic approach based on Kohn-Sham orbital energy differences to approximate the spectrum. Whilst Kohn-Sham virtual molecular orbital energies have no formal dependence on the excited state energies of a system, this procedure often leads to good results [315] and Savin et al. [317] have argued that such an approximation has a reasonable theoretical basis. With this in mind, the calculated spectra are shown in Figure 10.12. It is clear that the η2-O2 complex has a UV-vis resonance at 260,000 cm⁻¹, in contrast to the Ti(OH)(η2-OOH) complex, which, in agreement with experiment, strongly implicates the η2-O2 species in catalyst deactivation.

Deactivation of the catalyst on preloading of alkyl hydroperoxides cannot be as easily explained by the process shown in Figure 10.11, since, for example, transfer of a -CH₂CH₃ group from the -OOR to the -OH ligand has a calculated barrier of 222 kJmol⁻¹ (detailed results not shown). However, it must be noted that the alkyl groups of the peroxides that have been used to study this effect, e.g., ⁷butyl, form carbenium ions that are much more stable and it is expected that the barrier will then be lower.

10.6 Acidity Effects

The calculated activation barrier reported by Neurock and Manzer [292, 306] of 210 kJmol⁻¹ for epoxidation by the Clerici mechanism implies that this pathway is unlikely to be active (although we note that their calculations, like the present ones, neglect long range and solvent contributions). The 5-membered, solvent coordinated, Ti(η₁-OOH) ring complex (Species I, Figure 8.8, Chapter 8), could, however, be appreciably acidic. In this respect, the Ti(η2-OOH) complex suggested in the present work as the active oxygen donating species, could also be important. We have calculated the proton affinity of the Ti(OH)(η2-OOH) and Ti(OH)₂ complexes of the 3T models
Figure 10.12: BP86 estimated UV-vis absorption spectra showing that the model for the deactivated $\eta_2$-O$_2$ complex gives rise to the observed 260,000 cm$^{-1}$ whilst the oxygen donating species, Ti($\eta_2$-OOH) does not.

which have only two siloxy bridges attached to the Ti$^{IV}$ centre; they are 1333 and 1380 kJmol$^{-1}$ respectively. Thus, we conclude that $\eta_2$ binding of the -OOH ligand can result in increased acidity relative to titanium (IV) hydroxide complexes, and can do so in the absence of protic solvent. How the acidity of the Ti($\eta_2$-OOH) complex compares with that of Clerici's model has not yet been studied.
10.7 The Epoxidation of Alkenes:

Summary and Discussion

We have presented a large number of results on the interaction of Ti\textsuperscript{IV} sites with ethene and hydrogen peroxide. Summarising, the calculations have indicated that ethene probably does not bind to the Ti\textsuperscript{IV} sites in an \( \eta_2 \) fashion, but can form a weak hydrogen bond with titanium (IV) hydroxyls. A rather large absolute barrier of 114–148 kJmol\(^{-1}\) for ethene activation (to form a Ti=0 and SiOCH\(_2\)CH\(_3\) complex) suggests that under the mild conditions used for epoxidation reactions, ethene is inert to this type of site. Reaction of ethene with Ti=0 groups, however, will readily form a TiOCH\(_2\)CH\(_3\) complex (calculated barrier of 43–56 kJmol\(^{-1}\)), implying that for Ti=0 in, for example, porphyrins [300] or Ti\textsuperscript{IV}-silicas (see Section 9.4, Chapter 9), formation of organic derivatives, TiOR, could be an important process; oxygen donating R groups were shown to lead to stronger Ti-OH and weaker Ti-OSi bonds (when attached to the same Ti\textsuperscript{IV} site) and to less electrophilic TiOR oxygens.

