Characterisation of New Molecular Sieves

Brian Hampson B.Sc., M.Sc., GRSC

Doctor of Philosophy
University of Edinburgh
1991
I declare that

(i) this thesis is my own composition and that, unless otherwise stated, the work described was carried out by myself at the Edinburgh University Chemistry Department between October 1986 and September 1991;

(ii) this work has not been submitted for any other degree;

(iii) the work described in Chapter 6 has been published as a scientific paper in the journal Zeolites.

Brian Hampson
Acknowledgements

I would like to acknowledge the following people, not necessarily in this order, without whom I would not have been able to carry out this work.

(i) Drs. H.F. Leach and B.M. Lowe for taking me on in the first instance.

(ii) The University of Edinburgh for financial assistance in the form of a part-time demonstratorship for my first two years, and for awarding me the James Watt Bursary for my final year.

(iii) Dr. R. Brown for his help and technical advice, Mr. J. Broom for all the times he mended my glass vacuum line, and all the other technicians that I begged, borrowed, and stole help from.

(iv) The Edinburgh University SEM facility and Mr. J. Findlay for use of the SEM and subsequent processing of pictures.

(v) ICI Runcorn for the donation of the Cahn microbalance used in the gravimetric adsorption studies, and to ICI Wilton for help in the identification of the material coded BH1.

(vi) All the members of the catalysis and zeolite groups for their friendship and the good times we had during the three years and beyond.

(vii) Everybody who has encouraged, pushed, and cajoled me during the last two years in the production of this work.
Courses Attended During Postgraduate Studies

Mass Spectroscopy
Visiting lecturer

Crystallography
Dr. R. Gould, Dr. A. Blake

Catalysis and the Chemical Industry
Dr. D. Whan, Dr. M.S. Spencer, Dr. J.P. Candlin

FORTRAN Computing Course (Chem Phys 3)
Dr. M.A.D. Fluendy

Multipulse NMR Spectroscopy
Dr. I. Sadler

Physical Properties and Chemical Structures (Zeolites, Chem 4)
Dr. B.M. Lowe

Business Management
Dept. Business Studies, Edinburgh University

Industrial Processes
Dept. Chemical Engineering, Edinburgh University

Zeolite Group Seminars and BZA Conferences 1986-1989
Abstract

A general introduction to zeolites and aluminophosphate based molecular sieves is followed by a more detailed review of EU-1 and AlPO₄-5, the two molecular sieves studied in this work.

The synthesis and characterisation of these molecular sieves is described. The characterisation techniques gave details of the framework structure and composition, surface area, and morphology. A time study of the crystallisation of AlPO₄-5 from an aluminophosphate gel containing two organic templates showed the formation of a hydrate phase before the AlPO₄-5 phase, the change in pH during hydrothermal crystallisation, and the transformation of the Kaiser alumina spheres to give the spherical morphology of AlPO₄-5 associated with this synthesis procedure.

Volumetric adsorption and subsequent desorption of but-n-ene isomers on both molecular sieves at room temperature showed that some strong adsorption of the molecules occurs, which could be removed at higher temperatures. The effect was more pronounced with EU-1.

Gravimetric adsorption of various organic compounds on AlPO₄-5 showed pore filling values and rates of uptake consistent with the kinetic diameters of the organic molecules. The Langmuir model, found to give the best fit for the adsorption isotherms, was seen to break down at mid-range values of P/Pₒ.

Thermal desorption of pyridine from H-EU-1 showed that
the acid sites probably exist in or close to the side pockets in the EU-1 channel system, and that a side pocket may contain more than one acid site. The AlPO₄-5 samples of spherical morphology were found not to have strong acid sites.

The framework of calcined AlPO₄-5 was seen to be degraded to a denser phase by aqueous salt solutions, whereas as-synthesised samples remained intact. The extent of the attack was dependant upon the anion and the solution concentration. AlPO₄-11 and AlPO₄-25 samples were also attacked but to a lesser extent.

EU-1 and AlPO₄-5 samples acted as acidic catalysts in the isomerisation of but-1-ene. Only but-1-ene, cis and trans but-2-ene were observed in the gaseous phase. A strongly bound residue was detected on the surface of EU-1 by TGA. This residue was seen to deactivate the catalyst in the first instance, but heating the sample with the residue in a vacuum was seen to change the catalytic nature of the zeolite. The activity of the AlPO₄-5 samples was lower than EU-1 under identical conditions. However, samples of the AlPO₄-5 spheres were seen to have a higher activity than the usual barrels. Investigations gave no solid evidence for the seat to this increased activity, but it is thought that framework defect sites may be responsible.
## Contents

**Chapter 1** An introduction to Molecular Sieves 1  
1.1 History 1  
1.2 Zeolites 4  
1.2.1 Structure 4  
1.2.2 Synthesis 11  
1.2.3 Ion Exchange 14  
1.2.4 Molecular Sieving, Adsorption, and Diffusion 19  
1.2.5 Catalysis 25  
1.3 Aluminophosphate Based Molecular Sieves 37  
1.3.1 Introduction 37  
1.3.2 Classification and Structure 37  
1.3.3 Synthesis 43  
1.3.4 Adsorption 48  
1.3.5 Catalysis 51  
1.4 References 59  

**Chapter 2** EU-1 and AlPO₄-5 Molecular Sieves 72  
2.0 Introduction 72  
2.1 Zeolite EU-1 72  
2.1.1 Introduction 72  
2.1.2 Structure 72  
2.1.3 Synthesis 77  
2.1.4 Properties 85  
2.1.4.1 Structural Stability 85  
2.1.4.2 Ion Exchange 85
3.6 Isomerisation Reaction

3.6.1 Introduction

3.6.2 Apparatus

3.6.3 Experimental

3.7 Adsorption Measurements

3.7.1 Introduction

3.7.2 Volumetric Measurements

3.7.2.1 Apparatus

3.7.2.2 Experimental

3.7.3 Gravimetric Measurements

3.7.3.1 Apparatus

3.7.3.2 Experimental

3.8 Ultraviolet/visible Spectroscopy

3.8.1 Introduction

3.8.2 Experimental

3.9 Atomic Absorption Spectroscopy

3.9.1 Introduction

3.9.2 Experimental

3.10 pH Measurements

3.10.1 Introduction

3.10.2 Experimental

3.11.1 References

3.11.2 Bibliography

Chapter 4 Synthesis and Characterisation

4.1 Zeolite EU-1

4.1.1 Introduction

4.1.2 Synthesis Procedure
4.1.3 Characterisation
4.1.3.1 X-Ray Diffraction
4.1.3.2 Thermal Analysis
4.1.3.3 X-Ray Fluorescence Analysis
4.1.3.4 Scanning Electron Microscopy
4.1.3.5 Nitrogen Adsorption
4.2 Aluminophosphate AlPO₄₋₅
4.2.1 Introduction
4.2.2.1 Synthesis Procedure (AlPO₄₋₅)
4.2.2.2 Synthesis Procedure (Dense Phases)
4.2.3 Characterisation
4.2.3.1 X-Ray Diffraction
4.2.3.1.1 Aluminophosphate AlPO₄₋₅
4.2.3.1.2 Dense Phases
4.2.3.2 pH Measurements
4.2.3.3 Thermal Analysis
4.2.3.4 Elemental Analysis
4.2.3.5 Scanning Electron Microscopy
4.2.3.5.1 Aluminophosphate AlPO₄₋₅
4.2.3.5.2 Dense Phases
4.2.3.6 Nitrogen Adsorption
4.3 References

Chapter 5 Sorption of Hydrocarbons
5.0 Introduction
5.1 Butene Sorption using Constant Volume Apparatus
5.1.1 Introduction
5.1.2.1 Zeolite EU-1 226
5.1.2.2 Aluminophosphate AlPO₄-5 232
5.2 Hydrocarbon Sorption using a Cahn Microbalance 241
5.2.1 Introduction 241
5.2.2 Aluminophosphate AlPO₄-5 241
5.3 Pyridine Desorption 251
5.3.1 Introduction 251
5.3.2 Experimental 251
5.3.3.1 Zeolite EU-1 252
5.3.3.2 Aluminophosphate AlPO₄-5 255
5.4 References 259

Chapter 6 Degradation of Aluminophosphate Molecular Sieves by Aqueous Salt Solutions 261
6.1 Introduction 261
6.2 Experimental 262
6.2.1 Synthesis of Aluminophosphates 262
6.2.2 Treatment with Salt Solutions 264
6.3 Effects of Treatment with Aqueous Salt Solutions 265
6.3.1 Action of Aqueous Salt Solutions 265
6.3.2 Action of Aqueous Acids 270
6.3.3 Damp Materials 271
6.4 Conclusion 273
6.5 References 277
<table>
<thead>
<tr>
<th>Chapter 7</th>
<th>n-Butene Isomerisation</th>
<th>278</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>278</td>
</tr>
<tr>
<td>7.1.1</td>
<td>The Mechanism of the n-butene Isomerisation Reaction</td>
<td>278</td>
</tr>
<tr>
<td>7.1.2</td>
<td>Interpretation of Catalytic Data</td>
<td>284</td>
</tr>
<tr>
<td>7.1.3</td>
<td>General Characteristics of the Isomerisation Reaction</td>
<td>289</td>
</tr>
<tr>
<td>7.2</td>
<td>Zeolite EU-1</td>
<td>295</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Assessment of System Reliability and Activation Optimisation</td>
<td>295</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Determination of the Activation Energy</td>
<td>309</td>
</tr>
<tr>
<td>7.2.3</td>
<td>Comparison of the Isomerisation of the Three n-butene Isomers</td>
<td>317</td>
</tr>
<tr>
<td>7.2.4</td>
<td>Establishment of Procedures for Catalyst Regeneration</td>
<td>322</td>
</tr>
<tr>
<td>7.3</td>
<td>Aluminophosphate AlPO₄-5</td>
<td>336</td>
</tr>
<tr>
<td>7.3.1</td>
<td>To Compare the Activity of AlPO₄-5 (Single and Dual Template) with EU-1</td>
<td>336</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Effect of Reaction Variables</td>
<td>341</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Isomerisation Reactions and Activation Energies</td>
<td>351</td>
</tr>
<tr>
<td>7.3.4</td>
<td>Comparison of the Isomerisation Reaction over Various Synthesis Batches</td>
<td>361</td>
</tr>
<tr>
<td>7.4</td>
<td>References</td>
<td>372</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 8</th>
<th>Summary</th>
<th>375</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Zeolite EU-1</td>
<td>375</td>
</tr>
<tr>
<td>8.2</td>
<td>Aluminophosphate AlPO₄-5</td>
<td>378</td>
</tr>
</tbody>
</table>
Appendix 1  Results of First Attempt to Synthesise Zeolite EU-1  383

Appendix 2  Reprints of Published Material  390
1.1 History

A zeolite was defined by Smith as "an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration" [1]. The word zeolite is based on two Greek words (ζειω means "to boil" and θός means "stone") and describes the observations of the Swedish mineralogist, Cronstedt, when he reported the action of heat on a new mineral he discovered in 1756 [2]. This mineral is now known as stilbite and Cronstedt's report was the first written record of a natural zeolite. The definition must now, however, be extended to include the many synthetic aluminosilicates, some of which have analogous structures to the naturally occurring minerals. Some people have even included the series of molecular sieves based on microporous aluminophosphates, though these should really be classed as zeotypes. There has been some discussion on a modified definition of a zeolite, a short revue of which has been presented by Smith [3].

Natural zeolites can be described as either igneous or sedimentary. The igneous zeolites form in the cavities and fractures of volcanic lava flows as they cool. The crystals are relatively large with well defined morphologies, but the occurrences are too small and too far scattered to merit large scale industrial exploitation. The sedimentary
zeolites are not so morphologically well defined. It was not until von Seebach [4] in 1862 found analcime crystals 1mm in size in a clay, and Murray and Renard [5] reported twinned phillipsite crystals of the same size from samples taken during the HMS Challenger oceanographic survey of the bed of the Pacific Ocean (1873-1876), that mineralogists recognised their presence. Their widespread occurrence was only realised after the arrival of X-ray powder diffraction, and this also revealed that there were many large deposits, and that clinoptilolite was the most abundant sedimentary zeolite.

The type of zeolite found depends upon the environment in which they form. The silica content of the rock plays an important role, determining which zeolites predominate. The pH also has an effect, in that it is thought to control the rate at which crystallisation occurs. Other factors include temperature, pressure (burial depth), and time. These are all factors which are controlled in modern zeolite synthesis.

Synthetic zeolites have been reported as far back as 1862 when Deville claimed to have made levynite [6]. Other early claims also exist, as summarised by Breck [7], but the identifications were based on appearance and chemical analysis and were limited by the lack of a definitive diagnostic technique. It was not until the advent of X-ray powder diffraction that zeolites could be reliably identified.

Up until the mid-1950s, zeolite synthesis was carried out at high temperatures and pressures, to imitate the
conditions believed to occur during their formation in igneous rocks. In 1956, Milton and co-workers at Union Carbide, reported the formation of a new synthetic zeolite, which they named Zeolite A, under conditions that resembled those for the sedimentary formation of zeolites [8]. Instead of the high temperatures and pressures formerly used, it was realised that zeolites could be synthesised at low temperatures and pressures provided that the reagent mixture was sufficiently reactive. Many synthetic zeolites can now be made at temperatures below 373K, using very alkaline gels.

There are presently about 39 known natural zeolite structures, as well as over 100 synthetic species, many with structures that are not isotypic with those of the natural ones.

The discovery of new synthetic zeolites and related structures is still continuing. As recently as 1982, a new field was established when workers at Union Carbide [9] announced a new family of framework structures based on aluminium and phosphorus tetrahedra. Further, new and analogous frameworks have been synthesised by including silicon and other elements in the reaction mixture. These materials are referred to as the silicoaluminophosphates (SAPOs) and by analogy as ElAPSOs and MeAPSOs. As mentioned earlier, these are really zeotypes, as they are analogous in behaviour to aluminosilicates, and they will be dealt with in more detail later.

In recent years the family of molecular sieves has become very wide indeed; the inter-relationship between
zeolites, aluminophosphates, and other molecular sieves is shown in Figure 1.1 [10].

1.2 Zeolites

1.2.1 Structure

The main source of structural information is X-ray diffraction, though now, new spectroscopic techniques such as solid state nuclear magnetic resonance, and Fourier Transform infrared are used. Large single crystals are needed for X-ray analysis, though new structure refinement programs are now being used to analyse results from X-ray and neutron powder diffraction.

Zeolites have three-dimensional crystalline frameworks. These frameworks are made from primary units, namely the \([\text{SiO}_4]^{4-}\) and \([\text{AlO}_4]^{5-}\) tetrahedra. These are joined together by the mutual sharing of oxygen atoms at the corners of adjacent tetrahedra. The presence of aluminium gives the framework a nett negative charge which is balanced by cations.

It has been observed that all zeolite structures are made from a limited number of repeating sub-units, called secondary building units (or sbus) by Meier [11]. Meier originally proposed eight sbus but this has recently been expanded to sixteen [12] (Figure 1.2). An example of how a framework is built up from its sbus is shown in Figure 1.3.

In some cases, the framework contains repeating polyhedra, or cages. Four of these cages, each designated by a Greek letter, are shown in Figure 1.4. The \(\beta\)-cage is also known as the sodalite cage, as it occurs in the
Figure 1.1 The family of molecular sieves [10]

- molecular sieves
  - silicas
    - titano silicates
  - metalloaluminates
  - aluminophosphates
    - ELAPOS
    - MeAPOs
    - MeAPSOS
  - other
    - carbons
    - gallo germanates
  - zeolites
  - gallo silicates
  - chromo silicates
    - boro silicates
    - ferro silicates
Figure 1.2 Secondary building units found in zeolite molecular sieves [12]
**Figure 1.3** Use of a 5-1 SBU to build the chain structure found in MFI zeolites
Figure 1.4 Cages found in zeolite structures [13]

α-cage e.g. faujasite

β-cage e.g. sodalite

γ-cage e.g. paulingite

ε-cage e.g. erionite
mineral sodalite. The void spaces of these cages and of the channels that link them are not normally empty, and in the natural and 'as made' synthetic materials they contain water molecules, framework charge balancing cations, and often other species such as salts and organic molecules. The actual sites that these occupy depend upon the nature of the ions and molecules present, and also on the structure and framework composition of the zeolite.

The balancing cations are needed as the isomorphous substitution of Si" by Al" gives the site a nett negative charge. Thus the framework can be regarded as a large polyanion. The cations are often free to move within the channels and cavities, and in many cases can take part in ion exchange as will be discussed later.

As the Si/Al ratio, cation species, and water content all vary, even for the same zeolite, the formula for the crystallographic unit cell will vary from sample to sample, but it can be written in general as

\[ \frac{M}{n}[\text{AlO}_2]_x (\text{SiO}_2)_y \cdot w\text{H}_2\text{O} \]

where \( M \) is the balancing cation of valence \( n \), and \( w \) is the number of water molecules. The ratio \( y/x \) must be \( \geq 1 \) if Lowenstein's rule [14] which excludes Al-O-Al linkages is obeyed.

The wide variation in chemical composition has led to claims for over a hundred synthetic zeolites and zeotypes, though many of them are isotypic, that is, they have the same framework topology and so give very similar X-ray diffraction patterns. Meier and Olson have identified sixty four individual structure types based upon framework
topology [15]. In this compilation, they have only included structures that have a framework density of less than 21 tetrahedral atoms per 1000Å³, which precludes dense phases such as quartz. Each structure is identified by a three capital letter code as designated by the IUPAC Commission on Zeolite Nomenclature. Studies of the way in which secondary building units can be linked together indicate that there are many more, as yet unsynthesised, structure types.

The zeolite pore systems can consist of cages, channels, or a mixture of the two. Access to the cavities is controlled by the size of the largest constriction, or window; the size depends on the number of T-atoms that form the window (Table 1.1) [16]. The various pore sizes lead to the phenomena of molecular sieving, that is the ability to

<table>
<thead>
<tr>
<th>number of tetrahedra in ring</th>
<th>maximum pore size /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.16</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>0.28</td>
</tr>
<tr>
<td>8</td>
<td>0.43</td>
</tr>
<tr>
<td>10</td>
<td>0.63</td>
</tr>
<tr>
<td>12</td>
<td>0.80</td>
</tr>
<tr>
<td>18</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Table 1.1 Maximum pore sizes formed by rings of tetrahedra found in zeolite structures [16]
sorb small molecules and reject larger ones. The molecular sieve cavities are also responsible for the phenomena in zeolite catalysis known as shape selectivity. For example, large cages with small windows will allow large reaction intermediates to be formed, but only small products will be able to diffuse out.

The channel systems themselves can be one dimensional, e.g. Nu-10 (TON structure), two dimensional, e.g. mordenite (MOR structure), or three dimensional, either with all the channels equidimensional, e.g. faujasite (FAU structure), or with none of the three equidimensional, e.g. phillipsite (PHI structure).

1.2.2 Synthesis

Zeolites are synthesised by the hydrothermal crystallisation of an aluminosilicate gel. The gel is usually prepared from water, a source of silicon, a source of aluminium, and a base, usually a hydroxide, to give a high pH. The composition of the gel has to be carefully controlled to give a successful synthesis. The crystallisations are usually carried out at temperatures below 473K.

The aluminium source is usually a soluble aluminate, or a solution prepared by the dissolution of an aluminium oxide or hydroxide or even aluminium metal in aqueous alkali. The silica source may be a soluble silicate, a silica sol, or a high surface area silica. The base is usually in the form of an inorganic hydroxide, and, especially in the case of high silica zeolites, organic
bases such as quaternary ammonium salts are also used. The cations from the bases balance the negative charge on the zeolite framework.

The route to a zeolite from the initial gel components is shown below for the Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O system.

$$\text{NaOH}(_{aq}) + \text{NaAl(OH)}(_{aq}) + \text{Na}_2\text{SiO}_3(_{aq}) \downarrow \text{Ti a 298K}$$
$$[\text{Na}_a(\text{AlO}_2)_b(\text{SiO}_2)_c\cdot\text{NaOH}•] \text{gel} \downarrow \text{T2 = 298 to 448K}$$
$$\text{in a closed hydrothermal system}$$

$$\text{Na}_x[(\text{AlO}_2)_x(\text{SiO}_2)_y]\cdot\text{mH}_2\text{O} + \text{solution zeolite crystals}$$

Many variables influence the final product. Their role is not yet fully understood, and it is beyond the scope of this introduction to discuss them in any detail. The major factors that come into play during the reaction are:

1) gel composition
2) temperature
3) time

These determine, either individually or combined, which zeolitic or non-zeolitic structure is formed, the final framework composition e.g. Si/Al ratio, and the crystal morphology i.e. crystal size and shape. The variables are inter-related. For example, an increase in temperature will shorten the crystallisation time for a specific zeolite phase to form.

Zeolite crystallisation occurs in three phases,
pre-nucleation, nucleation, and crystal growth. There is no satisfactory explanation as to how the framework grows from an amorphous gel. It is thought that precursors are formed during the pre-nucleation stage, and that these form the nuclei from which the final framework structure extends.