The calculations have also indicated that on interaction of a titanium (IV) hydroxyl with hydrogen peroxide, in the absence of solvent, a Ti(\( \eta_2\)-OOH) species is formed. We have shown that formation of this complex via hydrolysis of either a Ti-OH or a Ti-OSi function can occur with approximately the same activation barrier; 48–73 kJmol\(^{-1}\) and 46–60 kJmol\(^{-1}\) respectively. In addition, we have shown that reaction at a TiOH site with three siloxy functions to the Ti\textsuperscript{IV} centre is similar to reaction at a Ti(OH)\(_2\) site which only has two siloxy functions. Small differences in the absolute activation barrier of the latter two Ti\textsuperscript{IV} sites as well as the observation of geometrical strain in the system when hydrolysis of a Ti-OSi function takes place suggests that the actual barrier will be somewhat dependent on the nature and environment of the Ti\textsuperscript{IV} site. Finally, it was shown that reaction of hydrogen peroxide with a Ti=0 function is very favourable but that formation of the Ti(\( \eta_2\)-OOH) species is still dominated by generation of the Ti=0 group itself. Following Karlsen and Schöffel[293] and Ledon and Varescon[300], the Ti(\( \eta_2\)-OOH) complex was suggested as the active oxygen donating species.
Figure 10.13: Possible catalytic cycles for alkene epoxidation at Ti-OR sites based on the individual steps studied in the current work; an alternative active oxygen donating species would, however, lead to similar paths. See text for more details.

Once formation of the active Ti(η2-OOH) species has occurred, formation of the epoxide on interaction of ethene is rapid with the active peroxidic oxygen being the one attached to the TiIV centre. The activation barrier of 43-56 kJmol⁻¹ leads to an overall barrier relative to the [hydroxide-•·water] adsorption complex of 62–92 kJmol⁻¹ (the range includes reaction at both model titanium (IV) hydroxides and via hydrolysis of either hydroxy or siloxy functions) or 70-103 kJmol⁻¹ for epoxidation at a titanium (IV) hydroxide or Ti=0 species respectively, i.e., the calculations clearly indicate that Ti=0 groups are viable intermediates on the pathway for alkene epoxidation. Unlike the Clerici mechanism, coordination of a protic solvent is not required for activity. Solvent effects are presumed to arise from competitive
adsorption at Ti$^{IV}$ coordination sites that are required for $\eta_2$-OOH binding or from hydrophobic/hydrophilic and shape selectivity properties of the host. Analysis of the molecular orbitals of the reactants and transition state indicate that the major interaction leading to oxygen transfer is between the $\pi$-HOMO of the alkene and the $\sigma^*$-LUMO of the catalyst. ROOH oxidants, leading to Ti$^{IV}(\eta_2$-OOH) active sites will cause the activity for epoxidation to vary according to the nature of the R group; we expect that, because of opposing effects (electrophilicity of the active oxygen and degree of Ti···OR bond formation in the transition state), a range of similarly hindered oxidants, with varying electron donating abilities, will give rise to a volcano-type curve for activity. Lastly, frontier orbital analysis suggests that allyl chloride could participate in a competing reaction during epoxidation processes. However, the reduced activity of this alkene to oxidation is more likely to be due to other factors, e.g., electronic repulsion preventing initial approach of the substrate to the active site and/or formation of stable adsorption complexes of the reactant; it is unlikely that the reduced activity is directly related to changes in the oxygen donation step.

The Ti($\eta_2$-OOH) complex was shown to be more acidic than initial titanium (IV) hydroxides and was shown to deactivate to a Ti($\eta_2$-O$_2$) complex with a barrier of 63–81 kJmol$^{-1}$. This barrier is significantly higher than that for epoxide formation and suggests that deactivation of the catalyst via this pathway (leading to a yellow colouring of the catalyst) occurs more slowly than epoxidation and would therefore only occur in the absence of an oxidisable substrate.

The experimentally observed R dependence of TiOR derived octasilesqui­oxanes in epoxidation catalysis will now be discussed in some detail. We consider that this R dependence, as well as the observation that a Ti–O bond which, in the experiment reported was a Ti–OSi bond [289], must be cleaved during catalysis is crucial to a complete mechanistic understanding. Figure 10.13 shows the possible catalytic cycles for alkene epoxidation at Ti–OR sites based on the individual steps studied in the current work; an alternative active oxygen donating species would, however, lead to analogous paths. Path 1 assumes hydrolysis of a Ti–OR function on interaction with R'OOH. After alkene oxidation, the new Ti$^{IV}$ species is a Ti–OR' complex.
with ROH coordinated. R dependence on activity would therefore be lost unless ROH remained strongly coordinated through a large number of catalytic cycles; we consider this unlikely. Path 1 would also lead to different initial and steady state activities. If, instead, a siloxy function is hydrolysed on interaction of the Ti-OR complex with R'O0H (Path 2), alkene epoxidation results in formation of a Ti(OR)(OR') complex. This species could react in one of three ways:

a. On interaction of another molecule of R'O0H, hydrolysis of a second siloxy function takes place. On the basis of the current calculations, although there is little preference for hydrolysis of a hydroxy or siloxy function of Ti-OR complexes when using H2O2 as oxidant, we have shown that replacing the hydroxyl by an electron donating alkoxy group can lead to electronic preference for fracture of the siloxy group (reduced electrophilicity of the TiOR oxygen as well as stronger Ti-OR and weaker Ti-OSi bonds). Steric constraints when R is large will also favour attack at the siloxy function. Although this route would initially show the required R dependence, it would eventually lead to TiIV leaching.

b. Prior to further epoxidation cycles the initial Ti-OR species reforms. This process would be aided by the locality of the SiOH function nearest to the -OR' group and on host lattice constraints on the [Ti...O(H)Si] distance which may favour the (SiO)3Ti form. The partial charge on the oxygen atoms of an isolated model silanol (H3SiOH) and an ethanol molecule of -1.07 and -0.79 electrons respectively support this suggestion in as far as they indicate that the former will preferentially attack the positive TiIV centre. Route b is also consistent with the work of Abbenhuis et al. [289] on Ti-Cp derivatised octasilsesquioxanes and would lead to the R dependence on activity noted for Ti-OR derivatised octasilsesquioxanes [287, 291] (see also Section 8.2.3, Chapter 8). However, initial calculations of this self-repair step using clusters similar to those in Figure 10.7 and with the Si+ centre relaxed, for the case when R = R' = H, gave an activation barrier of 74–96 kJmol⁻¹ (detailed results have not been presented). Given that we have already
shown that electron donating TiOR derivatives strengthen the Ti-OR bond further, we suggest that this step could be rate determining. The variations in Ti-OR bond strengths with the nature of the R group is also consistent with the observed R dependence although it is noted that this electronic contribution is probably masked by steric effects for bulky R groups.

c. On interaction of another molecule of R'OOH, a Ti-OR or Ti-OR' bond cleaves. On the basis of the steric arguments suggested by Maschmeyer et al. [287], it is expected that the least crowded bond would be attacked, i.e., the Ti-OR bond if R' = t-But whilst R = Me, s-But or i-Pr. This would, of course, lead to loss of the R group and therefore its effect on reactivity. A different initial and steady state activity of the catalyst would also be observed.

On the basis of these arguments, Path lc of Figure 10.13 appears, therefore, to be the most satisfactory and we propose the mechanism shown in Figure 10.14 for alkene epoxidation over TiIV-silicas (and octasilasesquioxanes). The mechanism is consistent with both the current calculations and the open literature, including solvent effects, acidity, behaviour towards base, catalyst deactivation, and R dependence of TiOR derivatives.