The theory that cations act as templating agents has led to the idea that large organic cations and other molecules (e.g. amines) could give zeolites with larger channels and cages than those formed with inorganic cations. There is evidence for this, although the largest zeolite cage, that of faujasite, is formed in an organic free system. The real effect of the organic void filling species is to increase the Si/Al ratio of the framework, e.g. TMA-sodalite has a Si/Al ratio of 5, compared with 1 for Na-sodalite. This difference arises from the fact that only one TMA cation can be accommodated in each sodalite cage.

Perhaps the most well known example of the use of organic cations in high silica zeolite synthesis is that of the tetrapropylammonium (TPA) cation in the crystallisation of ZSM-5. The TPA cation is located in the ZSM-5 channel system such that the central nitrogen atom is at the channel intersection with each propyl chain down one of the channels. Templating is not always as well defined as in the TPA-ZSM-5 case. It is sometimes found that a single organic species can be used in the synthesis of more than one zeolite, and that a zeolite can be made using different organic species [17,18].

As explained above, the use of organic cations led to
the synthesis of high silica zeolites (Si/Al > 10). This is due in part to the fact that, as the organic cations are larger than the inorganic ones, fewer organic cations can be accommodated in the channel system, and so there must be less anionic AlO₄ tetrahedra in the framework. This is exemplified in the TMA-A/Na-A example mentioned above.

Large organic species are usually trapped in the channel system after crystallisation has occurred. They are normally too large to be removed by ion exchange, so for the zeolite to be useful as a molecular sieve, catalyst, or ion exchanger, it is usually necessary to remove the organic void filler by thermal degradation, either oxidatively in air, or under an inert atmosphere.

1.2.3 Ion Exchange

The ion exchange properties of zeolites have been studied for two main reasons. The first reason is structure modification. In this, the catalytic or molecular sieving properties are changed to suit the required conditions by the introduction of various ions. The second reason is for the use of zeolites as ion exchangers in commercial processes.

One of the earliest investigations into zeolite ion exchange properties is reported to be by Eichorn in 1858 in which he observed that chabazite and natrolite reversibly exchanged Na⁺ and Ca²⁺ ions from dilute salt solution [19].

As mentioned earlier, the framework carries a negative charge associated with the aluminium tetrahedra, and this must be balanced by cations in the zeolite void
space. These cations are not rigidly bound and so are able to participate in ion exchange. The exchange capacity of the zeolite is, therefore, dependant upon the Si/Al ratio, the lower the ratio, the higher the capacity.

The exchange equilibrium for a zeolite containing cation B which has a valence $Z^+_B$ in a solution containing cation A having a valence $Z^+_A$ is written as:

$$Z^+_A A(s) + Z^+_B B(z) \leftrightarrow Z^+_B B(s) + Z^+_A A(z)$$

(the subscripts (s) and (z) refer to the solution and zeolite phases respectively).

The distribution of the ions in both phases can be measured at equilibrium. The fraction of the cation A in solution is expressed as

$$A(s) = \frac{Z_A m_A}{Z_A m_A + Z_B m_B}$$

where $m_{A,B}$ are the molar concentrations of the ions in solution. The fraction of the same ion in the zeolite is

$$A(z) = \frac{Z_A M_A}{Z_A M_A + Z_B M_B}$$

where $M_{A,B}$ are the concentrations of the ion in the zeolite. Plotting $A(s)$ against $A(z)$ gives the ion exchange isotherm. If there is no preference for the ion by the zeolite, then the isotherm is a straight line of $A(z) = A(z)$. The selectivity of the ion by the zeolite can be expressed by the equation

$$\alpha = \frac{A(z) m_B}{B(z) m_A}$$

where $\alpha$ is known as the separation factor. The selectivity for one ion over the other is represented by the extent to which $\alpha$ deviates from unity.
In addition to ion selectivity, zeolites also exhibit an ion-sieve effect, i.e. some ions cannot reach certain sites in the void space. For example, analcime, which has an aperture of 0.26\text{nm}, exchanges Na\text{+} with Rb\text{+} (diameter of 0.30\text{nm}) but not with Cs\text{+} (diameter of 0.33\text{nm}) [20]. Zeolite A displays a double ion-sieve effect. Small cations such as Na\text{+} can enter the \(\beta\)-cages by the single six rings whereas larger cation, such as Tl\text{+} (diameter of 0.28\text{nm}), can only enter the \(\alpha\)-cages, and larger organic cations such as the tetramethylammonium cation (TMA\text{+}), are completely excluded [21,22].

Some ions such as Li\text{+} might be thought to exchange with most zeolites quite readily, but they are in fact found not to do so. This is because the Li\text{+} ion has a strongly bound hydration sphere that increases its effective diameter. Similar complications occur with divalent cations, as these have a higher hydration energy than univalent cations, and their hydration shell is tightly bound.

The pH of the exchange solution has to be carefully controlled, otherwise effects due to the acidity of the solution become important. For example the hydronium ion, H\(_3\)O\text{+}, may exchange with cations within the zeolite [23], or multivalent cations within the zeolite may hydrolyse.

Direct treatment of silica rich zeolites with a dilute mineral acid results in the exchange of the cation by H\(_3\)O\text{+}, which, on dehydration of the zeolite, leaves a proton (attached to the aluminosilicate framework) as the balancing cation. This acts as a Brönsted acid site in catalysis. If, however, the solution is too acidic, or the
zeolite is left in contact with the solution for too long, aluminium is leached from the framework [24], as is shown in Figure 1.5 [25]. Because of this, zeolites with a low Si/Al ratio are unstable in acidic solutions, the framework eventually collapsing [26].

Although nearly all ion exchange is done with zeolite in contact with a solution phase, it has also been observed in solid state reactions [27,28]. Recently, Beyer et al. [29] observed reactions between ZSM-5 (the hydrogen and ammonium forms) and alkali metal halides when the mixture is heated. The results indicated that ion exchange had taken place.

The commercial use of zeolites as ion exchangers is limited by two main factors. The first is the instability of the zeolite at low pH as mentioned above. The second is that the crystallite size of synthetic zeolites is normally too small for them to be used in unpelleted form. The pelleting of the zeolite results in a reduction in the exchange rate. Furthermore the pellets tend to break up with use. Consequently for many purposes ion-exchange resins are preferred to zeolites.

Some of the applications in which zeolites have found extensive use include:

(1) the removal of $^{137}$Cs and $^{90}$Sr/$^{90}$Y from nuclear waste storage ponds using clinoptilolite [30,31];

(2) the removal of ammonia and ammonium salts from waste water, clinoptilolite again being used most often [32]; and
Figure 1.5 Mechanism of framework dealumination by a mineral acid [25]
the replacement of polyphosphates in detergents by zeolite A [33,34].

1.2.4 Molecular Sieving, Sorption, and Diffusion

Upon dehydration, zeolites usually have a large sorption capacity for molecules that can penetrate the pore windows, but exclude larger molecules. This ability to selectively adsorb molecules up to a certain critical dimension is known as "molecular sieving", a term introduced by J.W. McBain [35].

As shown previously, the window diameters depend on the number of T-atoms that enclose them and can be calculated in simple cases as shown in Table 1.1. These are however theoretical values based upon the assumption that the ring is circular and planar, which is not always the case. For example, mordenite has 12 T-atom windows which are elliptical, having an opening of 0.65nm x 0.70nm, compared to zeolite Y which has circular 12 T-atom windows of diameter 0.74nm.

The size of the windows can be modified by cation exchange. The best example of this effect is shown by Zeolite A (Table 1.2). The effect arises from the siting of the cations next to the S8R windows which give access to the supercage. Upon dehydration of Na-A and K-A, the three univalent cations adjacent to the S8R windows (site II cations) move towards the ring and thus reduce the aperture size (the sentinel effect). In Ca-A, the ions (4Ca^{2+} + 4Na^+) are situated such that there are no site II cations so the S8R rings are unrestricted.
Table 1.2 Approximate pore sizes of zeolite A ion-exchanged with various cations

<table>
<thead>
<tr>
<th>cation</th>
<th>aperture /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>0.29</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.36</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Another factor affecting the penetration of the window by molecules is the temperature. A molecule that is slightly larger than the aperture may eventually enter the channel system if the temperature is increased. This is due to the vibration in the T-O-T bonds of the window increasing as the temperature is increased, creating changes in the pore diameter. For example, at room temperature, NH₃ does not enter the β-cages of the faujasites, but as the temperature increases, it diffuses in slowly [36].

Two further factors that affect the sorption properties of zeolites are concerned with the Si/Al ratio. As the Al-O bond is longer than the Si-O bond, an increase in aluminium content will result in an increase in the size of the unit cell. For example, in faujasite, the cubic unit cell constant increases linearly from 2.46nm to 2.495nm as the Si/Al ratio changes from 3.0 to 1.18 [37]. The other effect that occurs is that as the zeolite becomes more siliceous in nature, its surface becomes more hydrophobic. The electric field set up within the zeolite void space by
charged species gives the zeolite the ability to preferentially sorb polar molecules, such as water, over non-polar molecules, such as n-paraffins, and it is this field that is reduced as the anionic nature of the framework becomes less.

Provided that the adsorbate will enter the pore system, the extent of the adsorption at equilibrium depends upon the temperature and sorbate pressure. The isotherms obtained by plotting the amount of gaseous material adsorbed against the sorbate pressure are usually of Type I as classified by Brunauer et al. [38], indicative of strong adsorption. This is because the potential fields from the pore walls overlap enhancing the interactive energies of the solid with the gas molecule. This increases adsorption at low relative pressures in comparison with sorption on non-microporous solids with similar surface structures. Figure 1.6 [39] shows the six different types of isotherms that can be obtained, and the method of filling that they represent.

Type I isotherms are characterised by a plateau (Figure 1.6) which corresponds to the maximum uptake of sorbate by the zeolite. The limit exists because the pore constraints prevent the phenomenon of multilayer adsorption. In some cases, sorbates, especially the larger organic molecules, will sit in the centre of the channel, resulting in less than monolayer adsorption. A direct consequence of these factors is that it is difficult to quantify the inside of the zeolite in terms of surface area. The Type II isotherm developed by Brunauer, Emmett

21
Figure 1.6 Adsorption isotherms as classified by Brunauer et al. [39]
and Teller [40] is based upon multilayer coverage of the surface by the sorbate molecules, and is not strictly applicable to zeolites. The most appropriate isotherm model is that developed by Langmuir [41] where adsorption is confined to monolayer coverage. The Type I isotherm fits well the Langmuir equation

\[
\frac{n}{n_a} = \frac{Bp}{1 + Bp}
\]

where \(n\) is the number of moles adsorbed by unit weight of sorbent, \(n_a\) is the maximum number of moles adsorbed, and \(B\) is an empirical constant. For a planar surface, the value \(n_a\) is used to calculate the specific surface area \(A\) from the equation

\[
A = n_a a_m L
\]

where \(a_m\) is the cross sectional surface area of the sorbed molecule, and \(L\) is the Avogadro constant. It must be noted, however, that in this equation, \(n_a\) is the monolayer capacity, and so in cases in which the maximum adsorption occurs at less than monolayer coverage, the true surface area is not measured.

The most satisfactory way to quantify the pore structure is in terms of void volume. The maximum amount sorbed corresponding to the plateau of the isotherm can be expressed as a volume of the adsorbate, provided a reasonable estimate of its density can be made. The volume of the sorbate is equivalent to the accessible void volume in the zeolite. This volume should be the same for different sorbates, provided that all or the same amount of the pore structure is accessible to each of them. This is
known as the Gurvitsch rule [42].

The forces that bring about sorption in zeolites include "dispersion" forces, which are forces of attraction and short-range repulsion, and, as mentioned earlier, electrostatic (coulombic) forces due to the zeolite surface being charged (polar). These electrostatic forces arise when the molecules are charged or have dipole or quadrupole moments. An example of the latter is seen in the separation of \( \text{N}_2 \) from \( \text{O}_2 \) in air [43] where \( \text{N}_2 \) is preferentially sorbed due to its quadrupole moment.

Diffusion plays an important part in sorption, as it is normally the rate-controlling step. The type of channel system within the zeolite can affect the rate of diffusion of a molecule, for example diffusion is slower in a sinusoidal channel than in a straight one. This has been demonstrated by comparing the diffusion of n-hydrocarbons in erionite and zeolite Ca-A [44].

Zeolites in commercial use as molecular sieves are usually pelleted. Hence intercrystalline diffusion must occur in the macropores of the pellet. Kondis and Dranoff [45] have shown, using zeolite A in powder and pellet form, that the adsorption and desorption was still controlled by intracrystalline diffusion, though the pellet form had a lower effective diffusivity.

Diffusion in three dimensional pore systems should be more rapid than in one dimensional systems. This is a consequence of counterdiffusion. In a monodimensional system, if the pore width is less than two molecular diameters, the diffusing and counterdiffusing molecules
will be unable to pass whereas in a three dimensional system, there are more passages and wider intersections. Counterdiffusion has been shown to occur quite readily in zeolite Y [46].

Recently, Choudhary et al. [47] investigated the difference in diffusion rates in medium pore zeolites of molecules with apparently similar kinetic diameters. For example, 2,3-dimethylbutane is not sorbed in ZSM-5, whereas 3-methylpentane is, yet both have $d_0=0.56\text{nm}$. They proposed a 'shuttlecock-shuttlebox' model for the sorbate molecule-zeolite channel system in which the flexibility of the molecule in the direction of diffusion plays an important role.

With the availability of more powerful computing facilities, it is now possible to simulate the diffusion of molecules through zeolite channels, with computer graphics showing the molecule's movement and location [48,49].

The commercial applications of zeolites as sorbents is varied and include:

(1) the removal of water from non-aqueous solutions by zeolite 4A;
(2) the removal of acidic gases, e.g. $\text{SO}_2$, in pollution control by mordenite; and
(3) the separation of n-paraffins from iso-paraffins by zeolite 5A.

1.2.5 Catalysis

A catalyst is a substance that alters the rate at which a reaction reaches equilibrium but which does not
appear in the stoichiometric equation for the reaction. It is said that Aristotle reported the phenomena in his *Meteorology*, though the actual concept of catalysis was not introduced until 1836 by Berzelius [50].

The full scale commercial use of zeolites began in the early 1960s with the use of rare earth exchanged zeolites X and Y as cracking catalysts [51-53]. This was the result of an extensive research programme by the Mobil Oil Company to improve on the product ratios given by the silica-alumina catalysts used at the time [54].

The field of zeolite catalysis is extensive and varied as can be seen from the many reviews on the subject [55-60].

Table 1.3 [61] shows the major commercial processes in which zeolites are employed as catalysts. As can be seen from this table, the applications are mostly in the petrochemical industry. Hölderich attributes this to the two major oil crises [62], and Vaughan suggests that it is the reason why few zeolites have been thoroughly evaluated catalytically [63]. This is now changing and research is now turning to the use of zeolites in the production of fine chemicals, as can be seen by the papers and reviews presented at the 8th IZA Conference [64].

The major applications of zeolite catalysis are in the transformation of hydrocarbons. These are acid catalysed reactions which require acidic sites in the zeolite. As mentioned in Section 1.2.3, the exchangeable cations can be replaced by protons using mineral acids. Alternatively for zeolites that are unstable in acidic media, the hydrogen
<table>
<thead>
<tr>
<th>process</th>
<th>zeolite catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>cracking</td>
<td>rare earth X and Y</td>
</tr>
<tr>
<td>hydrocracking</td>
<td>X and Y, erionite, mordenite, loaded with Co, Mo, W and Ni</td>
</tr>
<tr>
<td>selectoforming</td>
<td>Ni-erionite</td>
</tr>
<tr>
<td></td>
<td>Ni-erionite/clinoptilolite</td>
</tr>
<tr>
<td>hydroisomerisation</td>
<td>Pt-mordenite</td>
</tr>
<tr>
<td>dewaxing</td>
<td>Pt-mordenite, ZSM-5</td>
</tr>
<tr>
<td>benzene alkylation</td>
<td>ZSM-5</td>
</tr>
<tr>
<td>xylene isomerisation</td>
<td>ZSM-5</td>
</tr>
<tr>
<td>methanol to gasoline</td>
<td>ZSM-5</td>
</tr>
<tr>
<td>NO\textsubscript{x} reduction</td>
<td>H-mordenite</td>
</tr>
</tbody>
</table>

Table 1.3 Important industrial processes utilising zeolite catalysts [61]

Form can be generated by the calcination of an ammonium ion-exchanged form.

\[
\text{NaZ} + \text{NH}_4^+ (\text{aq}) \rightarrow \text{NH}_4\text{Z} + \text{Na}^+ (\text{aq})
\]

\[
\text{NH}_4\text{Z} \rightarrow \text{NH}_3(\text{g}) + \text{HZ}
\]

A third protonation method involves the dehydration of cations that have water of hydration.

\[
\text{M(H}_2\text{O)}^{n+} \rightarrow \text{M(OH)}^{(n-1)+} + \text{H}^+
\]

Reduction of the cation in a stream of hydrogen also results in the formation of acidic hydroxyl groups as well as dispersing the metal through the zeolite structure, giving it a bifunctional catalytic nature [65]

\[
\text{NiY} + \text{H}_2 \rightarrow \text{HY.Ni}^0
\]
In all four cases, the residual protons are associated with oxygen coordinated to an aluminium in the lattice.

Treatment of the zeolite by heating to temperatures in excess of 823K results in the generation of Lewis acid sites from the loss of these protons by dehydration (Figure 1.7) [66]. These tri-coordinate aluminium defect sites are thought to be unstable in the presence of water vapour at these temperatures, and annealing occurs [67], forming an extra framework oxyaluminate species. This octahedral aluminium has been distinguished from the normal tetrahedral framework aluminium by magic angle spinning nuclear magnetic resonance (MASNMR) spectroscopy [68].

The framework hydroxyl groups can be detected by infrared spectroscopy. There are at least two bands seen in the hydroxyl stretching region. The first is at around 3740cm\(^{-1}\) and is attributed to terminal hydroxyl groups. These occur either on the surface of the crystal where the three-dimensional lattice terminates, or at a defect site within the framework. The second band normally occurs between 3600-3650cm\(^{-1}\) and is attributed to bridging hydroxyls. This frequency is lower due to the fact that the proton is not as rigidly bound to the oxygen as it is in the case of the terminal hydroxyl group, and so is more acidic in nature. It has also been observed [69] that the frequency of the band at 3650cm\(^{-1}\) in NaHY decreases as the Si/Al ratio increases, making the hydroxyl group more acidic. In addition to this band, the faujasites show a band also attributed to bridging hydroxyls at 3540cm\(^{-1}\) [70]. These bands are usually referred to as high frequency (HF).
Figure 1.7 Mechanism for the dehydroxylation of ion-exchanged zeolites to form Lewis acid sites [66]
at 3650cm\textsuperscript{-1}, and low frequency (LF) at 3540cm\textsuperscript{-1}, and are attributed to protons being bound to oxygens in different framework environments.

Another type of acid site, termed a "superacid" site is also thought to occur. It was first reported by Jacobs and co-workers [71] in a study of cumene (isopropylbenzene) cracking and toluene disproportionation reactions. It is thought to result from a synergism between the ejected aluminohydroxyl species and the framework hydroxyls [72,73]. However the nature of the site has still not been resolved [74].

Many techniques have been used to determine the strength, number, nature, and environment of the acidic sites, though no single method can be used to obtain all of these [75-77].

Of the non-destructive techniques, infrared spectroscopy has proved to be one of the most useful, especially when used to study the interaction between adsorbed bases and the acid sites [78]. The basic molecules, of which nitrogenous bases such as ammonia and pyridine are the most widely used, give rise to distinct spectra upon adsorption [79,80].

The main chemical analysis techniques used to study acidic sites include titration using coloured indicators [81,82], the potentiometric titration of solutions following ion exchange [83,84], and the adsorption and desorption of bases [85,86].

Zeolite catalysis is not confined solely to acidic reactions. It is thought that basic centres are involved in
the toluene alkylation reaction over K⁺ and Rb⁺ exchanged zeolite X [87], and also in the decomposition of propan-2-ol over K⁺, Rb⁺, and Cs⁺ exchanged zeolite Y [88]. Ziolek observed that oxidation of H₂S decreased as the Na⁺ and K⁺ ions in zeolites X and Y were exchanged for H⁺ [89].

Zeolites are also used as bifunctional catalysts, in which the acid forms are loaded with a metal such as platinum or ruthenium [90,91]. In addition to some of the reactions listed in Table 1.3, metal loaded zeolites are also used in Fischer-Tropsch syntheses [92], and the watergas shift reaction [93]. The metals are usually introduced by ion exchange followed by reduction, though adsorption from the gas phase can also be used [94,95].

The majority of active sites are present within the channels and cavities of the crystallites. Because these are of molecular dimensions, the phenomena termed "shape selectivity" occurs [96,97]. This is one of the main reasons that zeolites have superceded the silica-alumina catalysts, which have pores upto 10nm in diameter.

The pore constraints can inhibit the entrance of the reactants, the exit of the products, and the formation of some transition state species. These constraints give rise to four types of shape selectivity.

(1) **Reactant shape selectivity:** only molecules of a kinetic diameter that is less than or close to the window size (depending on the reaction temperature as described in Section 1.2.4) can enter the channel system. This was first observed by Weisz [98]. He noted that Ca-A dehydrated n-butanol but not
isobutanol, whereas when Ca-X (which has a pore diameter that both molecules can enter) was used, isobutanol was dehydrated at a faster rate. In some cases, a small amount of catalysis, ~1-2%, has been observed when molecules should not be able to enter the pore system. This is thought to be caused by active sites that are present on the external surface of the crystallites [99,100].