Finally, we are now in a position to speculate on ways to improve the catalytic effectiveness of titanosilicates in alkene epoxidation processes. Obviously, the host material needs to be chosen with the reactants and products in mind, i.e., such that reactant and product shape selectivities as well as hydrophobic considerations are optimal. The first chemical step in the catalytic cycle, formation of the TiIV(η2-OOH) complex, could be accelerated by use, if possible, of TiOR derivatives, e.g., grafted onto a MCM-41 surface, that are optimum for cleavage of Ti-OSi bonds but that do not sterically inhibit other steps. Alternatively, choice of the best protic solvent which will favour the pathway via a Ti=O species but that will not compete too effectively with other steps, by strongly coordinating to the TiIV centre, may be profitable. The next chemical step, oxygen transfer to the alkene will be accelerated by careful choice of R'OOH such that the strength of the non-bonded Ti···OR interaction in the η2-OOH complex is maximised without excessively
reducing the electrophilicity of the activated oxygen. This end may also be achieved by use of electron withdrawing ligands at the Ti$^{IV}$ centre. The final chemical step, self-repair of the active site may be rate determining and optimisation of this step is therefore likely to be most effective. We suggest that electron-withdrawing ligands on the Ti$^{IV}$ centre, in order to increase its electrophilicity towards the neighbouring SiOH species as well as structural constraints leading to the hydrolysed form being energetically strained would aid this step. Of course, steric effects will be important in all steps, and may, in some cases dominate. Finally, we note that increasing activity via this heterolytic pathway may not have much effect on the epoxidation of alkenes such as allyl chloride. If the reduced activity is due to formation of stable adsorption complexes that reduce the alkene concentration at the active site, then careful catalyst engineering to remove these adsorption sites may help. If, however, the reduced reactivity is due to electronic repulsion between active site and alkene, then solution of the problem is more difficult. One possibility may be to include hydrogen-bonding functionality into the R group of TiOR derivatives in order to aid approach of the alkene to the active site (through H-bond formation). Indeed, it may be profitable in a more general sense to include such ‘reaction directing’ functionality into the active site, for example, to have more regioselective control or even to map chirality into the products. Our studies into these novel approaches continues.
Figure 10.14: The proposed mechanism for alkene epoxidation at Ti-OR sites based on the current work and that in the open literature. $R$ represents either $\equiv\text{SiOH}$, $H$, or an organic function. The calculations do not indicate a strong preference for either pathway 1 or 2 for formation of the active oxygen donating species ($\text{Ti}^{IV}(\eta_2-\text{OOH})$), although we note that path 2 is likely to be more strongly dependent on solvent. Formation of the active oxygen donating species will also depend upon the concentration of hydroperoxide at the Ti$^{IV}$ site and on competitive adsorption with solvent or base for two coordination sites. Steps 3 give rise to acidity in the presence of hydrogen, but not alkyl hydroperoxides. Steps 4 and 5 describe alkene epoxidation and catalyst deactivation respectively. These two processes are likely to compete, but since the activation barrier is less for Step 5 than for Step 4, deactivation will only be significant when the concentration of alkene becomes smaller than that of the active oxygen donating species. Finally, Step 6, self-repair of the catalyst and diffusion of the products closes the catalytic cycle; initial results suggest that catalyst self-repair could be rate limiting.
Summary and Conclusions

A large number of calculations have been presented and discussed concerning methodological problems (Chapter 4), the Methanol to Gasoline process (Chapter 6 and 7) and Ti^{IV}-silica oxidation catalysts (Chapter 9 and Chapter 10). Summarising briefly, Chapter 4 outlined a number of weaknesses of pure, gradient-corrected Density Functional Theory (DFT), particularly the problem of predicting vibrational frequencies and estimating activation barriers. We also noted that MP2 corrected HF methods are still a competitive alternative to pure gradient-corrected DFT methods for the study of reaction processes of well behaved closed-shell systems, giving errors in the activation barriers of up to +30% (MP2//HF) and -30% (DFT) respectively. A surprising result from this study was that our test reactions (see Figure 4.3, Chapter 4) with 1T and 5T clusters gave almost identical results. The cause of this similarity is unclear but probably reflects the concerted ‘push-pull’ nature of the mechanisms in which two active-site oxygens participate. The relative proton affinities of the two participating oxygens in a 1T and 5T cluster are expected to be similar by symmetry in a fully geometry relaxed system and, as suggested by Kramer and van Santen [222], this difference could drive the reaction. This result is, of course, an artefact of the cluster approximation where no geometry constraints or environmental effects are included.

Part II, the study of the MTG process, gave rise to two important conclusions. The first concerned the methodological problem of using cluster models for the study of methanol adsorption (see Chapter 6). A number of authors have now published work concerning this problem and it is increasingly apparent that cluster models overestimate the interaction of the conjugate base oxygen of the acid site with the hydroxyl of the methanol molecule. We conclude that the dominant form of adsorbed methanol is a physisorbed one in which there is only a single strong hydrogen bond between the surface and the methanol molecule. The results of Part II also led to the suggestion that a ‘carbene-like’ mechanism, different to those proposed on the basis of similar calculations by Blaszkowski and van Santen [174], could be active for MTG conversion. Consideration of errors in the
methods employed, however, indicate that the current techniques cannot be used to differentiate (on the basis of energetics) between the two 'classes' of pathway.