(2) Product shape selectivity: Product molecules that have dimensions close to that of the pore system may become trapped within a cavity, or have very much slower diffusion rates relative to that of smaller products, and may even undergo further reaction during the extra time within the crystallite. Weisz observed that during the methylation of toluene to xylenes, para-xylene was the dominant isomer seen in the products, having a diffusivity $10^4$ times greater than those of ortho- and meta-xylene [97]. When n-hexane is cracked over Ca-A [98], normal hydrocarbons are produced in preference to branched hydrocarbons with the same number of carbon atoms.

(3) Restricted transition state selectivity: some products are not formed because the transition state that needs to be formed from the reactant is too large for the space in which the active site resides. In true restricted transition state selectivity, the reactants and the potential products should be able to diffuse through the pore system unhindered. In the transalkylation of meta-xylene, toluene and either
1,3,5- or 1,2,4-trialkylbenzene is formed. The transition state for the symmetrical isomer is too large for the space available in H-mordenite and so is not seen in the products [101,102] even though it is predominant in the trialkylbenzene equilibrium mixture [103]. Similarly, the transalkylation of ortho-xylene also goes via a large diaryl intermediate. In addition to the transalkylation, isomerisation by a stepwise methyl shift to meta- and para-xylene can occur. It has been observed that as the channel size of the zeolite decreases, then the ratio of the rate of transalkylation to the rate of isomerisation decreases [104].

4 Molecular traffic control: zeolites such as ZSM-5 contain two types of intersecting channels, differing in size, shape, and path tortuosity. Derouane and Gabelica proposed a theory in which the reactant molecules preferentially enter the crystallite through one of the channel systems, and the product molecules diffuse out through the other, preventing counterdiffusion effects [105]. An investigation by Pope using adsorption techniques [106] did not support this theory, however the model was only intended to describe dynamic systems [107]. Lowe et al. have also suggested a model whereby small product molecules diffuse out through pores too narrow for larger reactant molecules [108].

Shape selectivity can be controlled in a number of ways. One way is to increase the crystal size. This has two
effects. The first is that the ratio of external active sites, which have no shape selective properties, to internal active sites is reduced. This is thought to be the reason for the reduction in the production of durene (1,2,4,5-tetramethylbenzene) during the methanol to gasoline process when the size of the ZSM-5 crystals are increased [109]. The second effect of increasing crystal size is to increase the diffusion path lengths. This results in molecules with faster diffusivities occurring in greater proportion in the products. For example, in the alkylation of toluene with methanol, increasing the size of the ZSM-5 crystals increases the para-xylene content of the products [110,111]. The para-xylene content can also be increased by increasing the temperature [112], again showing the importance of diffusion limitations.

Another method of controlling the shape selectivity is to introduce various cations. For example, the xylene transmethylation reaction over mordenite becomes more selective to the 1,2,4-trimethylbenzene isomer on increasing the cation size [113].

Weisz [97] expressed shape selectivity as

$$ S = \frac{(k'_p/k'_a)}{(k_p/k_a)} $$

where $k'$ and $k$ are the observed rate constants for the products with and without structural constraints, and the subscripts p and a designate the "proselective" (favoured) and "antiselective" (unfavoured) products. Shape selectivity is occurring when $S > 1$.

Shape selective properties have been used to characterise zeolites [114]. Some of the more common test
reactions used are listed here.

(1) The Constraint Index (CI) compares the relative rates of the cracking of n-hexane and 3-methylpentane [115].

\[
CI = \frac{\log(\text{fraction nC6 remaining})}{\log(\text{fraction 3MC5 remaining})}
\]

(2) The isomerisation of meta-xylene compares the rates of formation of the isomeric products [116].

\[
R = \frac{k_{r}o-xylene \text{ from m-xylene}}{k_{r}p-xylene \text{ from m-xylene}}
\]

(3) The hydroconversion of n-decane uses eight criteria based on the products to characterise the structure and dimensions of the channel system [117,118].

(4) The Spaciousness Index uses the hydrocracking of butylcyclohexane [119].

\[
SI = \frac{\text{amount of i-butane in products}}{\text{amount of n-butane in products}}
\]

A side effect of hydrocarbon reactions is the formation of carbonaceous deposits, or "coke", in the channels. Coke is considered to be hydrogen deficient organic residues. As the reactions continue, the deposits build up, eventually blocking the channels. This is known as "aging". If the channel system is non-interconnecting, then coking can result in the rapid deactivation of the catalyst as the molecular pathways become blocked. With intersecting channel systems, more routes are available for the diffusing molecules to bypass the blockages, though the pathways are more tortuous and so increase the selectivity for molecules with faster diffusion rates [120]. Occurrence of coke deposits within large cages could also reduce the effective cage size and so alter the transition state.
selectivity of the zeolite. However, as these deposits become larger, the cages, which are also channel intersections, become filled and again a rapid deactivation of the catalyst occurs. Furthermore the deposits become more difficult to remove under mild regeneration conditions. This has been referred to as the "faujasite trap" [121].

It is thought that coke is formed from the cyclisation or condensation of alkyl aromatics to form fused ring polycyclics. Rollman and Walsh [122,123] observed that erionite and ferrierite, which have pore openings that will not accept aromatics, had coke yields less than that of mordenite and ZSM-5 which do accept aromatic molecules. However, because of the channel constraints of ZSM-5, the alkylaromatics formed are unable to react further to form coke. Dejaifve et al. [124] observed that the coke deposits that were formed in ZSM-5 occurred only on the surface.

Alkenes are also thought to contribute to coke formation. Venuto [125] proposed a scheme in which carbonium ions, whilst acting as hydrogen donors in hydrogen transfer reactions to form alkanes, become larger through a "building block" process, then further cyclise, whilst remaining strongly adsorbed to the catalyst surface, and eventually become coke.
1.3 Aluminophosphate Based Molecular Sieves

1.3.1 Introduction

In the late 1970s, the Union Carbide laboratories initiated a research program specifically to create a new class of molecular sieves, using known concepts of crystal chemistry. This resulted in the discovery of the aluminophosphate (AlPO₄) molecular sieves reported by Wilson et al. in 1982 [9,126]. This was followed in 1984 by the incorporation of silicon into the framework to make silicoaluminophosphates (SAPOs) [127,128]. Further investigations resulted in the incorporation of metals in the framework to form MeAPOs, where Me is Mg, Mn, Fe, Co, and Zn [129-131], and also the incorporation of one or more of the elements Li, Be, B, Si, Ti, Ga, Ge, and As to synthesise the derivatives known as ELAPOs [132].

In addition to those synthesised at Union Carbide, other laboratories have reported aluminophosphate based molecular sieves [133-136] including the 18-membered ring VPI-5 [137-139].

1.3.2 Classification and Structure

There are similarities between AlPO₄ and SiO₂ which pointed to the use of aluminophosphates as a potential source of microporous frameworks.

(1) AlPO₄ is isoelectronic with Si₂O₄;

(2) the average of the ionic radii of Al³⁺ (0.039nm) and P⁵⁺ (0.017nm) is 0.028nm, which is close to that of Si⁴⁺ (0.026nm) [140];
(3) there are crystalline dense phases of AlPO₄ with structures analogous to those of SiO₂ [141].

The nomenclature of the Union Carbide molecular sieves consists of an acronym followed by a number.

The acronym is derived from a normalised TO₂ formula where T represents the tetrahedral atom, and O is oxygen. It provides a simplified picture of the elemental composition of the framework tetrahedral sites and takes the form

$$(El_xAl_yP_z)O_2$$

where El is one or more of the incorporated elements, and x, y, and z are the mole fractions of the respective elements.

The number refers to the structure type of the molecular sieve, e.g. AlPO₄-11 and SAPO-11 have the same framework topology. The numbers are not related to any zeolite series number. There are presently over fifty structure types, not all of which have been determined. They include novel structures, structures analogous to known zeolites, and also layered materials. The latter, however, tend to collapse on removal of the organic material [142]. Typical structures, grouped into pore size categories, are shown in Table 1.4 [143-146]. Some of the established structure types have also been incorporated into Meier and Olson’s Atlas of Zeolite Structures [12].

In the AlPO₄ frameworks, the AlO₄ and PO₄ tetrahedra are in strict alternation. This gives a neutral framework and a TO₂ formula of

$$(Al_{0.5}P_{0.5})O_2$$
<table>
<thead>
<tr>
<th>AlPO₄ structure</th>
<th>structure type</th>
<th>pore size /nm</th>
<th>pore volume /cm³g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>large pore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5, 36, 37</td>
<td>n,d</td>
<td>0.8</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.8</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>Faujasite</td>
<td>0.8</td>
<td>0.35 (0.37)</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.7</td>
<td>0.33</td>
</tr>
<tr>
<td>medium pore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11, 31, 41</td>
<td>n,d</td>
<td>0.6</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.65</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.6</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>n,d</td>
<td>0.62</td>
<td>0.28</td>
</tr>
<tr>
<td>50</td>
<td>n</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>small pore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14, 17, 18, 26, 33, 34, 35, 39, 42, 43, 44, 47, 52</td>
<td>n,d, n, n, n, n, n, Linde type A, Gismondine, Chabazite-like, Chabazite-like</td>
<td>0.4, 0.43, 0.43, 0.43, 0.43, 0.43, 0.43, 0.43, 0.31</td>
<td>0.19, 0.28 (0.23), 0.35, 0.23, 0.3, 0.32, 0.23, 0.34 (0.32), 0.3</td>
</tr>
<tr>
<td>v. small pore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16, 20, 25, 28</td>
<td>n</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Sodalite</td>
<td>0.3</td>
<td>0.24 (0.20)</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.3</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.3</td>
<td>0.21</td>
</tr>
</tbody>
</table>

a n = novel,  d = determined  
b measured by water adsorption  
c void volume of zeolite counterpart

Table 1.4 Structure data for aluminophosphate molecular sieves [143-146]
The structures seem to obey Lowenstein's rule [14] by avoiding Al-O-Al bonds. Whereas in aluminosilicates Si-O-Si linkages occur, the corresponding P-O-P linkages are not observed in the aluminophosphates. Possibly this is because they are unstable due to the closeness of the two positive charges. The lack of these two type of linkage result in the structures containing only even numbered rings.

From the above $T_0$ formula, it can be seen that substitution of $\text{Al}^{3+}$ and $\text{P}^5^-$ ions by nonisoelectronic species will result in a nett charge on the framework and will require charge balancing species in the void space. This will impart ion exchange capabilities to the substituted aluminophosphate, and hence the possibility of Brönsted acid sites for catalysis.

Depending on the charges on the tetrahedral cations, the framework will be positive, negative, or electroneutral. To date, no anion exchange has been reported in the open literature for aluminophosphates; this suggests that substitutions leading to an overall positive charge are unlikely. Table 1.5 [147] shows the bonding types and their occurrence.

From this table it can be seen that only some of the possible substitutions occur. A metal can only be incorporated into an aluminium site. With silicon, there are two possible mechanisms.
bonds observed | unlikely bonds
---|---
Al - O - P° | P - O - P°
Si - O - Si° | P - O - Si°
Si - O - Al° | Al - O - Al°
Me - O - P° | Me - O - Me°
Me - O - P - O - Me° |  

o = electroneutral framework
e = electropositive framework
e = electronegative framework

Table 1.5 Bonding concepts and occurrence in aluminophosphate frameworks [147]

(1) Si can substitute for P, imparting an overall negative charge;

(2) two Si can substitute for Al+P, which is electroneutral, however some mechanism (1) must occur to avoid Si-O-P linkages [132].

Magic angle spinning nuclear magnetic resonance (MASNMR) spectroscopy has helped to verify these substitutions. Freude [148] and Saldarriaga [149], investigated samples of SAPO-5 and SAPO-37 respectively. Both observed only a single peak in the ²⁹Si spectra at about -90ppm, the shift for a Si(4Al) environment. This is indicative of Si substituting for P only (mechanism (1)).

Hasha et al. [150] observed a broad, unresolved band between -90 to -120ppm for various samples of SAPO-20, the sodalite analogue, which indicates that Si-O-Si linkages,
including Si\((4\text{Si})\) environments (-115ppm) in the higher substituted samples, are present. Therefore there is evidence that both mechanisms occur.

In all cases, the \(^{31}\text{P}\) spectra showed only a single peak in the low 30ppm region, corresponding to a P\((4\text{Al})\) environment. No resonance was observed for P-O-Si.

It is interesting to note that the \(^{27}\text{Al}\) spectra in these cases show only one resonance peak in the tetrahedral Al region, indicating only one aluminium environment, Al\((4\text{P})\) being the most obvious, when clearly some Al-O-Si linkages must occur. Hasha concludes that the Al\((4\text{P})\) and Al\((\text{Si,3P})\) environments are indistinguishable.

For some aluminophosphates a peak is also observed in the octahedral Al region at around -14ppm. This has been assigned as extraframework aluminium [148,149], but it has also been suggested that it could be due to secondary coordination of some tetrahedral Al\((4\text{P})\) sites with strongly adsorbed water [151]. Martens and co-workers question the latter explanation [152]. They observed a decrease in the intensity of the octahedral peak during a time study of the hydrothermal crystallisation of SAPO-37, whilst the tetrahedral peak increased in intensity. They also observed results consistent with silicon substituting via mechanisms (1) and (2).

Silicon substitution by both mechanisms is further indicated using base probe molecules to measure the number of acid sites. At low levels of silicon substitution, upto 1%, Milestone and Tapp [153], using \text{n}-propylamine on SAPO-5, observed that the number of Si in the framework
equalled the number of acid sites, but above this level of substitution, there was more Si than acid sites, indicating Si grouping. Grouping was also observed by Xu Qinhua using pyridine [154].

The ElAPO substituted series contains elements with oxidation states from +1 to +5 [132]. The substitutions follow similar rules to those above. Elements of oxidation states +1, +2, and +3 go into the P site, c.f. Me for P. Elements in the +4 state substitute via the two mechanisms proposed for silicon substitution, and those in the +5 state substitute isoelectronically for P [147].

AlPO₄₈ and SAPOs have very good thermal and hydrothermal stabilities, and the other substituted aluminophosphates have stabilities dependant on their chemical composition and crystal form [132,142].

1.3.3 Synthesis

The synthesis of the aluminophosphate molecular sieves is very similar to that for aluminosilicate zeolites. They are both crystallised hydrothermally from a reactive gel mixture at temperatures of between 373K and 523K, and templating agents are used to aid the synthesis.

The gel for AlPO₄ based zeotypes contains sources of aluminium and phosphorus, an organic templating agent, water, and, in the case of the substituted series, a source of the additional framework elements.

The sources of the materials can vary, as in zeolite synthesis. The phosphorus is usually added as 85% orthophosphoric acid. The aluminium is from a reactive
source such as pseudoboehmite (AlOOH) or aluminium isopropoxide (Al(OCH(CH\(_3\))\(_2\))_3\). Silicon can be added in the form of a reactive silica. The source of the elements should be such that it permits the formation of a reactive species that can become a framework tetrahedral unit. The compounds can be inorganic, such as halides, or organic (organometallic), such as alkoxides. The organic templating agent is usually an amine or quaternary ammonium salt, of which over 85 different molecules have been used successfully.

Tapp et al. have warned about the use of nitrates in the synthesis procedure [155]. They detected the presence of di-n-propylnitrosamine, a known carcinogen, in the mother liquor from the synthesis of AlPO\(_4\)-11 when using aluminium nitrate and di-n-propylamine. They recommend that under no conditions should nitrates be used in any syntheses involving amines in acidic conditions, as this may lead to the formation of other nitrosamines.

The major difference between the two synthesis mixtures is the initial gel pH. With aluminosilicates, the pH is high, whereas with aluminophosphates it is low. This low pH has the benefit of being able to ensure adequate solubility of a greater range of organic amines than is possible in zeolite synthesis. It also facilitates the incorporation of the elements into the framework by inhibiting the precipitation of oxides and hydroxides.

As in aluminosilicate synthesis, variations in the concentrations of one or more of the gel components, and/or variations in the reaction conditions will produce
Table 1.6 Effect of changes in reaction conditions on final product from the gel composition R:Al₂O₃:P₂O₅:40H₂O

different structures as can be seen in Table 1.6 [156,157]. Also, one organic template can be used to form more than one structure, and a given structure may be formed with different templates. Examples of this can be seen in Table 1.7 [147]. The two structures that are the least template specific, 5 and 11, are both unidimensional tubular channel systems. This may be the reason why they are relatively insensitive to the size and shape of the organic molecule.

Due to the acidic conditions of the synthesis, it is expected that the template within the pore structure will be in a cationic state. In the case of amines, they are protonated, as has been observed by Milestone and co-workers using NMR [153]. In the substituted aluminophosphates where there is a charge on the framework, it is expected that the cationic templates will
<table>
<thead>
<tr>
<th>template</th>
<th>AlPO₄ structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-n-propylamine</td>
<td>11, 31, 39, 41, 43, 46, 50</td>
</tr>
<tr>
<td>tetraethylammonium hydroxide</td>
<td>5, 18, 34</td>
</tr>
<tr>
<td>tripropylamine</td>
<td>5, 36</td>
</tr>
<tr>
<td>quinuclidine</td>
<td>16, 17, 35</td>
</tr>
<tr>
<td>diethyl ethanolamine</td>
<td>5, 47</td>
</tr>
</tbody>
</table>

Table 1.7(a) Templates that can be used in the formation of more than one aluminophosphate molecular sieve [147]

<table>
<thead>
<tr>
<th>AlPO₄ structure</th>
<th>No. of templates giving structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>large pore</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>25+</td>
</tr>
<tr>
<td>36</td>
<td>2</td>
</tr>
<tr>
<td>37</td>
<td>1 (dual)</td>
</tr>
<tr>
<td>medium pore</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>7+</td>
</tr>
<tr>
<td>31</td>
<td>2</td>
</tr>
<tr>
<td>41</td>
<td>2</td>
</tr>
<tr>
<td>46</td>
<td>1</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>small pore</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
</tr>
<tr>
<td>34</td>
<td>3</td>
</tr>
<tr>
<td>44</td>
<td>1</td>
</tr>
<tr>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>v.small pore</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 1.7(b) AlPO₄ structure/template specificity [147]
counterbalance this charge. Hasha observed $^{13}$C NMR shifts for TMA$^+$ rather than TMA(OH) in the SAPO-20 sodalite cage indicating balancing of framework charge [150]. Cationic templates require to be charge balanced by anions in electroneutral structures such as AlPO$_4$s, and also when there is an excess of template molecules over negative framework sites. It is thought that OH$^-$ is the counterion, and indeed, single crystal X-ray structure determinations have indicated the presence of OH$^-$ in AlPO$_4$-5 [158] and AlPO$_4$-17 [159], and $^{13}$C NMR produces a peak thought to be associated with TMA(OH) in AlPO$_4$-20 [150].

Bibby et al. observed that the amine template diffused out of the AlPO$_4$-11 channel without decomposition. However, on substituting another element into the framework, the amine degraded to an alkene and ammonia due to the protonation by the acid site [160].

Calculation of the template volume compares well with the saturation oxygen volumes, indicating the space filling role of the organic template. This is further observed as the template/TO$_2$ ratio remains constant for varying framework charge [147]. Tapp has shown that there are approximately two amine molecules per channel unit in AlPO$_4$-11 [153], and Wilson has shown that AlPO$_4$-20 has one TMA per sodalite cage, and that AlPO$_4$-17, an erionite analogue, has four template molecules per unit cell [142].

Calcination of the final crystalline product between 673K and 873K results in the removal of the organic molecule and leaving an open structure.
1.3.4 Adsorption

As with other microporous materials, sorption has been used to characterise the framework and surface of the aluminophosphate based zeotypes.

The pore diameters shown in Table 1.4 were measured using hydrocarbons of known kinetic diameter. The pore volumes were assessed from water vapour adsorption data. Lower pore volumes are measured with $O_2$ [9]. The difference arises because, unlike $H_2O$, $O_2$ cannot penetrate 6 T-atom rings. AlPO$_4$ based structures analogous to known aluminosilicates have pore volumes similar to their counterparts (Table 1.4).

The surfaces of all the aluminophosphate structures (including the electroneutral AlPO$_4$s) are hydrophilic. This is in contrast to the electroneutral silica zeolites which are hydrophobic. In the case of AlPO$_4$s, the hydrophilicity is thought to be due to the difference in electronegativity between Al (1.5) and P (2.1) [142].

The attraction of AlPO$_4$s for water was observed by Milestone and Tapp when trying to measure pore volumes using nitrogen [153]. The AlPO$_4$s sorbed trace amounts of water which affected the measurements.

Table 1.8 [126] shows how the hydrophilicity varies for the different structures. The most hydrophilic structures are comparable to the zeolite NaY, and the hydrophobic nature of the silica zeolites is also shown. The AlPO$_4$s and substituted structures can be used to dry permanent gases, and organic liquids [161-166].

The sorption of hydrocarbons and permanent gases
Table 1.8 Adsorption of water from an aqueous organic solution (4% water in butanone) [126]

<table>
<thead>
<tr>
<th>adsorbent</th>
<th>% water removal</th>
<th>% loadinga</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO$_4$-5</td>
<td>55</td>
<td>23</td>
</tr>
<tr>
<td>AlPO$_4$-8</td>
<td>74</td>
<td>45</td>
</tr>
<tr>
<td>AlPO$_4$-11</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>AlPO$_4$-14</td>
<td>&gt;80</td>
<td>&gt;45</td>
</tr>
<tr>
<td>AlPO$_4$-15</td>
<td>&gt;80</td>
<td>&gt;45</td>
</tr>
<tr>
<td>AlPO$_4$-17</td>
<td>77</td>
<td>41</td>
</tr>
<tr>
<td>AlPO$_4$-20</td>
<td>87</td>
<td>58</td>
</tr>
<tr>
<td>NaY</td>
<td>80</td>
<td>37</td>
</tr>
<tr>
<td>Silicalite</td>
<td>-5</td>
<td>—</td>
</tr>
</tbody>
</table>

a calculated from theoretical capacity

follows a Type I isotherm (Section 1.2.4), typical of micropore filling. The isotherms for water adsorption, however, vary (Figure 1.8) [142,157]. AlPO$_4$-11, -17, and -18 all show Type I isotherms, whereas AlPO$_4$-20 shows a Type IV isotherm, indicative of mesoporosity, and AlPO$_4$-5 and -31 show Type V isotherms, indicative of weak gas-solid interactions in microporous materials. Table 1.9 [126,161-164] shows that this anomaly only occurs for the nonsubstituted structure 5. This is discussed further in Section 2.2.4.2.
Figure 1.8 Adsorption of water by various aluminophosphate molecular sieves [142,157]
Table 1.9 Pressure dependence on the adsorption of water by AlPO$_4$-5 analogues at room temperature [126,161-164]

<table>
<thead>
<tr>
<th>adsorbent</th>
<th>pressure /mmHg</th>
<th>%wt adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO$_4$-5</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>26.4</td>
</tr>
<tr>
<td>SAPO-5</td>
<td>4.6</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>27.2</td>
</tr>
<tr>
<td>MgAPSO-5</td>
<td>4.6</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>21.3</td>
</tr>
<tr>
<td>TiAPSO-5</td>
<td>4.6</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>23.4</td>
</tr>
<tr>
<td>ZnAPSO-5</td>
<td>4.6</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>17.5</td>
</tr>
</tbody>
</table>

1.3.5 Catalysis

The substituted aluminophosphates should show catalytic activity as a result of the anionic nature of the framework. The protonic form of these molecular sieves are expected to have Brönsted acid sites which should be observed in the hydroxyl stretch region in the infrared spectrum (4000 to 3400 cm$^{-1}$).

In AlPO$_4$-5 and -11, a weak absorbance at around 3677 cm$^{-1}$ is observed [147] attributed to v(P-OH), the terminal groups at the crystal surface. Xu Qinhua also observed a very weak absorbance at 3630 cm$^{-1}$ attributed to v(Al-OH), also terminal groups [154].

On substituting silicon into the framework, these bands become more intense, and other bands also appear. With SAPO-5, the absorbances occur at 3745, 3677, 3630, and
Martens and coworkers report slightly different frequencies [167], 3743, 3672, 3618, and 3528 cm\(^{-1}\). The absorbance at 3745 cm\(^{-1}\) is attributed to \(v(\text{Si-OH})\), terminal hydroxyls, and is observed in zeolites. This absorbance increases slightly in intensity on increasing the silicon content, but the others were unaffected [167]. The absorbance at 3520 cm\(^{-1}\) has been attributed to \(v(\text{Al-OH})\) [154].

The acidic nature of these hydroxyls has been observed by the reduction in intensity of the absorbances on addition of a base [154, 167], and the shift in frequency following rapid exchange with D\(_2\)O [154]. The adsorption of pyridine also produces new absorbance frequencies due to the C-C stretches in the pyridine molecule in the presence of Brönsted and Lewis acid sites. Xu Qinhua observed absorbances using SAPO-5 at 1635 and 1550 cm\(^{-1}\) for Brönsted sites, 1624 and 1455 cm\(^{-1}\) for Lewis sites, and 1490 cm\(^{-1}\) common to both.

Absorbances for other substituted aluminophosphates are shown in Table 1.10 [147, 168], indicating how the different structures and substitutions alter the frequencies.

The temperature programmed desorption of NH\(_3\) can be used to assess the strength of the acid sites. Xu Qinhua et al. [154] observed single maxima for AlPO\(_4\)-5 and SAPO-5 occurring at 473K and 513K respectively, compared to two maxima for H-ZSM-5 occurring at 473K and 653K. Khouzami et al. [168] observed two maxima for AlPO\(_4\)-11 and SAPO-11 occurring at 413K and 513K, and 473K and 623K respectively,
Table 1.10 Infrared absorbances for various substituted aluminophosphate molecular sieves [147,168]

<table>
<thead>
<tr>
<th>substituted AlPO₄</th>
<th>absorbance frequency /cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAPO-11</td>
<td>3746 3710³ 3678 3632 3535</td>
</tr>
<tr>
<td>SAPO-11</td>
<td>3740 3710 3675 3605</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>3744³ 3626 3605</td>
</tr>
<tr>
<td>MgAPO-34</td>
<td>3675⁷h 3591</td>
</tr>
<tr>
<td>MgAPO-34</td>
<td>3744³ 3673³ 3621 3595</td>
</tr>
<tr>
<td>SAPO-37</td>
<td>3744³ 3642 3576</td>
</tr>
<tr>
<td>SAPO-41</td>
<td>3744 3673 3616</td>
</tr>
<tr>
<td>SAPO-46</td>
<td>3744³ 3673³ 3627 3532</td>
</tr>
</tbody>
</table>

* = very weak absorbance  sh = shoulder

The difference in the temperature of desorption between the aluminophosphate structures is probably caused by the difference in channel dimensions, structure 11 being the narrower.

Most of the catalytic reactions that have been studied are, obviously, those in which zeolites have been used. The aluminophosphates have been compared with zeolites and with each other to assess performance. Some of the processes that have been successful on the laboratory scale have been patented, examples of which are shown in Table 1.11 [153].

53
Table 1.11 Catalytic reactions reported to be successful on a laboratory scale [153]

The Union Carbide laboratories use the cracking of n-butane at 773K to assess the reactivity of new molecular sieves [132] by comparing the first order rate constants, $k_A$, for each catalyst. Table 1.12 [132] shows how $k_A$ varies for the different structures, substitution elements, and extent of substitution. As expected, the unsubstituted AlPO$_4$s are virtually inactive. SAPO-5, on the other hand, gives a range of activities from low to high. However metal incorporation gives a low activity. Structure 34 gives a range of activities depending on the incorporated element, the range including the measured $k_A$ value for its aluminosilicate analogue, chabazite. There does not seem to be any simple relationship between the $k_A$ value and the
<table>
<thead>
<tr>
<th>substituted AlPO₄</th>
<th>$k_A$/cm³min⁻¹g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO₄-5</td>
<td>∼0.05</td>
</tr>
<tr>
<td>BeAPO-5</td>
<td>3.4</td>
</tr>
<tr>
<td>CoAPO-5</td>
<td>0.4</td>
</tr>
<tr>
<td>MgAPO-5</td>
<td>0.5</td>
</tr>
<tr>
<td>MnAPO-5</td>
<td>1.2</td>
</tr>
<tr>
<td>SAPO-5</td>
<td>0.2-16</td>
</tr>
<tr>
<td>MgAPSO-5</td>
<td>2.6</td>
</tr>
<tr>
<td>ZnAPSO-5</td>
<td>1.5</td>
</tr>
<tr>
<td>AlPO₄-11</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>SAPO-11</td>
<td>0.5-3.5</td>
</tr>
<tr>
<td>MgAPO-36</td>
<td>11-24</td>
</tr>
<tr>
<td>CoAPO-36</td>
<td>11</td>
</tr>
<tr>
<td>MnAPSO-36</td>
<td>6.8</td>
</tr>
<tr>
<td>MgAPSO-36</td>
<td>18</td>
</tr>
<tr>
<td>BeAPO-34</td>
<td>3.7</td>
</tr>
<tr>
<td>CoAPO-34</td>
<td>5-15</td>
</tr>
<tr>
<td>FeAPO-34</td>
<td>0.1-0.6</td>
</tr>
<tr>
<td>MgAPO-34</td>
<td>7-29</td>
</tr>
<tr>
<td>MnAPO-34</td>
<td>2.5-5.2</td>
</tr>
<tr>
<td>ZnAPO-34</td>
<td>13</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>0.1-7.6</td>
</tr>
<tr>
<td>BeAPSO-34</td>
<td>7.6</td>
</tr>
<tr>
<td>GeAPSO-34</td>
<td>10.0</td>
</tr>
<tr>
<td>MgAPSO-34</td>
<td>0.05</td>
</tr>
<tr>
<td>Chabazite</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 1.12 Activity of substituted aluminophosphate molecular sieves for the cracking of n-butane [132]

concentration of a specific element incorporated into the framework [147].

AlPO₄-5 was also found to be inactive in the cracking of cumene. The incorporation of silica into the framework greatly enhanced the catalytic activity [154].

The conversion of methanol to hydrocarbons can be written as

$$\text{CH}_3\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{OCH}_3 \xrightarrow{+\text{H}_2\text{O}} \text{alkenes} \rightarrow \text{aliphatics, aromatics}$$

55
The formation of dimethylether requires only weak acid sites, whereas the conversion of alkenes to aliphatics and aromatics requires strong acid sites. This explains why dimethylether is the only product observed using unsubstituted AlPO₄-s [168,169]. The substitution of metals into the AlPO₄-5 framework has various effects upon the production of hydrocarbons [169]. The order of reactivity is

$$\text{Ga} < \text{Mn} < \text{B} < \text{Be} = \text{Si}$$
gallium having virtually no effect, whereas silicon produces up to 98% conversion. The introduction of iron, titanium, and especially vanadium result in the formation of CO and CH₄.

Large concentrations of methylated aromatics were found in the products, e.g. 40% hexamethylbenzene in Si and Co substituted AlPO₄-5 [153], and 30% 1,2,4-trimethylbenzene in SAPO-11 [168]. The difference in the number of methyl groups is a consequence of shape selectivity.

SAPOs have also been found useful in the methylation of toluene [170]. The SAPOs were found to be less active than the ZSM-5 type reference zeolite, LZ 105. The medium pore SAPOs, however, gave very high methylation selectivity with less than 2% disproportionation occurring, whereas the large pore SAPO-5 gave 60% disproportionation, and LZ 105 80%. It was also observed that, due to shape selectivity, the medium pore SAPOs produced para-xylene in concentrations greater than the equilibrium concentration, SAPO-11 producing up to 50%, compared to 24% for LZ 105.

The shape selective properties of medium pore SAPOs
are further illustrated in the isomerisation of meta-xylene. All the substituted aluminophosphates gave the equilibrium concentrations of the xylenes, but the medium pore structures gave less disproportionation products (toluene and trimethylbenzene) due to the restricted channel dimensions [170]. AlPO₄-5 was found to be inactive for the isomerisation of ortho-xylene [154].

The conversion of small alkenes over AlPO₄s and SAPOs has also been studied [170-172]. The reaction of propene over large pore SAPO-5 results in very rapid deactivation of the catalyst, with virtually no conversion. At the other end of the scale, with small pore SAPO-34, the major products were no larger than C₄ [172]. It is thought that, in SAPO-5, the large size of the channel allows the formation of coke precursors, whereas with SAPO-34, oligomerisation occurs within the cages, but the molecules are too large to diffuse out through the pores and so have to be cracked first. In contrast, the reaction using the medium pore structures AlPO₄-11 [171], and SAPO-11 and -34 [170] give liquid products, the major components of which are alkenes. It has been shown that the stronger the acidity of the catalyst, the higher the aromatic content of the products [173], the formation of aromatics from alkenes occurring by a hydrogen transfer reaction. The lack of aromatics using the aluminophosphate based catalysts can be considered as arising from their lack of strong acid sites.

The reaction of 1-hexene over a range of substituted aluminophosphates gives strength to the above observations [172]. Double bond isomerisation was mainly observed over
SAPO-5. As this will occur on very weak acid sites, it indicates the rapid coking of the channel system. The medium pore SAPOs were again quite active, giving both double bond and skeletal isomers. SAPO-11 was observed to keep its activity throughout the reaction. The channels in this structure are thought to be sufficiently narrow to inhibit the formation of coke precursors. Incorporation of transition metals into the structure enhances the formation of skeletal isomers.

All the aforementioned reactions show that the aluminophosphate based catalysts show a range of acid strengths dependent on the substituted elements, and that they exhibit shape selective properties, as do the aluminosilicates. It is clear that further work must be carried out to evaluate the materials more fully.
1.4 References

[1] Smith J.V., Mineralogical Society of America
    Special Paper, 1, 281, (1963)
    17, 120, (1756)
    334 (1862)
    Scientific Results of the Voyage of HMS Challenger, 1873-1876, Eyre and Spottiswood, London (1891)
[6] Deville St.C., Compt. Rend., 54, 324 (1862)
[7a] Breck D.W., Zeolite Molecular Sieves,
[7b] Morey G.W., Ingerson E., Econ. Geol.,
    38, 607, (1937)
[8] Breck D.W., Eversole W.G., Milton R.M., Reed T.B.,
[13] Reference 7a, p46
[15] Reference 12, (all)
[16] Reference 7a, p65
[18] Reference 7a, p305-307
[19a] Reference 7a, p11
[25] Reference 7a, p569
[26] Reference 7a, p569

60


Breck D.W., United States Patent 3723308 (1973)


Reference 7a, p640


Reference 7a, p94


[56] Venuto P.B., Reference 45, p260
[61] Reference 17, p127
[64] Reference 62, (all)
[66] Reference 7a, p474


[83] Skeels G.W., Flank W.H., Reference 45, p369
[129] Messina C.A., Lok B.M., Flanigen E.M.,
[130] Wilson S.T., Flanigen E.M.,
[131] Wilson S.T., Flanigen E.M.,
Reference 48, p103
[133] Bond G.C., Gelsthorpe M.R., Sing K.S.W.,
[134] Tapp N.J., Milestone N.B., Wright L.J.,
18, 173, (1985)
[136] Derouane E.G., Vallyocsik E.W., von Ballmoos R.,
[137] Davis M.E., Saldarriaga C., Montes C., Garces J.,
[138] Davis M.E., Saldarriaga C., Montes C., Garces J.,
Crowder C., Zeolites, 8, 362, (1988)
[139] Davis M.E., Montes C., Hathaway P.E., Garces J.M.,
Reference 62, p199
40, 604, (1953)
[142] Wilson S.T., Lok B.M., Messina C.A., Cannan T.R.,
Flanigen E.M., Reference 43, p79

68

[144] Reference 7a, p133


[154] Xu Qinhua, Yan Aizhen, Bao Shulin, Xu Kaijun,
Reference 48, p835

[155] Tapp N.J., Bibby D.M., Milestone N.M., Zeolites,
8, 157, (1988)

[156] Tapp N.J., Milestone N.M., Bibby D.M., Zeolites,
8, 183, (1988)

Reference 72, p97

[158] Bennett J.M., Cohen J.P., Flanigen E.M.,

[159] Pluth J.J., Smith J.V., Bennett J.M.,


[161] Lok B.M., Celeste A.M., Patton R.L., Gajek P.J.,
Cannan T.R., Flanigen E.M., European Patent 103117
(1984)

[162] Lok B.M., Marcus B.M., Flanigen E.M.,
European Patent 161488 (1985)

[163] Lok B.M., Vail L.D., Flanigen E.M.,
European Patent 158348 (1985)

[164] Lok B.M., Vail L.D., Flanigen E.M.,
European Patent 158975 (1985)

[165] Lok B.M., Marcus B.M., Messina C.A., Patton R.L.,
Wilson S.T., Flanigen E.M., European Patent 158349
(1985)

[166] Flanigen E.M., Lok B.M., Marcus B.M., Messina C.A.,
Reference 145, p97

[168] Khouzami R., Coudurier G., Mentzen B.F.,
Vedrine J.C., Reference 145, p355

[169] Kikhtyanin O.V., Mastikhin V.M., Ione K.G.,

[170] Pellett R.J., Long G.N., Rabo J.A., Reference 48,
p843


[172] Pellet R.J., Coughlin P.K., Shamshoum E.S.,
Rabo J.A., in "Perspectives in Molecular Sieve

[173] Givens E.N., Plank C.J., Rosinski E.J.,
2.0 Introduction
This thesis is largely concerned with the acidic nature of two molecular sieves: the zeolite EU-1, and the aluminophosphate AlPO₄-5. Both these materials are relatively new, and their properties are summarised in this Chapter.

2.1 Zeolite EU-1

2.1.1 Introduction
In 1981, Casci et al. [1] reported the synthesis of a novel, medium pore, high silica zeolite. It was the first of a series from Edinburgh University Chemistry Department, and so was designated EU-1.

2.1.2 Structure
It has been known since its discovery that the channel system of EU-1 has a maximum window size of 0.58nm, corresponding to a 10 tetrahedral (T) atom ring. This was determined from sorption experiments using hydrocarbons of various critical diameters [1].

EU-1 commonly crystallises in an ellipsoidal habit [2]. Initial X-ray powder diffraction measurements produced the pattern shown in Figure 2.1, and the corresponding d-spacings (Table 2.1).

It was only recently, however, that the full framework topology was determined [3]. The channel system is
Figure 2.1 X-ray powder diffraction pattern for the zeolite EU-1 [2]
<table>
<thead>
<tr>
<th>EU-1</th>
<th>ZSM-50</th>
<th>TPZ-3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>inter-planar spacing (d) /nm</td>
<td>rel. peak intensity(^a) (I/I(_o))</td>
<td>inter-planar spacing (d) /nm</td>
</tr>
<tr>
<td>1.103</td>
<td>vs</td>
<td>2.01</td>
</tr>
<tr>
<td>1.010</td>
<td>s</td>
<td>1.11</td>
</tr>
<tr>
<td>0.972</td>
<td>w</td>
<td>1.01</td>
</tr>
<tr>
<td>0.684</td>
<td>w</td>
<td>0.97</td>
</tr>
<tr>
<td>0.586</td>
<td>vw</td>
<td>0.577</td>
</tr>
<tr>
<td>0.466</td>
<td>vs</td>
<td>0.464</td>
</tr>
<tr>
<td>0.431</td>
<td>vs</td>
<td>0.435</td>
</tr>
<tr>
<td>0.400</td>
<td>vs</td>
<td>0.430</td>
</tr>
<tr>
<td>0.382</td>
<td>s</td>
<td>0.400</td>
</tr>
<tr>
<td>0.371</td>
<td>s</td>
<td>0.385</td>
</tr>
<tr>
<td>0.344</td>
<td>m</td>
<td>0.370</td>
</tr>
<tr>
<td>0.338</td>
<td>m</td>
<td>0.342</td>
</tr>
<tr>
<td>0.326</td>
<td>s</td>
<td>0.335</td>
</tr>
<tr>
<td>0.316</td>
<td>vw</td>
<td>0.327</td>
</tr>
<tr>
<td>0.311</td>
<td>vw</td>
<td>0.324</td>
</tr>
<tr>
<td>0.296</td>
<td>vw</td>
<td>0.294</td>
</tr>
<tr>
<td>0.271</td>
<td>vw</td>
<td>0.253</td>
</tr>
<tr>
<td>0.255</td>
<td>w</td>
<td>0.248</td>
</tr>
<tr>
<td>0.242</td>
<td>vw</td>
<td>0.233</td>
</tr>
<tr>
<td>0.230</td>
<td>vw</td>
<td>0.213</td>
</tr>
</tbody>
</table>

\(a\) relative intensity (%)

vs 60-100
s 40-60
m 20-40
w 10-20
vw <10
sh shoulder

b The example X-ray patterns in the patent for this zeolite contain peaks that are not present in all of the samples: these are the peaks common to all the patterns.

Table 2.1 Interplanar spacings for as synthesised zeolites with the EUO topology [1,5,6]

74
unidimensional, consisting of elliptical rings of
dimensions 0.58 x 0.41nm, running in the (100) direction.
Coming off these channels are side pockets of dimensions
0.68 x 0.58 x 0.81nm deep (Figure 2.2).

The unit cell is orthorhombic and has cell parameters
of a=1.3695nm, b=2.2326nm, and c=2.0178nm. It contains 112
T-atoms, and hence has the composition

\[ \text{Na}_n[\text{Al}_{112-n}\text{Si}_{224}] \cdot 26 \text{ H}_2\text{O} \]

where 1.5 < n < 19, in accordance with the patent.

The framework itself is made up of a combination of
four 5-1 and one single 4 ring secondary building units.
Because the framework is unique, it has been given the code
EUO by the Structure Commission of the IZA [4]. Two other
zeolites, TPZ-3 [5] and ZSM-50 [6], have similar d-spacings
and peak intensities as measured by X-ray powder
diffraction, and so it is assumed that these zeolites have
isotypic framework structures. The d-spacings are given in
Table 2.1 for comparison with EU-1.