Lastly, Part III discussed the nature and oxidative activity of Ti\textsuperscript{IV}-silica catalysts. Again, a number of important results were found; we were able to distinguish between a number of different Ti sites and their behaviour towards hydrolysis and hydration in complete agreement with experiment. In addition, we were able to show that a long debated species, the Ti=0 species is, in fact, energetically accessible from a titanium hydroxide in the presence of protic solvents. Further, we were able to rationalise all aspects of the epoxidation behaviour of Ti\textsuperscript{IV}-silicas in the presence of sacrificial oxidants, e.g., solvent effects, the response to additives, the effect of changing the oxidant, deactivation to $\eta_2-\text{O}_2$ etc. We were also able to show, on the basis of calculated energetics, that an epoxidation pathway via a Ti=0 species is just as likely as not, provided that there is a kinetic pathway for initial formation of the Ti=0 species.

In conclusion, we have clearly demonstrated the ability of computational quantum chemistry to be, in favourable cases, a predictive tool for the study of reactivity in zeolites. We stress that larger clusters, combined quantum/classical techniques or periodic quantum chemical methods are likely to be necessary to solve difficult problems like the mechanism of the MTG process and answer questions that concern the activity of specific molecular sieves. Finally, it is clear that our ability to direct experimentalists in the improvement of catalytic systems will have a huge impact on the future development of new industrial technologies.
References


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[99] R. Amos et al., Cadpac 6.0, 1995, Cadpac, Cambridge Analytical Derivatives Package version 6.0, is a suite of codes including, amongst others HF, MP2 and DFT functionality.


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Appendix A

Cartesian Coordinates of Optimised Structures

The Cartesian coordinates (in Å) of structures shown in Figures discussed throughout this thesis are listed below. If a given Figure contains multiple structures, they will be listed from left to right, top to bottom. Only structures that have not previously appeared are listed.
A.1 Chapter 4

Figure 4.1; the water dimer, BLYP/TZVP.

Figure 4.2; the methanol dimer, BLYP/TZVP.

Figure 4.3; HF/6-31G**; 1.

Figure 4.4; HF/6-31G**; 2.

Figure 4.5; HF/6-31G**; 3.

Figure 4.6; HF/6-31G**; 4.

Figure 4.7; HF/6-31G**; 5.

Figure 4.8; HF/6-31G**; 6.
A.2 Chapter 6

Figure 6.1; BLYP/TZVP.

\[
\begin{align*}
C & : 0.099440 -0.064910 0.113930 \\
H & : -0.305070 0.696970 -0.565770 \\
N & : -0.024200 0.200570 1.153020 \\
O & : -0.010460 -0.105410 -0.116000 \\
Si & : 2.228580 1.343920 0.196930 \\
Al & : 1.512580 -0.003490 0.039680 \\
B & : -0.479760 0.259890 0.819700 \\
Li & : 2.690020 2.471260 -1.944280 \\
Be & : 0.383750 0.744880 -2.378650 \\
\end{align*}
\]

\[C -0.000185 0.000920 0.001715 \]

\[H -1.700280 -1.151796 -0.704086 \]

\[N -0.444035 1.683301 1.120304 \]

\[O 1.533549 -0.091569 0.896071 \]

\[Si 0.811767 1.733433 0.388777 \]

\[Al 6.192567 -0.000615 -0.000635 \]

\[B 7.740021 0.194812 -0.050868 \]

\[Li 1.782978 4.682002 -2.317449 \]

\[Be 0.883646 0.910531 -2.514246 \]

\[Be 1.658106 -1.344258 -4.796449 \]

\[N 0.816588 -3.778782 -3.456281 \]

\[O 4.077030 -1.355822 -5.316019 \]

\[Si 1.206638 -0.724652 -7.069579 \]

\[Be 0.069440 -0.049010 0.119330 \]

\[Al -0.444035 1.683301 1.120304 \]

\[Si 0.329015 -0.173890 -3.619850 \]

\[B -2.644240 -1.466480 -3.871510 \]

\[Li 4.791090 -0.487270 -3.838260 \]

\[Be 3.441840 0.514240 -4.852890 \]

\[B 1.224920 3.441780 -2.030090 \]

\[Li 4.230520 0.384860 -2.495040 \]

\[Be 4.412720 4.037750 -3.560550 \]

\[Li 2.739610 2.286330 -0.038380 \]

\[B 3.067070 3.346400 1.233200 \]