The infrared spectrum of EU-1 shows two main
absorption regions, the Si-O stretch near 1100 cm\(^{-1}\), and the
Si-O deformation near to 500 cm\(^{-1}\). Table 2.2 lists these in
more detail and also compares them with the same regions
for ZSM-5 and ZSM-11. It can be seen that, though the
differences are small, they are significant enough to
distinguish the three materials.

An analogue of EU-1 recently reported in which all the
framework aluminium was isomorphously substituted by iron
[7] showed a slight shift to lower vibrational frequencies,
e.g. 575cm\(^{-1}\) to 560cm\(^{-1}\), attributed to the presence of iron
a) 10 T-atom ring of the zeolite EU-1 [4]

b) Schematic of channel system of the zeolite EU-1 to show side pockets [3]

Figure 2.2 Pore structure of the zeolite EU-1
Table 2.2 Infrared absorptions for the zeolites EU-1, ZSM-5, and ZSM-11 [1]

<table>
<thead>
<tr>
<th>Wave-length /cm⁻¹</th>
<th>EU-1 comment</th>
<th>Wave-length /cm⁻¹</th>
<th>ZSM-5 comment</th>
<th>Wave-length /cm⁻¹</th>
<th>ZSM-11 comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1213</td>
<td>medium weak</td>
<td>1228</td>
<td>medium</td>
<td>1221</td>
<td>medium strong</td>
</tr>
<tr>
<td>1080</td>
<td>very strong</td>
<td>1095</td>
<td>very strong</td>
<td>1090</td>
<td>very strong</td>
</tr>
<tr>
<td>570</td>
<td>doublet centre</td>
<td>545</td>
<td>doublet centre</td>
<td>548</td>
<td>symmetrical doublet</td>
</tr>
<tr>
<td>470</td>
<td></td>
<td>455</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

in the framework. This was accompanied by a slight shift in the 2θ values in the XRD pattern indicating a change in lattice dimensions.

2.1.3 Synthesis

EU-1 is usually formed by the hydrothermal crystallisation of a gel with the stoichiometric composition

\[ v\text{Na}_2\text{O} \quad w\text{HEX} \quad x\text{Al}_2\text{O}_3 \quad y\text{SiO}_2 \quad z\text{H}_2\text{O} \]

where \( v, w, x, y, \) and \( z \) are the molar ratios of the components, \( X \) is an anion, and HEX is the hexamethonium ion \((N,N,N',N',N'-\text{hexamethyl-1,6-hexane diammonium ion})\), a bis-quaternary ammonium cation (Figure 2.3). It is thought that EU-1 was the first zeolite to be synthesised using this type of cation.

It has been claimed that other elements may also be incorporated in the framework by using different oxides in
a) hexamethonium cation

b) dibenzyl dimethylammonium cation

Figure 2.3 Two structure directing agents used in the synthesis of the EUO framework
the gel [1]. For example, silicon can be replaced by germanium, and aluminium can be replaced by iron, gallium, or boron. The iron analogue of EU-1 was synthesised by replacing the aluminium source with Fe(NO$_3$)$_3$.9H$_2$O [7].

It is not necessary for the organic diamine to be the hexamethonium cation. Casci and co-workers [1] claim that any of the alkylated derivatives of a polymethylene $\alpha$-$\omega$ diamine can be used, where the amine groups are separated by up to 12 carbon units, and the R groups range from H to C$_8$ alkyls, and they give an example using decamethonium bromide.

In the synthesis of the isostructural zeolites, the hexamethonium cation was used for TPZ-3 [5], and, more interestingly, the dibenzyltrimethylammonium cation (Figure 2.3), a quaternary ammonium ion, was used in the synthesis of ZSM-50 [6]. Sumitani and co-workers have also successfully used a mixture of the hexamethonium cation with either the tetramethylammonium cation or the tetraethylammonium cation, which had the effect of increasing the rate of TPZ-3 formation.

The zeolite EU-1 can be made from a range of gel compositions. Table 2.3 gives the optimum range of molar component ratios, along with those for TPZ-3 and ZSM-50 for comparison. The most interesting feature is that ZSM-50 can be produced with much higher SiO$_2$/Al$_2$O$_3$ ratios than EU-1, and even forms an all silica analogue. Gels with SiO$_2$/Al$_2$O$_3$ > 120 result in the formation of other phases in EU-1 syntheses with the hexamethonium ion [2].
Table 2.3 Preferred ranges of component ratios for the synthesis of zeolites with the EUO topology [1,5,6]

As discussed in Section 1.2.2, changes in reaction variables affect the formation of the zeolite. Casci et al. have studied the effects of some of these variables with respect to EU-1 formation [2].

In addition to XRD, they used the change in pH of the synthesis gel to monitor the progress of the zeolite crystallisation [8]. Figure 2.4 shows the relationship between the gel pH and the % crystallinity as a function of time. The sudden rise in pH is attributed to the increase in the free base/silica ratio, i.e. ([M\textsubscript{7}O]-[Al\textsubscript{2}O\textsubscript{3}])/SiO\textsubscript{2}, in the mother liquor as the silica is incorporated into the framework.

It was found [2] that increasing the reaction
Figure 2.4 Variation in gel pH during EU-I crystallisation

[8]
temperature increased the rate of crystallisation such that an Arrhenius type plot of \( \ln(\text{crystallisation time}) \) against the reciprocal temperature gave \( E_a = 95.4 \text{kJ mol}^{-1} \) for the rate of formation of EU-1, compared to 46 kJ mol\(^{-1}\) for zeolite A, and 63 kJ mol\(^{-1}\) for zeolite X.

An increase in the stirring speed of the reaction mixture was found to decrease the crystallisation time, and the effect was largest at speeds below 300 rpm. An increase in speed from 300 to 750 rpm decreased the crystallisation time by 1 hour, compared to a decrease of 3 hours for a stirring speed increase from 210 to 300 rpm.

Both Sumitani [5] and Casci [2] observed that 'seeding' the reaction mixture, i.e. adding a small quantity of TPZ-3 and EU-1 respectively, could reduce the crystallisation time. Furthermore, Casci found that this enabled him to increase the \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio in the reaction gel and still obtain a pure EU-1 phase.

EU-1 itself is a metastable phase, and the hydrothermal crystallisation reaction can overrun, causing the EU-1 to dissolve and recrystallize as \( \alpha \)-cristobalite and quartz. Dodwell et al. [9] found that substitution of some of the \( \text{Na}_2\text{O} \) with \( (\text{NH}_4)_2\text{O} \) increased the lifetime of the fully crystalline EU-1 phase in the mother liquor. This led to two undesirable side effects. The first was a tenfold increase in crystallite size, to one which would be unsuitable for most catalytic processes. The second was that the crystallisation time was also increased from about 70 hours to 120 hours. It was found that by stirring the reaction mixture and increasing the temperature part way
through the crystallisation process, a method previously used to reduce the particle size of ZSM-5, gave a product that was 100% EU-I of submicron particle size, in 72 hours. The authors also made EU-I from an alkali free system i.e. no alkali metal oxide. They used an initial gel of composition

\[2.5\text{NH}_4\text{O}_2 \quad 5\text{HEX(OH)}_2 \quad \text{Al}_2\text{O}_3 \quad 60\text{SiO}_2 \quad 3000\text{H}_2\text{O}\]

This provides a zeolite that contains only protons after calcination, so no further ion exchange is necessary to produce an acid catalyst.

Calcination of the 'as-synthesised' EU-I product, and its analogues, at 723K to 823K for up to 48 hours results in the removal of occluded water and the organic amine to leave the open framework with protons and the alkali cations (if used in the synthesis) as the framework charge balancing cations in the channels. Figure 2.5 shows the thermal analysis of an 'as-synthesised' sample of EU-I. The initial endothermic decrease in weight of about 0.5% is due to the loss of water. This is followed by a weight loss of about 14% occurring between 573K and 973K which is caused by the oxidative decomposition of the hexamethonium ion. The 3 stage loss of the organic, indicated by the 3 exotherms in the DTA, could be due to a combination of the zeolite's novel structure, and the strong association between the charge centres of the organic molecule and the zeolite framework.
Figure 2.5 Thermal analysis of EU-1 [2]
2.1.4 Properties

As the zeolites EU-1, ZSM-50, and TPZ-3 are isostructual, they should show similar physical and chemical properties.

2.1.4.1 Structural Stability

EU-1 demonstrates a very high thermal stability. The lattice begins to collapse at about 1523K, indicated by the endotherm at this temperature in Figure 2.5. Subsequent X-ray analysis confirmed the presence of amorphous material [2]. TPZ-3 was reported to have no significant change in its XRD pattern on heating to 1073K for over 12 hours [5].

As with other high silica zeolites, the framework of EU-1 is resistant to attack by mineral acids. The amount of aluminium leached from the framework by a solution of 1M HCl at 333K during an ion exchange procedure was found not to be very significant [2].

2.1.4.2 Ion Exchange

EU-1, TPZ-3, and ZSM-50 all show ion exchange capabilities typical of zeolites, the capacities being dependant upon the aluminium content of the framework. Exchange will occur with solutions containing most cations, especially the alkali metals, the alkaline earth metals, the rare earth metals (lanthanides), and the group VIII metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) [1, 5, 6]. The ion exchange procedure can be carried out either batchwise or continuously. A proton exchanged form for acid catalysis can be produced by either direct contact with a mineral
acid, or by exchanging with ammonium chloride followed by calcination.

The ion exchange behaviour of EU-1 could prove useful in processes similar to those discussed in Section 1.2.3.

2.1.4.3 Sorption

Table 2.4 gives the sorption capacities of EU-1 for adsorbates of various kinetic diameters [1]. The results show that EU-1 has a significant sorption capacity of \(14.4 \text{cm}^3\text{g}^{-1}\) as measured by n-hexane sorption. The low sorption capacities for hydrocarbons with \(\sigma\) greater than that for para-xylene confirms that the pore size is 0.58nm, and that EU-1 has molecular sieving capabilities, which could be used for industrial processes such as the separation of xylenes.

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>(\sigma)/nm</th>
<th>(P)/mmHg</th>
<th>time/h</th>
<th>weight sorbed/g100g(^{-1})</th>
<th>void volume/cm(^3)/100g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>0.27</td>
<td>4.5</td>
<td>2</td>
<td>6.9</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>4.5</td>
<td>16</td>
<td>11.0</td>
<td>11.0</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.43</td>
<td>45.8</td>
<td>2</td>
<td>9.5</td>
<td>14.4</td>
</tr>
<tr>
<td>p-xylene</td>
<td>0.58</td>
<td>1.6</td>
<td>2</td>
<td>10.5</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>18.5</td>
<td></td>
<td>10.6</td>
<td>12.2</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0.59</td>
<td>1.6</td>
<td>2</td>
<td>2.3</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td></td>
<td></td>
<td>5.5</td>
<td>6.3</td>
</tr>
<tr>
<td>cyclo-hexane</td>
<td>0.60</td>
<td>2.7</td>
<td>2</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td></td>
<td></td>
<td>1.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*Table 2.4 Sorption properties of EU-1 at 298K [1]*
The slow uptake of water is indicative of the hydrophobic nature of EU-1, which it has in common with other high silica zeolites.

TPZ-3 and ZSM-50 showed similar results [5,6], however no data is available for the silica analogue of ZSM-50.

Using computer simulation, Pickett et al. [10] have studied the passage of benzene through the channel system of EU-1. They have predicted that the molecule can pass unhindered through the straight channels, but can also get caught in the side pockets. If the molecule is located in the pocket, then it should not affect the diffusion of another molecule in the channel. This should prove beneficial in catalysis as the diffusion and catalytic processes should have a measure of independence.

2.1.4.4 Catalysis

As the Na⁺ ions in 'as synthesised' EU-1 can be exchanged for the catalytically active ions (e.g. H⁺ and rare earth cations) it is expected to be a useful catalyst in many reactions in which zeolites are employed, e.g. alkylation of alkanes or aromatics, disproportionation, isomerisation, catalytic cracking, hydrodesulphurisation, hydrodenitrification, catalytic dewaxing, dealkylation, dehydration, oxidation, and polymerisation [1]. The impregnation of the zeolite with metals such as Ni, Co, Pt, Pd, Re, and Rh imparts the ability to perform hydrogenation/dehydrogenation reactions.

As a catalyst, EU-1 can be used alone, or in an inorganic matrix, such as silica, alumina, or
montmorillonite, to act as a binder in the manufacture of pellets.

Before the structure of EU-1 was elucidated, Kumar et al. [11] employed catalytic test reactions to probe the shape selective properties of EU-1, loaded with 0.5 wt% platinum. The Spaciousness Index (SI, the ratio of i-butane to n-butane in the products from the hydrocracking of butylcyclohexane) measured for this catalyst was slightly larger than that for ZSM-12, which has a unidimensional pore structure of 12 T-atom channels. This suggested that EU-1 must have an effective pore width greater than that for ZSM-12. The products from the isomerisation of n-decane pointed to a 10 T-atom window, as did the sorption experiments. However, when n-dodecane was used, the products indicated 12 T-atom windows, as did the hydrocracked products of n-decane. EU-1 showed typical behaviour for a zeolite with 10 T-atom windows for the disproportionation of ethylbenzene. It can now be deduced, with knowledge of the structure, that it was the side pockets that gave the impression that EU-1 had 12 T-atom windows and was more spacious than ZSM-12.

Dewing [12] measured the diffusional constraints of various zeolites by comparing the ratio of ortho- to para-xylene from pure meta-xylene at 50% equilibrium conversion. EU-1 was found to lie between mordenite (which has wider channels than EU-1 and hence gave a higher ortho/para ratio) and ZSM-5 (which has similar channel dimensions but, because they are sinusoidal, a longer effective path length).
In a similar reaction, Kumar et al. [13] observed that ZSM-50 gave a lower ortho/para ratio (extrapolated back to 0% conversion of meta-xylene) than ZSM-5, the reverse of the result reported by Dewing. It should be noted, however, that the ZSM-5 crystallites used were smaller than those of the ZSM-50, and the reaction temperature used for ZSM-5 was slightly lower than that used for ZSM-50, and both were much lower than those used by Dewing. The use of smaller crystallites and lower temperatures is known to increase the ortho/para ratio (Section 1.2.5).

More interestingly in this reaction, the large side pockets in the ZSM-50 structure allowed the formation of a higher concentration of trimethylbenzenes (TMBs) than was observed for ZSM-5. This is an example of reduced restricted transition state shape selectivity. This was also observed in the methylation of toluene over the two catalysts. In this case the TMBs/xylenes ratio was higher for ZSM-50 than for ZSM-5, again due to the former's large side pockets.

Table 2.5 gives an example of the catalytic activity of EU-1 for the isomerisation of a non-equilibrium mixture of xylenes containing other hydrocarbons. The results for a 90% SiO₂/10% Al₂O₃ catalyst is given for comparison. It can be seen that EU-1 gave a better performance than the amorphous silica-alumina catalyst, by producing a higher percentage of para-xylene in the product, a greater ethylbenzene loss, and a lower xylene loss at a higher space velocity, though increasing the space velocity reduces the ethylbenzene conversion.
<table>
<thead>
<tr>
<th>catalyst</th>
<th>EU-1</th>
<th>SiO₂/Al₂O₃</th>
<th>initial feed comp (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>723</td>
<td>723</td>
<td>673</td>
</tr>
<tr>
<td>WHSV h⁻¹</td>
<td>13</td>
<td>84</td>
<td>59</td>
</tr>
<tr>
<td>Product comp (wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>0.69</td>
<td>0.20</td>
<td>0.10</td>
</tr>
<tr>
<td>toluene</td>
<td>3.69</td>
<td>2.06</td>
<td>2.03</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>6.67</td>
<td>8.34</td>
<td>8.35</td>
</tr>
<tr>
<td>para-xylene</td>
<td>19.75</td>
<td>19.65</td>
<td>17.22</td>
</tr>
<tr>
<td>meta-xylene</td>
<td>42.51</td>
<td>43.58</td>
<td>44.38</td>
</tr>
<tr>
<td>ortho-xylene</td>
<td>19.39</td>
<td>20.82</td>
<td>22.46</td>
</tr>
<tr>
<td>C₉⁺ aromatics</td>
<td>6.41</td>
<td>4.11</td>
<td>4.08</td>
</tr>
<tr>
<td>% ethylbenzene loss</td>
<td>22.1</td>
<td>2.6</td>
<td>2.4</td>
</tr>
<tr>
<td>% xylene loss</td>
<td>3.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 2.5 Activity of EU-1 for xylene isomerisation [1]

Sumitani and co-workers have made a comprehensive investigation of the catalytic properties of various samples of TPZ-3 [5]. For the reactions employed, the following general observations were reported.

1) Disproportionation of toluene

TPZ-3 had a higher catalytic activity within the temperature range used (573K to 823K) than the ZSM-5 and mordenite catalysts. The TPZ-3 samples also had a long active lifetime, with the activity being maintained at relatively low temperatures.
Methylation of toluene
The activity of the catalysts was not appreciably reduced, even after long term usage. The toluene conversion to xylenes was maintained at a high level, with ortho-xylene being produced in the greatest proportion.

Isomerisation of xylenes
The catalysts had a long active lifetime at relatively low temperatures (573K) and atmospheric pressure, with a production of para-xylene higher than that found for equilibrium conversion.

Isomerisation of ethylbenzene to xylenes
The catalysts again had a long active lifetime at relatively low temperatures and pressures, similar to those in (3), with a high level of selectivity for xylenes over ethylbenzene.

It can be seen that EU-1, and the isostructural zeolites ZSM-50 and TPZ-3, have properties typical of high silica zeolites, and have possible uses in industrial processes.

2.2 Aluminophosphate AlPO$_4$-5

2.2.1 Introduction

AlPO$_4$-5 was the first of the microporous aluminophosphate molecular sieves to be synthesised [14], and was reported by Wilson et al. in 1982 [15]. Its X-ray diffraction pattern (Figure 2.6) did not correspond to that for any known crystalline structure and hence it was recognised as a novel material [15].
Figure 2.6 X-ray powder diffraction pattern for AlPO$_4$-5 [17]
2.2.2 Structure

Typically AlPO₄-5 crystallises in a hexagonal barrel shaped habit, being either a single crystal, or an agglomerate of hexagonal platelets [14].

Initial X-ray powder diffraction measurements gave the pattern shown in Figure 2.6. The calculated powder pattern is also shown for comparison, and the observed and calculated d-spacings are given in Table 2.6 [16].

The use of 'plug gauge' adsorption gave an estimated pore size of 0.8nm, indicating a ring containing 12 tetrahedral (T) atoms, and the intracrystalline pore volume was measured at 0.18cm³g⁻¹ using oxygen [15]. Water vapour, however, gave a larger apparent pore volume of 0.31cm³g⁻¹ indicating that smaller pores may be present in the framework.

Single crystal X-ray diffraction techniques have been used on AlPO₄-5 containing tetrapropylammonium hydroxide (TPA(OH)), the organic structure directing agent, to determine its framework structure [17].

The framework is made up of strictly alternating tetrahedrally coordinated aluminium and phosphorus atoms. These are arranged in a 2D network of 4, 6, and 12 T-atom rings using three linkages of each tetrahedron (a 3-connected 4.6.12 2D net, Figure 2.7). The fourth linkage of each tetrahedron projects alternately up and down to connect a stack of these 2D nets into a 4 connected 3D network. This results in the formation of unconnected 12-ring cylindrical channels, the surfaces of which are made solely of 6-rings.
<table>
<thead>
<tr>
<th>Interplanar spacing (d) /nm</th>
<th>Relative peak intensities (I/I₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.19 - 1.16</td>
<td>vs</td>
</tr>
<tr>
<td>0.686 - 0.673</td>
<td>vw - w</td>
</tr>
<tr>
<td>0.597 - 0.583</td>
<td>w - s</td>
</tr>
<tr>
<td>0.451 - 0.442</td>
<td>m - vs</td>
</tr>
<tr>
<td>0.427 - 0.419</td>
<td>m - vs</td>
</tr>
<tr>
<td>0.399 - 0.392</td>
<td>vs</td>
</tr>
<tr>
<td>0.363 - 0.358</td>
<td>vw</td>
</tr>
<tr>
<td>0.344 - 0.339</td>
<td>w - m</td>
</tr>
<tr>
<td>0.309 - 0.306</td>
<td>w</td>
</tr>
<tr>
<td>0.298 - 0.294</td>
<td>w - m</td>
</tr>
<tr>
<td>0.267 - 0.265</td>
<td>vw</td>
</tr>
<tr>
<td>0.260 - 0.256</td>
<td>w</td>
</tr>
<tr>
<td>0.244 - 0.242</td>
<td>vw</td>
</tr>
<tr>
<td>0.240 - 0.238</td>
<td>vw - w</td>
</tr>
<tr>
<td>0.221</td>
<td>vw</td>
</tr>
<tr>
<td>0.218 - 0.215</td>
<td>vw</td>
</tr>
<tr>
<td>0.214 - 0.213</td>
<td>vw</td>
</tr>
<tr>
<td>0.212 - 0.211</td>
<td>vw</td>
</tr>
<tr>
<td>0.208 - 0.206</td>
<td>vw</td>
</tr>
<tr>
<td>0.201 - 0.200</td>
<td>vw</td>
</tr>
<tr>
<td>0.196</td>
<td>vw</td>
</tr>
<tr>
<td>0.190</td>
<td>vw</td>
</tr>
<tr>
<td>0.190 - 0.187</td>
<td>vw</td>
</tr>
<tr>
<td>0.177</td>
<td>vw</td>
</tr>
<tr>
<td>0.176</td>
<td>vw</td>
</tr>
<tr>
<td>0.165 - 0.154</td>
<td>vw</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Relative intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vs</td>
</tr>
<tr>
<td>s</td>
</tr>
<tr>
<td>m</td>
</tr>
<tr>
<td>w</td>
</tr>
<tr>
<td>vw</td>
</tr>
<tr>
<td>sh</td>
</tr>
</tbody>
</table>

Table 2.6 Interplanar spacings and peak intensities for AlPO₄-5 [16]
Figure 2.7 The 3 connected 4.6.12 2D net of AlPO₄-5
This confirms the early adsorption measurements to
determine the pore size. As can be seen, the main channels
are surrounded by alternating 4- and 6-ring channels with
parallel axes. Water molecules present in the
'as-synthesised' structure, between six and ten molecules,
are thought to reside in both these smaller channels and
the main channel [18].

The unit cell, contains twelve phosphorus and twelve
aluminium atoms, and has hexagonal symmetry with
$a=1.3724\text{nm}$, $c=0.8484\text{nm}$, and $\gamma=120^\circ$. It has the space group
symmetry $P6/mcc$ [4].

The unique topology of the AlPO$_4$-5 has been assigned
the IUPAC zeolite structure code (Section 1.2.1) AFI [4].
Other structures that are isotypic are the substituted
AlPO$_4$-5 molecular sieves (SAPO-5, MeAPO-5, EIAlPO-5).

The electroneutral framework resulting from the
alternating $[\text{AlO}_2]^-$ and $[\text{PO}_2]^-$ species means that the
quaternary ammonium cations (trapped in the framework
during synthesis) do not have any framework charge
balancing function. In the case of the tetrapropylammonium
ion with the hydroxyl counter-ion in AlPO$_4$-5, X-ray
diffraction shows that the cation is in a tripod
configuration with the OH$^-$ anion suspended between the three
feet of one tripod and the head of the next [17]. The van
der Waals length of the molecule in this conformation,
$0.84\text{nm}$, coincides well with unit cell length of
approximately $0.85\text{nm}$ along the c axis, the direction of the
channel system. Chemical analysis of AlPO$_4$-5 containing
TPA(OH) shows that there is one organic molecule per unit
cell [14], in agreement with the structure analysis. When other organic species are occluded in AlPO₄-5 the number of molecules per unit cell depends on the molecular size (Table 2.7). As a full structure determination has only been carried out on TPA(OH)-AlPO₄-5 the exact positions of these encapsulated species are unknown.

<table>
<thead>
<tr>
<th>organic species</th>
<th>No. of organic species per unit cell</th>
<th>No. of carbon and nitrogen atoms per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrapropylammonium cation</td>
<td>1.0</td>
<td>12</td>
</tr>
<tr>
<td>tripropylamine</td>
<td>1.0</td>
<td>9.1</td>
</tr>
<tr>
<td>tetraethylammonium cation</td>
<td>1.0</td>
<td>8.7</td>
</tr>
<tr>
<td>triethylamine</td>
<td>1.2</td>
<td>8.4</td>
</tr>
<tr>
<td>N-methyl piperidine</td>
<td>1.3</td>
<td>9.0</td>
</tr>
<tr>
<td>N,N-diethyl ethanolamine</td>
<td>1.3</td>
<td>9.2</td>
</tr>
<tr>
<td>2-methyl pyridine</td>
<td>1.3</td>
<td>9.9</td>
</tr>
<tr>
<td>1,4 diazabicyclo (2,2,2) octane (DABCO)</td>
<td>1.8</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 2.7 Packing of organic templates in AlPO₄-5 [14]

As described in Section 1.3.2, in addition to X-ray diffraction other non-destructive analytical techniques can be used to give further information on the environments of the framework elements.

Using X-ray photoelectron spectroscopy (XPS), Suib et al. [19] investigated the chemical states of aluminium and phosphorus in the AlPO₄-5 structure. The results showed that the aluminium chemical state strongly resembles that
found in the more aluminous zeolites such as X and A. Various phosphorus containing compounds were studied, and Na$_3$PO$_4$ was found to have phosphorus in a chemical state closest to that in AlPO$_4$-5.

$^{27}$Al and $^{31}$P NMR spectra [20,21,22] both display essentially one single resonance line, with shifts consistent with tetrahedral environments for both aluminium, Al(4P), and phosphorus, P(4Al). Similar results have been observed for other aluminophosphate molecular sieves (Section 1.3.2).

Goepper et al. [20] observed a shift in the peaks of the $^{31}$P and $^{27}$Al spectra upon template and water removal from AlPO$_4$-5. They attribute this to the direct influence of the encapsulated molecules on the aluminium and phosphorus environments, and/or the Al-O-P bond angles. They consider that the observed asymmetry in the peak shapes is due to the atoms not being in completely symmetrical environments, i.e. it has the same cause as the shift in peaks mentioned above, but in this case only a fraction of the tetrahedra are affected. Asymmetry to high field in the $^{27}$Al spectra has also been reported by Blackwell and Patton [21].

Hydrated AlPO$_4$-5 shows a resonance in the $^{27}$Al spectra at -12.7ppm (aluminium in an octahedral environment). The disappearance of this resonance upon dehydration indicates a reversible interaction between the framework aluminium and water producing an octahedral region chemical shift. This result is in agreement with the proposal of Blackwell and Patton [21] who disagree with other arguments that the
peak is due to extralattice aluminium [23].

The $^{31}$P spectra for both the 'as synthesised' and dehydrated structures show small shoulders. The shoulder in the 'as synthesised' spectrum is attributed to interactions with the organic molecules occluded in the micropores. In the case of the dehydrated sample, one of the two lines is attributed to P-OH defect sites. This has been deduced from the appearance of a single resonance using ($^1$H-$^{31}$P) cross-polarisation NMR techniques, which indicate phosphorus-proton interactions. $^1$H MASNMR produces a spectrum containing a single peak at 1.5ppm attributed to terminal hydroxyl groups [24].

The presence of hydroxyl groups is also observed using infrared spectroscopy. As mentioned earlier (Section 1.3.2), the main, though very weak, absorbances observed in the hydroxyl stretching region are at 3677cm$^{-1}$ and 3630cm$^{-1}$, attributed to $\nu$(P-OH) and $\nu$(Al-OH) respectively.

The interaction of benzene with these hydroxyl groups has also been investigated [25,26]. The results show a very slight shift to lower wavenumbers; this indicates that the benzene molecules are only very weakly adsorbed and hence the hydroxyl groups have no strong acidic properties. Adsorption of hydrogen gas produces bands at 4100cm$^{-1}$ and 4060cm$^{-1}$, attributed to H$_2$ complexed with hydroxyl groups [26].
2.2.3 Synthesis

The general procedure for the synthesis of AlPO$_4$-5 involves the hydrothermal crystallisation of a reactive aluminophosphate gel. The gel composition normally employed, in molar ratios, is

$$0.5-1.5R \quad 1.0Al_2O_3 \quad 1.0P_2O_5 \quad 40-50H_2O$$

where R is an organic amine.

The sources of aluminium and phosphorus have already been discussed (Section 1.3.3). Over twenty five different organic amines have been successfully used to crystallise the AlPO$_4$-5 structure [27]; some of these are shown in Figure 2.8. As the main AlPO$_4$-5 micropore system is essentially a cylinder of uniform cross-section, it would seem that the only steric constraint placed on the organic molecule is that its width is no greater than 0.8nm.

The use of different templates, as well as varying other reaction conditions, can affect the outcome of the reaction. The reaction times and temperatures to produce the AlPO$_4$-5 phase using various amines, as first observed by the Union Carbide workers, are shown in Table 2.8.

Table 2.9 illustrates the effect that occurs on altering the reaction temperature. As expected, the higher the temperature, the shorter the crystallisation time. Wilson [18] suggests that the framework collapse to a dense phase at 473K is due to the tripropylamine diffusing in and out of the channel system at a faster rate than at 423K, reducing the amine's stabilising effect on the framework. This is further substantiated by the structure being stable under identical conditions if TPA(OH), a larger molecule
Figure 2.8 Some structure directing agents used in the synthesis of AlPO₄-5 [14]
<table>
<thead>
<tr>
<th>structure directing agent</th>
<th>reaction time /hrs</th>
<th>reaction temp /K</th>
</tr>
</thead>
<tbody>
<tr>
<td>tripropylamine</td>
<td>70</td>
<td>423</td>
</tr>
<tr>
<td>tetrapropylammonium hydroxide</td>
<td>65</td>
<td>423</td>
</tr>
<tr>
<td>triethylamine</td>
<td>27</td>
<td>473</td>
</tr>
<tr>
<td>tetraethylammonium hydroxide</td>
<td>24</td>
<td>473</td>
</tr>
<tr>
<td>triethanolamine</td>
<td>72</td>
<td>423</td>
</tr>
<tr>
<td>piperidine</td>
<td>24</td>
<td>423</td>
</tr>
<tr>
<td>2-methyl pyridine</td>
<td>168</td>
<td>423</td>
</tr>
<tr>
<td>cyclohexylamine</td>
<td>168</td>
<td>423</td>
</tr>
<tr>
<td>N,N-diethyl benzylamine</td>
<td>168</td>
<td>423</td>
</tr>
<tr>
<td>N,N-dimethyl ethanolamine</td>
<td>24</td>
<td>473</td>
</tr>
<tr>
<td>dicyclohexylamine</td>
<td>24</td>
<td>423</td>
</tr>
<tr>
<td>N,N-dimethyl ethanolamine</td>
<td>24</td>
<td>423</td>
</tr>
<tr>
<td>N,N,N-trimethyl ethanolamine hydroxide</td>
<td>52</td>
<td>423</td>
</tr>
<tr>
<td>N,N-dimethyl piperazine</td>
<td>24</td>
<td>473</td>
</tr>
<tr>
<td>1,4-diazabicyclo (2,2,2) octane</td>
<td>192</td>
<td>473</td>
</tr>
<tr>
<td>N-methyl diethanolamine</td>
<td>24</td>
<td>473</td>
</tr>
<tr>
<td>N-methyl ethanolamine</td>
<td>24</td>
<td>473</td>
</tr>
<tr>
<td>N-methyl piperidine</td>
<td>24</td>
<td>473</td>
</tr>
<tr>
<td>3-methyl piperidine</td>
<td>168</td>
<td>423</td>
</tr>
<tr>
<td>N-methyl cyclohexylamine</td>
<td>24</td>
<td>473</td>
</tr>
<tr>
<td>3-methyl pyridine</td>
<td>24</td>
<td>423</td>
</tr>
<tr>
<td>4-methyl pyridine</td>
<td>168</td>
<td>423</td>
</tr>
</tbody>
</table>

Table 2.8 Reaction time and temperature for AlPO$_4$-5 synthesis gel composition 1.0R:Al$_2$O$_3$:P$_2$O$_5$:40H$_2$O using various structure directing agents [16]
<table>
<thead>
<tr>
<th>reaction temperature /K</th>
<th>reaction time /hrs</th>
<th>product phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>AlPO$_4$-5 (major)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>boehmite (minor)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>AlPO$_4$-5</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>AlPO$_4$-5</td>
</tr>
<tr>
<td>423</td>
<td>4</td>
<td>AlPO$_4$-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AlPO$_4$-tridymite (minor)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>AlPO$_4$-5 (major)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AlPO$_4$-tridymite</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>AlPO$_4$-cristobalite (major)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AlPO$_4$-tridymite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AlPO$_4$-5 (minor)</td>
</tr>
</tbody>
</table>

Table 2.9 Effect of temperature on crystallisation time in synthesis of AlPO$_4$-5 from gel composition PR$_3$N:Al$_2$O$_3$:P$_2$O$_5$·40H$_2$O [18]
<table>
<thead>
<tr>
<th>Structure directing agent</th>
<th>Reaction temperature /K</th>
<th>Reaction time /hrs</th>
<th>Product phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>tripropyl amine</td>
<td>373</td>
<td>168</td>
<td>AlPO$_4$-H3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>metavariscite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>variscite</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>24</td>
<td>AlPO$_4$-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AlPO$_4$-H3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>metavariscite</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>24</td>
<td>AlPO$_4$-5</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>24</td>
<td>AlPO$_4$-tridymite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AlPO$_4$-cristobalite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AlPO$_4$-5</td>
</tr>
<tr>
<td>tetrapropyl ammonium hydroxide</td>
<td>328</td>
<td>284</td>
<td>boehmite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>metavariscite</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>168</td>
<td>metavariscite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AlPO$_4$-H3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>variscite</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>24</td>
<td>AlPO$_4$-5</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>24</td>
<td>AlPO$_4$-5</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>24</td>
<td>AlPO$_4$-5</td>
</tr>
</tbody>
</table>

a  $\text{AlPO}_4\text{-H3} = \text{AlPO}_4\ 1.67\text{H}_2\text{O}$
metavariscite = $\text{AlPO}_4\ 2\text{H}_2\text{O}$
variscite = $\text{AlPO}_4\ 2\text{H}_2\text{O}$
boehmite = $\text{AlOOH}$

Table 2.10 Effect of structure directing agent and temperature on the crystallisation time of the aluminophosphate gel of composition $R:\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:4\text{O}_2\text{O}$ [18]

104
and hence having a slower diffusion rate, is used as the template (Table 2.10).

Table 2.10 also shows the necessity for temperatures to be greater than 373K before the AlPO₄-5 structure forms, unlike silica rich zeolite phases which can be synthesised at temperatures below 373K. The AlPO₄ phases produced at the lower temperatures all contain octahedral alumina, and the authors suggest that higher temperatures are needed for tetrahedral aluminium to crystallise from the acidic gel.

To determine the relationship between the concentration of the gel components and the formation of tetrahedral aluminium, Jahn and co-workers studied a system using $^{27}$Al MASNMR [28]. They observed that the addition of phosphoric acid to a suspension of Al(OH)$_3$ gave a tetrahedral aluminium species (40ppm shift) which converted to aluminium octahedrally coordinated to four phosphorus atoms and two water molecules (-15ppm shift) if no amine was added. The rate of conversion increased on increasing the P$_2$O$_5$/Al$_2$O$_3$ ratio. They suggest that conversion from tetrahedral to octahedral aluminium is caused by water molecules entering the aluminium sphere of coordination, and that this is prevented by the addition of the amine. This would explain why Wilson and co-workers obtained hydrate phases if low concentrations of amines were used, and also if the P$_2$O$_5$ content is increased, in effect lowering the amine concentration [18].

Hydrothermal crystallisation of gels that had been allowed to form significant amounts of the octahedrally coordinated aluminium species gave products containing the
AlPO₄-H₃ (AlPO₄ 1.67H₂O) phase, an aluminophosphate hydrate having a three-dimensional structure based on two kinds of sheets which contain tetrahedrally and octahedrally coordinated aluminium [29].

Jahn [28] found that the optimum gel preparation to obtain pure AlPO₄-5 was to use a composition of

$$2.5\text{Et}_3\text{N} \quad 1.0\text{Al}_2\text{O}_3 \quad 1.7\text{P}_2\text{O}_5 \quad 300\text{H}_2\text{O}$$

and to mix the amine with the phosphoric acid before adding the Al(OH)₃. The $^{27}\text{Al}$ spectrum of the solid phase of this mixture showed a strong resonance at 41.6ppm, indicating that the aluminium in the tetrahedral coordination was the most favoured.

If a gel is hydrothermally treated in the absence of an amine, dense phases such as berlinite (the AlPO₄ analogue of quartz), AlPO₄-tridymite, and AlPO₄-cristobalite are obtained [18,30], and thus it appears that organic bases are essential for the crystallisation of microporous aluminophosphates.

Figure 2.9 shows the crystallisation of AlPO₄-5 from a gel of initial composition

$$1.5\text{Pr}_3\text{N} \quad 1.0\text{Al}_2\text{O}_3 \quad 1.0\text{P}_2\text{O}_5 \quad 40\text{H}_2\text{O}$$

at 423K as observed by Choudhary et al. [31]. It can be seen that the crystallinity increases to a maximum at 24 hours, with a nucleation period of up to 4 hours. The phase transformation from AlPO₄-5 to dense AlPO₄ phases after 24 hours is inconsistent with Wilson's observations [18] that Pr₃N-AlPO₄-5 is stable in its mother liquor even after 120 hours at 423K. The degradation reported by Choudhary et al. could be a result of the way the gel was prepared; dense
Figure 2.9 Crystallisation of AlPO₄-5 from an aluminophosphate gel [31]

Running conditions
sample weight: 50mg in Pt crucible
sample reference: α-alumina
heating rate: 10K min⁻¹ in air

Figure 2.10 Thermal analysis of AlPO₄-5 [31]
phases were observed by Jahn et al. [28] in their investigations if the gel was not prepared in a certain way.

To obtain the open framework structure the occluded amine and water molecules are removed by calcination of the 'as synthesised' AlPO4-5 at temperatures between 773 to 873K for 12 to 18 hours. Figure 2.10 shows results for the thermal analysis in air of Pr3N-AlPO4-5 [31]. The first two endotherms are due to the diffusion from the framework of water and tripropylamine respectively, whilst the two exotherms correspond to oxidative degradation of the remaining amine.

2.2.4 Properties
2.2.4.1 Structural Stability

Workers at Union Carbide have reported the excellent thermal and hydrothermal stabilities of AlPO4-5, resisting loss of structure when heated to 1273K in air, and also when hydrothermally treated in 16% steam at 873K [17]. Choudhary et al. [32] subjected a sample of AlPO4-5 to temperatures in excess of 973K, and observed an 18% loss in the original crystallinity on reaching 1433K, with some phase transition to tridymite, though the crystals appeared to be morphologically stable. These results confirm Union Carbide's thermal stability claim.

The results they observed [32] for hydrothermal treatments, however, where not supportive of the Union Carbide results. Treatment of calcined AlPO4-5 with water vapour at 773K resulted in a 33% loss of the original
crystallinity after 48 hours, though no phase transitions were observed even after seven days treatment. High pressure steam treatment at 473K caused an almost complete phase transformation to tridymite, as did treatment with water at 473K under autogenous pressure.

The AlPO₄-5 structure is also unstable in extreme acidic and alkaline conditions [32,33]. Complete dissolution occurs at pH≤1 and ≥12.5 (HCl and NaOH concentrations ≥ 0.1mol dm⁻¹). Etching can be observed on the surface of crystals after treatment at pH 11.5 and pH 1.6. Treatment at pH 1.6 resulted in the hydrate aluminophosphate phase AlPO₄ 1.67H₂O, which contains octahedral aluminium [33]. This was observed using XRD and by comparing thermal analysis (DTA and TG) traces with prepared samples of the hydrate phase. Winiecki and Suib [33] suggest that dissolution occurs followed by recrystallisation, though the continual loss in crystallinity observed by Choudhary [32] suggests an interaction of polar species with the framework aluminium causing it to revert to octahedral coordination in these severe conditions, the Al-O and P-O bonds becoming weaker and leading to structural collapse.

2.2.4.2 Adsorption

The most interesting sorption property of AlPO₄-5 is that for water. As stated earlier (Section 1.3.4) the surface of the aluminophosphate is hydrophilic, despite the framework being electroneutral, and this has been attributed to the difference in electronegativities between
aluminium and phosphorus [14].

The structure has a pore volume capacity of 0.22-0.30 cm$^3$g$^{-1}$ for water, and 0.15-0.18 cm$^3$g$^{-1}$ for oxygen, the difference being due to the access of water through the 6-rings into the channels surrounding the main 12-ring channel.

The adsorption isotherm for water (Figure 2.11) is of Type V and is indicative of weak sorbent-sorbate interaction (Section 1.2.4). Lohse and co-workers [34] have connected this with Blackwell and Patton's observations [21] on the octahedral coordination of water with framework aluminium. In a personal communication to Lohse, Müller reported that a sample of AlPO$_4$-5 showed the same NMR characteristics as those of Blackwell's AlPO$_4$-17; this has also been observed by Goepper et al. [20]. This information, as well as the observation that the measured heat of adsorption is greater than that for condensation [34,35], led Lohse to postulate that a crystal hydrate is formed and that the process is not merely physisorption. This reversible hydration reaction also explains the large hysteresis loop observed.

The water sorption capabilities of AlPO$_4$-5 have been tested by drying organic liquids (Table 1.8), and removing water vapour from moist air [16].