\[Li 3.735080 2.394170 2.339190 \]

\[Be 1.791220 3.952920 1.717620 \]

\[Al 3.963950 4.374110 0.639260 \]

\[Li 2.690020 2.471260 -1.944280 \]

\[Be 0.383750 0.744880 -2.378650 \]

\[Al 3.912500 -0.173890 -3.619850 \]

\[Si -2.644240 -1.466480 -3.871510 \]

\[B 4.791090 -0.487270 -3.838260 \]

\[Li 3.441840 0.514240 -4.852890 \]

\[Be 1.224920 3.441780 -2.030090 \]

\[Li 4.230520 0.384860 -2.495040 \]

\[Be 4.412720 4.037750 -3.560550 \]

\[Li 2.739610 2.286330 -0.038380 \]

\[B 3.067070 3.346400 1.233200 \]

\[Li 3.735080 2.394170 2.339190 \]

\[Be 1.791220 3.952920 1.717620 \]

\[Al 3.963950 4.374110 0.639260 \]

Figure 6.2; BLYP/TZVP (top); 1.

\[
\begin{align*}
C & : -5.996426 -2.399573 -1.923721 \\
H & : -4.854411 -4.033732 -2.537304 \\
N & : -5.170141 -1.542371 0.559510 \\
O & : -8.875836 -0.872046 -3.348662 \\
Si & : -7.928397 -2.983230 -1.731326 \\
Al & : -0.388669 -0.351707 -0.021304 \\
B & : 1.277752 5.633391 0.004988 \\
Li & : 1.543210 1.848665 1.151294 \\
Be & : 2.475960 7.268875 -0.010663 \\
B & : -0.240527 3.266973 1.261383 \\
Li & : -7.949367 5.196722 3.214511 \\
Be & : -4.166546 7.542384 0.045966 \\
B & : -2.892045 8.319994 3.851536 \\
Si & : -1.959882 7.549788 4.017924 \\
Al & : -2.949783 9.135390 1.154807 \\
H & : -3.665560 10.052122 5.671731 \\
Li & : -8.976195 5.779666 5.497974 \\
Al & : -9.090451 6.013040 5.707579 \\
Li & : -9.185991 6.331997 0.360132 \\
Be & : -10.870943 7.972623 0.328900 \\
B & : -8.204400 1.572272 3.040426 \\
Li & : -10.114568 -2.963230 0.001211 \\
Si & : -9.953386 -2.971642 0.007920 \\
Al & : -9.126549 -1.707089 7.675406 \\
H & : -12.751401 0.713861 4.837376 \\
H & : -6.957891 0.481132 1.972633 \\
Al & : 0.501778 6.207057 1.411891 \\
H & : -2.034064 2.188368 -1.639043 \\
Si & : -1.700413 4.117528 -4.320504 \\
Si & : 2.639460 0.102395 -1.353351 \\
Be & : 5.819922 0.644577 -2.226328 \\
B & : 6.559069 -1.508502 -3.737580 \\
Li & : 7.297336 9.761111 0.927288 \\
Al & : 5.732510 2.978537 -3.801494 \\
\end{align*}
\]
Figure 6.3; MP2/6-31G**//HF/6-31G** (top); 3. Figure 6.3; BLYP/DZVP (bottom); 2.

H 4.163558 1.165244 1.140718
Si 5.391418 1.200892 1.137919
Al 2.246358 -0.287815 1.069361
P 2.585163 1.447729 0.116641
O 1.557923 -1.479714 -0.891371
N 0.209482 -1.364605 -0.483294
H -0.125704 -1.499117 -1.236500
Si -1.745800 -1.456503 -0.481877
H -0.607312 0.471417 0.946341
O -2.023349 -0.012377 0.476260
H -0.228142 0.651330 -1.110337
Si -3.953377 0.622309 0.223503
C -1.366442 0.775145 1.246655
O 0.962952 2.160529 -0.366644
C 1.838410 2.906892 -1.379360
H 0.971271 3.777576 -1.812333
H 2.071985 3.246971 -1.081360
H 1.878516 2.331129 -2.09686
H 1.071055 1.381513 -0.191903
H -0.029084 1.505701 0.581611
H -0.007528 0.085632 1.583069
H 1.088413 1.217155 2.076803
H -3.816769 1.820609 -0.114774
H -4.087072 0.027613 1.653833
H -4.736089 -0.456199 -0.393809
H -2.389773 -2.547316 0.259046
H -2.433292 -2.208119 -1.748812
H 2.028265 -2.974618 -0.536836
H 4.724521 -1.127389 0.750538
H 3.293995 -0.533335 2.865183

Figure 6.3; BLYP/DZVP (bottom); 1.

Si -0.042463 0.028797 -0.001828
Si 5.375228 -0.690504 -1.385975
Al 2.807343 1.310042 0.011798
O 1.610561 0.077089 -0.016064
Al 2.783401 1.700837 0.000000
H -0.492322 -1.381032 0.372925
H -0.430379 0.432885 1.320579
H -0.404421 0.094453 -1.066269
C 3.279480 2.130434 -1.037787
C 2.815385 3.261347 1.764114
C 2.767542 2.712266 1.477052
H 3.361335 3.025295 1.588660
H 6.810555 -0.651470 0.277442
H 5.722048 -2.565215 0.893444
C 4.614885 -2.141095 0.854766
Al 2.289416 -0.290037 0.005833
C 3.152280 -2.347223 -0.020792
C 1.718588 -3.447112 0.009711
C 0.877558 0.353708 0.019393
C 1.702813 -2.585331 0.775086
C 1.817283 -5.008584 -0.356906
H 6.828271 -0.191918 -0.066860
H 5.311123 0.350152 -2.672474
H 6.120352 2.114412 -1.156481
H 2.288820 -6.961038 -0.474465
H 4.110519 -0.074412 -1.617530
H 6.1980824 -0.902999 -1.080052

Figure 6.3; BLYP/DZVP (bottom); 3.

Si 0.169270 -0.074044 -0.189823
Si 0.870613 1.500184 -0.879374
A1 2.885529 1.447729 0.116641
A1 1.777317 0.007779 0.093293
H -0.215704 -1.499117 -1.236500
H -0.607312 0.471417 0.946341
H -0.228142 0.651330 -1.110337
H -3.953377 0.622309 0.223503
H 0.962952 2.160529 -0.366644
C 1.838410 2.906892 -1.379360
H 0.971271 3.777576 -1.812333
H 2.071985 3.246971 -1.081360
H 1.878516 2.331129 -2.09686
H 1.071055 1.381513 -0.191903
H -0.029084 1.505701 0.581611
H -0.007528 0.085632 1.583069
H 1.088413 1.217155 2.076803
H -3.816769 1.820609 -0.114774
H -4.087072 0.027613 1.653833
H -4.736089 -0.456199 -0.393809
H -2.389773 -2.547316 0.259046
H -2.433292 -2.208119 -1.748812
H 2.028265 -2.974618 -0.536836
H 4.724521 -1.127389 0.750538
H 3.293995 -0.533335 2.865183

248
A.3 Chapter 7

Figure 7.1; BLYP/DZVP; 4.

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Figure 7.1; BLYP/DZVP; 5.

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Figure 7.2; MP2/6-31G***/HF/6-31G**; 1.

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Figure 7.2; MP2/6-31G***/HF/6-31G**; 2.

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Figure 7.3; BLYP/DZVP; 6.

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249
## Chapter 9

### Figure 9.1: BPE/DZVP (top: 1)

| Ti       | -0.212221 | 0.101998 | -0.085783 |
| G       | -1.781610 | -0.180486 | -1.007517 |
| O       | -0.236517 | 1.681227 | 0.828042 |
| C       | 1.017953 | 0.473988 | -1.377125 |
| N       | 0.628881 | -1.265313 | 0.873392 |
| Si      | 0.675242 | 2.020271 | 1.948775 |
| H       | 1.907152 | 1.781390 | 2.316270 |
| N       | -0.149863 | 2.890666 | 3.191590 |
| H       | 1.077273 | 3.841680 | 4.115000 |
| Si      | -1.872101 | 2.209090 | 1.385311 |
| H       | 2.711881 | -2.676762 | -0.137607 |
| N       | 1.325361 | -3.590553 | 1.729062 |
| H       | 2.888560 | -1.528311 | 2.118990 |
| B       | 1.045289 | 1.340652 | -2.549538 |
| P       | -1.348570 | 0.850760 | 0.922067 |
| 8       | 3.310195 | 1.031840 | -2.652568 |
| D       | 1.636729 | 2.812127 | -2.355125 |
| Z       | -1.833786 | 0.192620 | -0.893043 |
| V       | 3.583555 | 1.653549 | -1.753787 |
| P       | -2.311870 | 0.612677 | 1.920267 |
| 8       | -3.940245 | -0.132180 | 0.466012 |
| D       | -1.630843 | -0.488922 | 1.803268 |
| Z       | -1.728289 | 0.283589 | 2.046526 |
| V       | -0.952807 | -1.058711 | 2.135827 |