The isotherms for permanent gases, e.g. oxygen, and hydrocarbons are of Type I [14,18,27,34,36]. Table 2.11 shows sorption data for various hydrocarbons. AlPO$_4$-5 displays molecular sieving properties by excluding molecules of kinetic diameter >0.8nm, the size of the 12
Figure 2.11 Adsorption isotherm for water on AlPO₄-5 at 298K

[34]
<table>
<thead>
<tr>
<th>absorbate</th>
<th>( \sigma /\text{nm} )</th>
<th>( T /\text{K} )</th>
<th>( P/P_0 )</th>
<th>max volume uptake ( \text{cm}^3/\text{g} )</th>
<th>time to equilibrate /hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>0.265</td>
<td>303</td>
<td>0.84</td>
<td>0.275</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>0.88</td>
<td>0.270</td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.43</td>
<td>303</td>
<td>0.88</td>
<td>0.134</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>0.92</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>0.585</td>
<td>303</td>
<td>0.87</td>
<td>0.150</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>0.93</td>
<td>0.150</td>
<td></td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.60</td>
<td>303</td>
<td>0.88</td>
<td>0.143</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>para-xylene</td>
<td>0.58</td>
<td>303</td>
<td>0.84</td>
<td>0.160</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meta-xylene</td>
<td>0.68</td>
<td>303</td>
<td>0.83</td>
<td>0.161</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>0.78</td>
<td>303</td>
<td>0.83</td>
<td>0.127</td>
<td>4</td>
</tr>
<tr>
<td>triethylamine</td>
<td>0.78</td>
<td>303</td>
<td>0.80</td>
<td>0.125</td>
<td>3</td>
</tr>
<tr>
<td>tripropylamine</td>
<td>0.79</td>
<td>303</td>
<td>0.80</td>
<td>0.008</td>
<td>( \geq 3 )</td>
</tr>
<tr>
<td>tributylamine</td>
<td>0.81</td>
<td>303</td>
<td>0.84</td>
<td>0.0001</td>
<td>( &gt;6 )</td>
</tr>
</tbody>
</table>

Table 2.11 Adsorption characteristics for AlPO₄⁻5 [34]

T-atom ring window. The sorption capacities for the sorbed molecules are comparable to that for oxygen. This indicates that there are no effects caused by strong specific interactions between the polar molecules and the AlPO₄⁻5 surface, or due to the configuration and/or molecular size of sorbates. The rate of uptake decreases with increasing molecular diameter (\( \sigma \)) as observed with zeolites (Section 1.2.4).

The heats of sorption of various hydrocarbons on AlPO₄⁻5 have been studied by both Choudhary et al. [36] and
Stach et al. [35]. Both groups observed that with n-hexane, cyclohexane, and benzene the heats varied with sorbate loading. This behaviour suggested that adsorption heats are influenced by the polar nature of the surface, and by molecular interactions. Similar behaviour is observed with the same sorbates on zeolite Y [35]. Stach et al. obtained $-\Delta H_0$ values (the heat of adsorption at zero coverage, found by extrapolation of a graph of the heat of adsorption against amount adsorbed) of between 58-60kJ mol$^{-1}$, and Choudhary et al. obtained slightly lower values between 53-55kJ mol$^{-1}$. With pyridine, Choudhary obtained $-\Delta H_0=89kJ$ mol$^{-1}$, and attributed the higher value to its dipole moment.

The changes in entropy upon sorption [36] suggest that the sorbed molecules are mobile, and that the mobility is dependent on the sorbate loading. Cyclohexane mobility increases with increased loading, however that for n-hexane and benzene decreases. The latter is attributed to a restriction in translational motion parallel to the surface.

2.2.4.3 Catalysis

The polar nature of the AlPO$_4$-5 surface and the presence of terminal hydroxyl groups imparts a mildly acidic nature to the structure, as shown by temperature programmed desorption of bases (Section 1.3.5).

From this, it would be expected that AlPO$_4$-5 would not be very catalytically active, and this has been shown to be the case, unless extreme conditions such as high
temperatures are employed. Table 1.12 shows how low the activity is in the cracking of n-butane compared to other, mostly substituted, aluminophosphates.

It has a low activity in the cracking of cumene \([25,37,38]\), 20% conversion being observed at 773K compared with 97.5% conversion for H-ZSM-5 under identical conditions \([25]\). Choudhary and Akolekar \([38]\) reported the deactivation of AlPO\(_4\)-5 during the reaction, and its subsequent regeneration on removal of the coke deposits by heating. The main 12 T-atom channel is large enough to allow the formation of coke precursors, as observed with SAPO-5 (Section 1.3.5). They also observed that there was virtually no activity in the cracking of n-hexane and iso-octane, which require stronger acid sites than in cumene cracking.

AlPO\(_4\)-5 has been reported to have very low activity in the isomerisation of ortho-xylene \([31,37,38]\).

The presence of weak acid sites has been used to explain why dimethyl ether is the major product in the conversion of methanol (Section 1.3.5). Tapp et al. \([39]\) observed only dimethyl ether, and Kikhtyanin et al. \([22]\) and Choudhary et al. \([38]\) observed the formation of a small amount of hydrocarbons at higher temperatures.

The use of AlPO\(_4\)-5 as a support for a metal catalyst could prove to be very useful with respect to its low catalytic activity, and the uniform channel size. In view of this, Czarnetski and van Hooff \([40]\) investigated the preparation of a nickel loaded AlPO\(_4\)-5. As is to be expected from its structure, they found that ion exchange procedures
were inadequate. Wet impregnation techniques using 1.0M solutions of Ni(NO$_3$)$_2$ or K$_2$[Ni(CN)$_4$] resulted in a 3wt% loading of nickel, but the pore volume was only reduced by 5% of its original value, indicating that the particles were located mainly on the surface of the crystallites. Chemical vapour deposition by subjecting AlPO$_4$-5 to a mixture of nickelocene, helium and hydrogen at 473K gave a loading of up to 10wt% of nickel, with a reduction in pore volume of up to 70%. No catalytic testing of the product was reported, however.

It would seem that unsubstituted AlPO$_4$-5 has little use as an industrial catalyst, however the use of the structure as a support for a metal catalyst could prove most interesting.

2.3 Aims of This Work

In the preceding pages, an attempt has been made to summarise the general properties of two new, novel molecular sieves, namely the zeolite EU-1 and the aluminophosphate AlPO$_4$-5. The aim of this work was to characterise further these two molecular sieves in the following manner.

The studies with EU-1 were a continuation of Henderson's work [41]. The aim was to synthesise fresh samples and subject them to a wide range of standard characterisation techniques, such as X-ray powder diffraction, thermal analysis, adsorption, X-ray fluorescence analysis, and scanning electron microscopy; to characterise the acid sites by pyridine desorption and
ion exchange; and to study their catalytic properties using butene isomerisation as a test reaction. The latter has been employed successfully by other workers to investigate the catalytic properties of solid acid catalysts (Section 7.1.1). In the present work it was planned to use it to establish links between the catalytic and structural properties of EU-1, and also to investigate the deactivation and subsequent regeneration of the zeolite.

The studies with $\text{AlPO}_4$-5 were carried out for a different purpose. As seen on the previous pages, $\text{AlPO}_4$-5 has virtually no catalytic activity. However, a new preparative procedure for this particular aluminophosphate molecular sieve developed at Edinburgh [42] resulted in a higher catalytic activity for the butene isomerisation reaction [43]. The aim of the present investigation was to determine the cause of the increased activity using the techniques mentioned above.
2.4 References

[1a] Casci J.L., Lowe B.M., Whittam T.V.,

[1b] Casci J.L., Lowe B.M., Whittam T.V.,
United States Patent 4593138

in Proc. 6th Int. Conf. Zeo., Eds. Olson D.,

[3] Briscoe N.A., Johnson D.W., Shannon M.D.,
Kokotailo G.T., McCusker L.B., Zeolites,
8, 74, (1988)

Structures (2nd Edition), Butterworths, (1987)

[5] Sumitani K., Sakai T., Yamamsaki Y., Onodera T.,


Zeo., (Zeolites for the 90’s: Recent Research
Reports), Eds. Jansen J.C., Moscou L.,


Zeolites, 5, 153, (1985)

[10] Pickett S.D., Nowak A.K., Thomas J.M.,


[42] Williams C.D., unpublished results
CHAPTER 3
Experimental Techniques

3.1 Introduction

This chapter describes the experimental techniques employed in the characterisation of the molecular sieves, both qualitatively and quantitatively. It also gives a description of the apparatus, the chemicals used, and the procedure, each section begins with a brief background to the technique. More detailed accounts can be found in standard texts.

It was mentioned in Section 1.1 how important it was to fully characterise samples that had been synthesised in order to verify their authenticity. In the case of the early synthetic work, many claims were unsubstantiated due to the lack of suitable analytical techniques.

3.2 X-Ray Powder Diffraction (XRD)

3.2.1 Introduction

The use of X-ray powder diffraction is probably the single most important tool in the identification of microcrystalline materials such as zeolites.

Monochromatic X-rays are directed from a suitable source at the sample, and are diffracted by the lattice planes in the crystals according to the Bragg equation
\[ n\lambda = 2d\sin \theta \] (3.1)

where

- \( n \) is the reflection order of the plane and is an integer,
- \( \lambda \) is the wavelength of the radiation,
- \( d \) is the interplanar spacing, and
- \( \theta \) is the angle of incidence of the radiation to the plane.

Each crystalline structure has its own set of lattice planes, and hence its own individual X-ray diffraction pattern.

For samples that contain no lattice planes, i.e. amorphous materials, broad diffuse peaks are observed as a result of the X-rays being diffracted from a continuous range of \( d \) values. An example of this is shown in Figure 3.1, and is a continuous scanning pattern for Cab-O-Sil M5 (BDH), an amorphous silica.

3.2.2 Experimental

The equipment used was a Philips semi-automatic X-ray powder diffractometer. The X-rays were produced from a PW1730/10 X-ray generator fitted with a copper fine focus X-ray tube, providing CuK\(_\alpha\) radiation of wavelength \( \lambda = 0.15418 \text{nm} \).

Samples were ground to a fine powder and packed into diffractometer slides. These slides were loaded into a PW1965/60 goniometer by a PW1170 automatic sample changer, and scanning was controlled by a PW1394 control unit.
Figure 3.1 X-ray powder diffraction pattern for amorphous silica (Cab-O-Sil M5, BDH)

range $2 \times 10^3$ counts s$^{-1}$
output went via a PW1390 single channel control unit to a PM8203 chart recorder.

Unless otherwise stated, the operating conditions used were:

- tube voltage: 40kV
- tube current: 30mA
- scanning angle: 40 to 4°20
- time constant: 2s
- range: $4 \times 10^3$ counts s$^{-1}$
- step angle: 1°20 min$^{-1}$
- chart speed: 1cm min$^{-1}$

Qualitative and quantitative analysis of samples can be carried out by calculating the crystallinity of the material relative to that of a standard sample, one which is very pure and highly crystalline, by use of the equation

$$\% \text{ crystallinity} = 100 \frac{I}{I_o} \quad (3.2)$$

where

- $I_o$ is the integral peak intensity of the standard sample, and
- $I$ is the integral peak intensity of the sample to be compared.

Assuming that the peaks are symmetrical, the integral peak intensity can be calculated from

$$I = wh \quad (3.3)$$

where

- $h$ is the peak height, and
- $w$ is the peak width at half the peak height.

Equation (3.2) only holds for samples run under the
same operating conditions. Correction factors must otherwise be applied.

In this work, this type of analysis was used to compare the crystallinities of samples from various synthesis series where the preparation procedure was varied, and also to monitor the progress of crystallisation reactions.

The values of $I_0$ for the two molecular sieves studied, EU-1 and AlPO$_4$-5, were calculated from the most intense peak of the most crystalline samples. Table 3.1 gives the standards used.

<table>
<thead>
<tr>
<th>molecular sieve$^a$</th>
<th>synthesis code</th>
<th>peak position $^b$/2$\theta$</th>
<th>intensity $I_0$ (peak area /mm$^2$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EU-1 BH3</td>
<td>20.55</td>
<td>781.6</td>
<td></td>
</tr>
<tr>
<td>AlPO$_4$-5 ET/1/180/42</td>
<td>22.40</td>
<td>816.0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ as synthesised samples  
$^b$ corrected to standard running conditions  

Table 3.1 $I_0$ values for standard molecular sieves

The calculated intensities are subject to errors. The errors are associated with the measurements in peak height and width, the packing of samples in the sample holder, and variations in the tube intensity. Comparison of diffraction patterns of the same sample obtained on different occasions, which was carried out for a number of samples, gave a maximum variation in intensity of ±6.5%, and was independent of the crystalline material used.
3.3 Thermal Analysis (TA)

3.3.1 Introduction

In thermal analysis, a sample is heated and the changes that occur over the chosen temperature range are observed.

In thermal gravimetric analysis (TGA), the change in weight of the sample is recorded as a function of temperature.

Differential thermal gravimetry (DTG) is similar to TGA except that the rate of weight loss, \( \frac{dw}{dt} \), is recorded, giving a series of peaks and troughs, such that the peak maximum occurs at the maximum rate of weight loss, and the faster the weight loss, the sharper the peak.

Differential thermal analysis (DTA) records the thermal events (endothermic or exothermic processes) which occur when a sample is heated. This is done by comparison with a thermally inert reference material. The two samples must be in near identical conditions, i.e. approximately the same weight, in similar containers, and placed symmetrically on thermocouples in the furnace. An endo- or exothermic process results in a difference in temperature between the sample and reference material which is measured by the thermocouples and output as a function of temperature. (This is equivalent to a plot against time for a linear heating rate). It should be noted that it is not only weight changes that result in DTA events. Phase transitions such as the \( \alpha-\beta \) transition in quartz can give rise to endothermic peaks.
3.3.2 Experimental

Two types of thermal analysis equipment were used in this work.

The main piece of apparatus used was a Stanton Redcroft TG770, which only performed thermal gravimetric analysis. Approximately 7mg of sample was placed in a platinum crucible and suspended from a microbalance. The sample was surrounded by a close fitting furnace and heated in a flowing atmosphere. The output was sent to a Kipp and Zonen BD9 twin channel chart recorder.

Unless otherwise stated, the running conditions for the apparatus were:

- heating rate: $10 \text{ K min}^{-1}$
- temp. range: ambient to 1173K
- gas flow: air at $6 \text{ cm}^3 \text{ min}^{-1}$
- chart speed: $2 \text{ mm min}^{-1}$
- weight loss: 20% full scale deflection

A Stanton Redcroft STA780 simultaneous thermal analyser was used to record TGA, DTA, and DTG. Approximately 10mg of sample in a platinum crucible was placed on the hangdown opposite the alumina reference sample. The samples were surrounded by a close fitting furnace and heated in a flowing atmosphere. The data were collected on a BBC B+ microcomputer and processed using software written by Dr. K.R. Franklin. The output was produced on a Linear Graphics A4M Plotmate flatbed graph plotter, and an Epson MX-80 F/T III printer.
Unless otherwise stated, the running conditions for the apparatus were:

- heating rate: $10 \text{K} \text{min}^{-1}$
- temp. range: 298K to 1173K
- gas flow: air at $10 \text{cm}^3 \text{min}^{-1}$
- weight loss: 50% full scale deflection

3.4 Scanning Electron Microscopy (SEM)

3.4.1 Introduction

Scanning electron microscopy enables the accurate size and morphology of crystallites to be determined.

A collimated, high energy electron beam is directed at the sample, and the image is built up from the intensity of the reflected electrons i.e. crevices will reflect fewer electrons than a flat plane and so produce darker areas. The resolution of the image can be increased by narrowing the electron beam and increasing the acceleration voltage. However, this results in a build up of electrons on the sample (‘charging’) if it is non-conducting. Coating the sample with a thin film of gold provides a conductive layer and so reduces the amount of charging. The gold layer further reduces the effect of charging by the release of secondary electrons were the electron beam strikes the surface.

3.4.2 Experimental

A Cambridge Instruments Stereoscan 90 was used to obtain the majority of scanning electron micrographs and a Stereoscan 250 was used for the remainder.
A very small amount of the sample was placed on a clean aluminium stub, and dispersed with a drop of Arklone (trichlorotrifluoroethane, ICI) which was allowed to evaporate away. The stub was then coated with a thin layer of gold before being placed in the vacuum chamber of the electron microscope. Gold plating of the samples, the initial setting up of the instrument, and the film processing was carried out by Mr. J. Findlay of the Faculty of Science SEM unit.

Magnifications of up to 20 000x were obtained.

3.5 X-Ray Fluorescence Analysis (XRF)

3.5.1 Introduction

X-ray fluorescence can be used to determine the elements present in a sample. Primary X-rays from a suitable source strike the specimen, which generates X-rays of wavelengths characteristic of the elements present. The primary X-rays knock out an electron from an inner electron, e.g. 1s (K), shell, which is replaced by an electron from an outer shell, e.g. 2p (L) or 3p (M), producing secondary X-rays. For example, the 2p-1s transition generates Kα X-rays. The wavelength of the secondary radiation is related to the element by the equation

\[ \frac{1}{\lambda} \propto z^2 \]  

(3.4)

where \( z \) is the atomic number of the element. The proportionality constant is dependant upon whether the radiation is from the K or L series. The secondary X-rays are collimated and picked up by the detector. The intensity
of the X-rays are proportional to the amount of the element in the sample.

3.5.2 Experimental

The samples were made into glass discs by fusing a known amount of the sample with 5 times by weight of Johnson Matthey lithium borate Spectroflux 105 in a furnace at 1473K. The molten mixture was pressed into a disc and allowed to cool slowly.

Elemental analysis of the glass disc was carried out by Dr. J.G. Fitton on a Philips PW1450 X-ray spectrometer. The results were supplied as % composition by weight of metal oxides, and these were then converted to molar ratios.

X-ray fluorescence analysis could only be used on the zeolite EU-1 samples. Due to the highly aluminous nature of the AlPO₄-5 samples, the glass discs fractured on cooling, and so were unsuitable.

3.6 Isomerisation Reaction

3.6.1 Introduction

Catalytic microreactors are widely used for the evaluation of catalyst performance. There are two basic types of system in use, those in which the reactant is passed once over the catalyst and then analysed, such as a flow reactor, and those in which the reactant is kept in constant contact with the catalyst and samples are periodically removed, such as the recirculating system used in this study.
3.6.2 Apparatus

The apparatus can be broken down into two basic units, the gas line where the reaction is carried out, and the gas chromatographic analysis unit.

The gas line (Figure 3.2) was made from Pyrex glass, and was sectioned off with Springham ground glass vacuum taps. These taps were sealed with Apiezon 'L' grease to maintain the vacuum.

The vacuum was obtained by two mercury diffusion pumps backed by Edwards rotary vacuum pumps; this combination could maintain a vacuum of approximately $133 \times 10^{-6} \text{Nm}^{-2}$. Contamination in the system was prevented by the use of cold traps sited between the diffusion pumps and the gas line. The vacuum was measured with a McLeod gauge, and a mercury manometer was used to measure gas pressures.

The reaction vessel consisted of a U shaped Pyrex glass vessel that contained a ground glass sinter bed to support the catalysts and allow free flow of the gas. The vessel was connected to the gas line by Quickfit ground glass ball joints, sealed with Apiezon 'T' grease. A close fitting silica furnace that surrounded the reaction vessel was used to heat the sample. The furnace was controlled by a Eurotherm temperature controller, and the exact temperature over the catalyst was measured with a Comark 5000 digital thermometer. Both made use of thermocouples inserted in a pocket in the reaction vessel just above the glass sinter.

The gas was pumped around the system by a type MB21E circulating pump from the Metal Bellows Company. The flow
Figure 3.2 Vacuum line used for catalysis reactions

1 reaction vessel
2 vacuum pumps
3 gas chromatograph
4 recirculating pump
5 cold traps
6 pressure gauge
7 gas inlet
8 McLeod pressure gauge
9 gas storage bulbs
rate was read from a flow meter incorporated in the line.

Samples were withdrawn via a three way tap in the recirculating part of the gas line to a Carle minivolume sampling valve. This valve contained a 0.2cm$^3$ sampling loop, and the configuration of the chambers within the valve allowed the loop to be loaded before being mixed with the carrier gas and sent to the gas chromatograph for analysis.

The gas chromatograph was a model F33 from Perkin Elmer. Separation of the sample into its components was achieved in the column, using nitrogen as the carrier gas. The separated sample was passed through an air/hydrogen flame ionisation detector to measure the quantity of each component. The gas chromatograph was run under the following conditions:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>4m of 0.32cm o.d. stainless steel loaded with bis-methoxy ethyl adipate (13.5%) and di-2-ethyl hexyl sebacate on 80/100 chromosorb P</td>
</tr>
<tr>
<td>Gas inlet</td>
<td>nitrogen 103kNm$^{-2}$ (carrier gas)</td>
</tr>
<tr>
<td>Pressures</td>
<td>hydrogen 117kNm$^{-2}$ (FID)</td>
</tr>
<tr>
<td></td>
<td>air 172kNm$^{-2}$ (FID)</td>
</tr>
<tr>
<td>Column T</td>
<td>ambient</td>
</tr>
</tbody>
</table>

The signals were amplified and sent to a Servoscribe RE511.20 potentiometric recorder linked in parallel with a Hewlett Packard 3373B integrator. The raw data were output by the integrator as peak areas in microvolt seconds. These were then used to calculate the composition of each sample (Section 7.1.2).
3.6.3 Experimental

A known amount of catalyst (0.04g of EU-1, 0.1g of AlPO₄-5) which had previously been pelleted and sieved to particle size range of 250-500μm, was put in the reaction vessel, the pellet size being such that the catalyst did not pass through the sinter bed. The sample was then heated at 723K for 18 hours either in air, by leaving the reaction vessel open to the atmosphere, or under vacuum, by attaching the reaction vessel to the gas line and slowly evacuating it. The samples heated in air were then attached to the gas line and heated under vacuum at 723K for a further hour.