### Figure 9.1: BPE/DZVP (middle: 1)

| Ti       | -0.257042 | 0.049058 | -0.05676 |
| G       | -2.460651 | -0.201895 | 0.278731 |
| O       | -0.274369 | 1.764387 | 0.448601 |
| C       | 0.394589 | -0.716660 | 1.143610 |
| N       | -1.842789 | 0.797238 | 0.718725 |
| Si      | 0.638391 | 2.811620 | 1.390068 |
| H       | 2.058305 | 2.207093 | 1.479333 |
| N       | 0.051219 | 2.820545 | 2.770528 |
| H       | 1.631376 | 4.175203 | 0.746500 |
| Si      | 0.159994 | -3.303665 | 2.198185 |
| H       | 2.086744 | -2.490602 | -0.012072 |
| N       | 0.334748 | -3.470495 | 1.400808 |
| H       | 2.174519 | -2.202043 | 2.418156 |
| Si      | 0.124053 | 0.301804 | -0.319188 |
| H       | 0.693303 | -0.500114 | -2.435442 |
| N       | 2.397741 | -0.074655 | -2.566433 |
| H       | 1.022946 | 1.706997 | -3.673383 |
| H       | -2.89781 | -1.723987 | -2.567376 |
| H       | -1.397638 | -2.049189 | -1.627423 |

### Figure 9.1: BPE/DZVP (top: 2)

| Ti       | 0.000000 | 0.000000 | 0.000000 |
| G       | 0.087020 | -0.061384 | -1.441726 |
| O       | 0.819133 | 0.000000 | 0.000000 |
| C       | -0.687652 | -0.722836 | 1.892519 |
| N       | -0.604995 | 1.170409 | 0.000000 |
| Si      | -1.478444 | -1.302184 | -1.650500 |
| H       | -1.785053 | 2.986682 | 0.793308 |
| N       | -1.740736 | 2.341093 | 2.272242 |
| H       | -3.122794 | 2.036826 | 2.380658 |
| Si      | -1.577219 | 4.053666 | 0.531848 |
| H       | -0.736400 | -1.250559 | 3.112257 |
| N       | -2.150136 | -1.425860 | 3.142923 |
| H       | -0.406338 | -0.087775 | 4.024101 |
| Si      | -0.275158 | -2.335565 | 3.320370 |
| H       | 2.346880 | 0.745587 | 0.343930 |

### Figure 9.1: BPE/DZVP (middle: 2)

<p>| Ti       | 0.000008 | -0.006854 | 0.040980 |
| G       | -0.858889 | -1.241646 | -1.058053 |
| O       | 1.859914 | -0.095445 | 0.195057 |
| C       | -0.000293 | -0.459993 | 1.668394 |
| N       | -0.638230 | 1.687029 | 0.100675 |
| Si      | -0.184661 | 2.851662 | 0.887111 |
| H       | -1.755836 | 2.374632 | 2.373533 |
| N       | -3.253219 | 2.177705 | 0.431858 |
| H       | -1.642132 | 4.043181 | 0.587089 |
| Si      | -0.780998 | 1.285112 | 3.206961 |
| H       | -2.195634 | -1.731165 | 3.305053 |
| N       | -0.565641 | -0.183040 | 4.221989 |
| H       | 0.156198 | -2.373382 | 3.463393 |
| Si      | 2.151952 | -0.323776 | 1.108876 |
| H       | 0.734825 | 0.417692 | -2.051120 |
| Si      | 1.701174 | 0.310873 | -2.527304 |
| H       | 0.356685 | -0.305719 | -2.527304 |</p>
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