After outgassing, the catalyst was allowed to cool to the reaction temperature, and the reaction vessel isolated. A known quantity of reactant, usually about 1.66×10⁻³mol, was introduced into the circulating system. Details of the gases used are given in Table 3.2. The recirculating pump was switched on and the flow rate adjusted to the required level, normally 0.7dm³/min⁻¹. The taps were opened to the reaction vessel to admit the reactant, and the timer was started simultaneously.

<table>
<thead>
<tr>
<th>gas</th>
<th>supplier</th>
<th>grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>but-1-ene</td>
<td>Matheson</td>
<td>CP</td>
</tr>
<tr>
<td>cis but-2-ene</td>
<td>Fluka</td>
<td>Puriss</td>
</tr>
<tr>
<td>trans but-2-ene</td>
<td>Matheson</td>
<td>CP</td>
</tr>
</tbody>
</table>

Table 3.2 Details of gases used in catalysis experiments

134
The reaction was monitored by periodically removing samples for analysis by gas chromatography, and was usually carried out over a period of 150 minutes.

After the experiment was completed, the reaction vessel was evacuated, the sample allowed to cool to room temperature, and kept under vacuum for 30 minutes to remove any weakly adsorbed products. The catalyst was kept for thermal analysis in order to determine the carbonaceous residue ('coke') content. The reaction vessel was cleaned, rinsed in distilled water, and dried for reuse.

In some experiments with EU-1, the catalyst sample underwent further catalytic investigation. If this was the case, then, after the experiment, the catalyst was kept in the reaction vessel and pretreated as required, e.g. heated in air or vacuum for a predetermined period of time, before being used for the next isomerisation reaction.

Any other variations in procedure are given with the related results.

3.7 Adsorption Measurements

3.7.1 Introduction

This section describes two ways in which the adsorption of gases by solids can be monitored. The first technique involves the use of a constant volume apparatus, in which the amount of gas adsorbed is measured as the change in the pressure in a fixed volume. The second technique involves the use of a microbalance, in which the amount of gas adsorbed is measured as a change in the sample weight.
3.7.2 Volumetric Measurements

3.7.2.1 Apparatus

The gas line (Figure 3.3) was made from Pyrex glass, and was sectioned off with Springham ground glass vacuum taps sealed with Apiezon 'L' grease to maintain the vacuum.

The adsorption part of the gas line was constructed with 2mm i.d. capillary glass tubing to reduce the internal volume. The adsorption vessel was made from fused silica and was permanently attached to the capillary tubing. A change in the volume of the system was achieved by filling or emptying the five bulbs of known internal volume with mercury from the reservoir. The internal volumes for each section are shown in Figure 3.3.

The vacuum was obtained with a mercury diffusion pump backed up by an Edwards rotary vacuum pump, a combination that could attain a vacuum of $133 \times 10^{-6} \text{Nm}^{-2}$. Contamination of the system was prevented by the use of a cold trap sited between the diffusion pump and the gas line. The vacuum in the system was measured with a McLeod gauge. Two mercury manometers were also incorporated, one to give a rough measure of the gas pressure in the handling section, and the other to obtain an accurate reading of the pressure in the adsorption section.

A close fitting silica furnace that surrounded the adsorption vessel was used to heat the sample. The temperature was regulated with a Eurotherm temperature controller, and the exact temperature of the adsorption vessel was measured with a Comark 5000 digital thermometer. Both made use of thermocouples taped to the outside of the
Figure 3.3 Vacuum line used for volumetric adsorption measurements

1 vacuum pumps
2 cold trap
3 McLeod pressure gauge
4 gas storage bulb
5 gas inlet
6 pressure gauge
7 capillary tubing
8 mercury/air displacement bulbs for pressure increase
9 adsorption vessel

measured volumes

- capillary line $12.13 \text{cm}^3$
- adsorption vessel $10.56 \text{cm}^3$
- bulb 1 $134.30 \text{cm}^3$
- bulb 2 $53.46 \text{cm}^3$
- bulb 3 $23.64 \text{cm}^3$
- bulb 4 $13.93 \text{cm}^3$
- bulb 5 $5.97 \text{cm}^3$
adsorption vessel.

3.7.2.2 Experimental

An accurately known amount of sample, about 0.5g, was put in the adsorption vessel, which was subsequently reattached by glassblowing to the gas line. The vessel was evacuated slowly and outgassed at 723K for 18 hours, after which period it was cooled to room temperature and isolated. A known amount (by pressure) of adsorbate, details of which are given in Table 3.3, was introduced into the adsorption section of the line up to the isolated vessel. The nitrogen adsorption measurements were conducted at liquid nitrogen temperature whereas the adsorption of the butenes was carried out at room temperature. The tap to the adsorption vessel was then opened to allow in the adsorbate, and when equilibrium had been established, the change in pressure was recorded. The volume of the adsorption system was reduced by raising the mercury level to the top of the next bulb and equilibrium was then re-established. This procedure was repeated for all five bulbs for adsorption. Desorption measurements were taken.
in the same way except that the bulbs were emptied to increase the adsorption volume.

Between each experiment, the sample was outgassed under vacuum at 723K. In the case of butene sorption, the treatment was preceded by heating the sample in an atmosphere of oxygen to ensure that strongly adsorbed molecules did not form any carbonaceous residues on heating.

3.7.3 Gravimetric Measurements

3.7.3.1 Apparatus

The apparatus consists of 3 sections, the gas handling line, the adsorption section, and the microbalance control and data collection unit.

The gas line (Figure 3.4) was made from Pyrex glass, and was sectioned off with Springham high vacuum greaseless taps. The vacuum was obtained with two mercury diffusion pumps each backed up by an Edwards rotary vacuum pump, the combination could attain a vacuum of $1.33 \times 10^{-6} \text{Nm}^{-2}$. Contamination of the system was prevented by the use of cold traps sited between the diffusion pumps and the gas line. The vacuum in the system was measured with a McLeod gauge, and gas pressures were measured with a mercury manometer.

The hydrocarbons to be studied, details of which are given in Table 3.4, were stored in isolated glass ampoules permanently attached to the gas line. Other gases could be admitted into the system by suitable connection of the source to a Quickfit ground glass joint on the gas line.
Figure 3.4 Vacuum line used for gravimetric adsorption measurements

1 adsorbate storage bulbs
2 adsorbate inlets
3 pressure gauge
4 McLeod pressure gauge
5 vacuum pumps
6 cold trap
7 Cahn balance
<table>
<thead>
<tr>
<th>chemical</th>
<th>supplier</th>
<th>grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>Fisons</td>
<td>AR</td>
</tr>
<tr>
<td>n-hexane</td>
<td>BDH</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>ortho-xylene</td>
<td>BDH</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>meta-xylene</td>
<td>BDH</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>para-xylene</td>
<td>BDH</td>
<td>&gt;99.5%</td>
</tr>
</tbody>
</table>

*Table 3.4 Organic chemicals used in gravimetric adsorption experiments*

The adsorption section consisted of a Pyrex vacuum vessel (Figure 3.5) obtained from Cahn Industries, which housed the microbalance, a Cahn RG Automatic Electrobalance. Silica glass 'bucket' containers to hold the sample and counter-balance were suspended from the arms of the microbalance with nichrome wire. The hangdown tubes were constructed mainly from Pyrex glass, with the section that contained the sample bucket constructed from silica glass. The sections of the hangdown tubes were joined to each other and to the microbalance housing with Quickfit ground glass joints sealed with Apiezon 'T' grease to maintain the vacuum.

One end of the vacuum bottle had a metal plate on which was mounted the interface between the Cahn Electrobalance and the control unit. The seal between this plate and the housing was obtained with an O-ring and Apiezon 'L' grease.

The sample was heated by use of a close fitting silica
Figure 3.5 Adsorption section used for gravimetric adsorption measurements
furnace from Stanton Redcroft, the temperature of which was controlled by a Stanton Redcroft Linear Temperature Variable Rate Programmer. The exact temperature of the sample was measured by a Comark 5000 digital thermometer with thermocouple which was inserted into a silica glass pocket in the silica glass hangdown tube in a position level with the sample bucket.

The Cahn Electrobalance works on the null balance principle. As the sample gains weight, a current is applied to a servomotor that restores the balance to its original position. The voltage resulting from the restoring current is directly proportional to the change in sample weight. This voltage is the output from the control unit, and was sent to a Servoscribe RE541.20 potentiometric recorder attached to the microbalance control unit.

3.7.3.2 Experimental

The balance was calibrated using standard weights in accordance with the manufacturer’s instructions.

Approximately 0.03g of the powdered molecular sieve was loaded into the sample bucket, and was very slowly evacuated. The sample was outgassed under vacuum for 18 hours at 723K and then allowed to cool to room temperature. The sample weight recorded at this temperature was taken as the initial weight.

Adsorption measurements were carried out by admitting successive doses of the adsorbate into the adsorption section, and recording the equilibrium pressure of the system as well as the equilibrium weight of the adsorbent.
plus adsorbate. Adsorption of the hydrocarbons was carried at room temperature.

Removal of the adsorbate between each experiment was achieved by evacuation of the adsorption system, followed by the heating of the sample at 723K for 1 hour in an atmosphere of pure oxygen. The sample was then outgassed under vacuum at this temperature for 18 hours.

3.8 Ultraviolet/Visible Absorption Spectroscopy

3.8.1 Introduction

When a molecule absorbs ultraviolet and visible radiation, transitions occur between electronic energy levels. The wavelength of absorption is a measure of the separation of the energy levels, and the energy \( E \ (\text{kJ mol}^{-1}) \) is related to the wavelength \( \lambda \ (\text{m}) \) by the equation

\[
E = \frac{hc}{\lambda} \quad (3.5)
\]

where

- \( h \) is Planck's constant \((6.626 \times 10^{-34} \text{Js})\),
- \( c \) is the velocity of light \((2.998 \times 10^8 \text{ms}^{-1})\), and
- \( N_A \) is Avogadro's number \((6.022 \times 10^{23} \text{mol}^{-1})\).

Ultraviolet radiation and visible radiation absorption occurs between 200-400nm and 400-800nm respectively.

The fraction of light absorbed is proportional to the number of molecules in the path of the beam, i.e. the concentration \( c \) of the solution in a cell of length \( l \), such that
where $I_0$ and $I$ are the intensities of the incident and transmitted light respectively, hence $\log(I_0/I)$ is the absorbance.

3.8.2 Experimental

The phosphorus content of some AlPO$_4$-5 samples was determined using a method based on Denigès' process [1]. The method involves the combination of phosphorus with ammonium molybdate to form ammonium phosphomolybdate $\left((\text{NH}_4\right)_3\text{PMo}_{12}\text{O}_{40}\left,$ a heteropolyanion that consists of a PO$_4$ unit sharing oxygen atoms with MoO$_6$ groups), which is subsequently reduced to molybdenum blue (MoO$_2$.2MoO$_3$) under conditions where the excess ammonium molybdate is not reduced.

The stock solutions were prepared as follows.

(1) *Phosphate:* about 0.2g of monopotassium phosphate (KH$_2$PO$_4$, BDH Analar) was weighed exactly, dissolved in distilled water and made up to 1000.00cm$^3$ in a volumetric flask.

(2) *Ammonium Molybdate:* 25.0g of ammonium molybdate $\left((\text{NH}_4\right)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O},\text{ BDH Analar}\right)$ was dissolved in 200cm$^3$ of distilled water at 333K and then allowed to cool. 280cm$^3$ of sulphuric acid (S.G. 1.84, BDH Analar) was slowly added to 450cm$^3$ of distilled water and also allowed to cool. The ammonium molybdate solution was added to the sulphuric acid solution slowly with constant agitation, allowed to cool, and made up to
1000.00 cm$^3$ in a volumetric flask.

(3) L-Ascorbic Acid: 19.6 g of l-ascorbic acid (Vitamin C, \( \text{CH}_2(\text{OH})-\text{CH(0)}-\text{CH(0)}-\text{C(OH)}=\text{C(OH)}-\text{C}=\text{O}, \) BDH Analar) was dissolved in 1000.00 cm$^3$ of 1.0 mol dm$^{-3}$ hydrochloric acid in a volumetric flask.

(4) AlPO$_4$-5 Solutions: about 4x10$^{-3}$ g of calcined dry AlPO$_4$-5 was weighed exactly, dissolved in 5 cm$^3$ of hydrochloric acid (S.G. 1.18, BDH Aristar) and made up to 50.00 cm$^3$ with distilled water in a volumetric flask.

All the solutions were stored in plastic bottles to reduce the possibility of contamination by silica from the glassware, the procedure is sensitive to silica concentrations in excess of 10$^{-2}$ mol dm$^{-3}$.

The standard phosphate solutions for the calibration graph were prepared as follows. 0.2 cm$^3$ of the stock phosphate solution was pipetted into a 10.00 cm$^3$ volumetric flask. To this was added 0.4 cm$^3$ and 0.05 cm$^3$ of the ammonium molybdate and ascorbic acid solutions respectively. The mixture was then made up to 10.00 cm$^3$ with distilled water. This was repeated to prepare a series of solutions containing 0 to 0.2 cm$^3$ of the stock phosphate solution, and gave a calibration range of phosphate concentrations from 0 to 2.9x10$^{-5}$ mol dm$^{-3}$.

The AlPO$_4$-5 test solutions were prepared in a similar manner, except that 0.25 cm$^3$ of each stock AlPO$_4$-5 was used. The unit cell of dry AlPO$_4$-5 is [AlPO$_4$]$_{12}$ [2], and has a molecular mass of 1463.40 g. The stock solutions therefore have an approximate phosphate concentration of
Hence the test solutions have an approximate phosphate concentration of

\[
\frac{4 \times 10^{-3} \times 12}{1463.40} \times \frac{1000}{50} = 6.6 \times 10^{-4} \text{ mol dm}^{-3}
\]

which is within the calibration range.

A calibration curve was constructed from the standard solutions on a Perkin Elmer 402 Ultraviolet-Visible Spectrophotometer. The solutions were put in quartz cells, and the absorbance measured against a reference solution which was the standard solution that did not contain phosphate anions. This was also used as the 'blank' solution to determine the baseline. The spectrum was scanned between 300 and 450nm. The concentration of phosphorus in the test AlPO$_4$-5 solutions were determined from the calibration plot.

The baseline was recorded after analysis of the standard solutions, and again after analysis of the test solutions. In both cases, the baseline had shifted by 0.5 absorbance units. This means that there is an error of not greater than ±2% in the absorbance of the test solutions.

3.9 Atomic Absorption Spectroscopy (AAS)

3.9.1 Introduction

When a ground state atom is irradiated by an energy source, energy of certain wavelengths are absorbed by the atom causing transitions to higher electronic, vibrational, and rotational energy levels, the wavelength of the
absorbed radiation being a measure of the energy level separation. An atom can have a number of these absorbances resulting in dark lines appearing in the irradiating spectrum, each element producing its own set of absorption bands.

In atomic absorption spectroscopy, a hollow-cathode lamp is used to emit the spectrum of the element to be analysed (the analyte). The beam from the lamp is passed through a flame into which a solution of the analyte has been introduced. The beam, now weakened by absorption by the element passes to a monochromator which isolates a single line of the analyte spectrum. A device such as a photocell is used to measure the intensity of the line.

Quantitative analysis can be carried out by construction of a calibration curve from measurements on solutions of known concentration.

3.9.2 Experimental

The aluminium content of some AlPO₄-5 samples was determined by the following procedure, carried out with the guidance of Dr. J. Farmer.

The stock AlPO₄-5 solutions were those prepared in Section 3.2.7.2, and so had an aluminium concentration of about 6.6x10⁻⁴ mol dm⁻³.

Standard aluminium solutions were prepared from a stock solution of 0.371 mol dm⁻³ aluminium nitrate in 0.5 mol dm⁻³ nitric acid (Al(NO₃)₃, BDH Spectrosol). 1.00 cm³ of this solution was added to 8.84 cm³ of hydrochloric acid (S.G. 1.18, BDH Aristar) and made up to 100.00 cm³ with
distilled water in a volumetric flask. The HCl was added to give a 1mol dm\(^{-3}\) concentration as was present in the stock AlPO\(_4\)-5 solutions. This was repeated for a series of solutions containing 0 to 1.0cm\(^3\) of the stock aluminium solution, and gave a calibration range of aluminium concentrations from 0 to 3.71x10\(^{-3}\)mol dm\(^{-3}\). The stock AlPO\(_4\)-5 solutions had concentrations within this calibration range, and so could be used without further dilution.

The analysis was carried out on a Pye Unicam SP9 Atomic Absorption Spectrophotometer. The solutions were fed into a nitrous oxide and acetylene flame which was irradiated with an aluminium source lamp. The intensity of absorption was measured at 309.3nm. The raw data was provided in digital form as the intensity of absorbance. The spectrophotometer was set up and run by Dr. Farmer.

The concentrations of the AlPO\(_4\)-5 test solutions were determined from the calibration plot.

The baseline was set using the standard solution that did not contain aluminium. This solution was further analysed between each standard and test solution so that any fluctuations in the baseline could be observed and hence used to reduce the consequent errors. The baseline deviation was no more than 1.5 absorbance units, resulting in a maximum error of ±4.5% in the absorbances for the test solutions.
3.10 pH Measurements

3.10.1 Introduction

pH measurements were used for three separate purposes in this work;

(i) for monitoring AlPO$_4$-5 synthesis;
(ii) for potentiometric titrations; and
(iii) for monitoring the degradation of the aluminophosphate molecular sieves.

The method described in this section is concerned solely with the measurements in (i), however the apparatus used for (ii) and (iii) was the same.

As mentioned in Section 2.1.3, the change in pH of the mother liquor is an indication of the crystallisation of a zeolite phase from the amorphous gel, and this method is a simple and rapid way of monitoring the reaction.

In the same way, the crystallisation of aluminophosphate molecular sieves can also be monitored. The gel has an initial pH of about 3, which rises to about 8.5 when crystallisation is complete. The rise in pH is due to the equimolar consumption of aluminium and phosphorus from the mother liquor into the framework [3].

3.10.2 Experimental

The pH measurements were taken with a Philips PW9422 pH meter. The pH electrode was an EIL combination electrode type 1180/200/UKP. As measurements were to be taken in acidic media, the electrode was standardised with pH=4.00 and pH=7.00 buffer solutions (tablets, BDH).

The AlPO$_4$-5 syntheses were carried out in static bombs.
The bombs were allowed to cool to room temperature after the appropriate reaction period had elapsed. The pH electrode was rinsed thoroughly in distilled water, and the excess water removed. The electrode was placed directly in the reaction vessel and left to stand for 10 minutes, after which time the reading had stabilised. The electrode was rinsed and dried between each reading. A plot of pH against reaction time for each synthesis series could then be produced.
3.11.1 References


3.11.2 Bibliography


Birks L.S., X-Ray Spectrochemical Analysis, Interscience, New York, (1959)
CHAPTER 4
Synthesis and Characterisation

4.1 Zeolite EU-1

4.1.1 Introduction

Three batches of EU-1 were used in this work, one provided by ICI, coded ICIEU1, the other two synthesised 'in house', coded BH2 and BH3.

This section deals with the preparation of BH2 and BH3, especially noting any differences in procedure, which might give the products different characteristics. To this end, the materials were characterised as completely as the available facilities would allow.

ICIEU1 was also subjected to characterisation. However, as the batch was supplied already hydrogen exchanged, the investigations were limited to this form.

The first attempt to synthesise EU-1 resulted in the formation of a crystalline product which gave an X-ray diffraction pattern similar to that for ZSM-5. The sample was coded BH1 and is discussed in further detail in Appendix 1.

4.1.2 Synthesis Procedure

Both BH2 and BH3 were synthesised from gels of the molar composition

\[ 10\text{Na}_2\text{O} \ 3\text{Al}_2\text{O}_3 \ 60\text{SiO}_2 \ 10\text{C}_{12}\text{H}_{30}\text{N}_2\text{Br}_{2/7} \ 3000\text{H}_2\text{O} \]

An initial gel of weight 400.00g was prepared as follows. 347.90g of distilled water was weighed out. 0.35g of aluminium, as aluminium wire (BDH, Analar), was cut up
finely and dissolved completely in a warm solution of 5.16g of sodium hydroxide (pellets, M&B) in an equal weight of the distilled water taken from that weighed earlier. 23.26g of silica (Cab-O-Sil M5, BDH) was weighed into a tared 1000cm$^3$ plastic bottle. To this was added the sodium aluminate solution, and a solution of 23.37g of hexamethonium bromide (C$_{12}$H$_{33}$N$_2$Br$_2$, Fluka, purum) in an equal weight of the original distilled water, along with the rinsings. The remainder of the distilled water was added, approximately 319g, and the contents of the bottle made up to a weight of 400.00g. This was mixed with a Braun Multiprac hand blender into a homogeneous paste.

The hydrothermal crystallisation was carried out at 433K and stirred at 300rpm in a 500cm$^3$ stainless steel autoclave built by Baskerville and Lindsay Ltd.

The gel composition and reaction conditions were the same as those used by Casci et al. for the construction of their Arrhenius plot for EU-1 [1]. From their results, the gel was expected to crystallise after 81.5 hours at 433K. Samples were removed from the autoclave at periodic intervals before this time, and studied with a Vickers model M41 Photoplan optical microscope. In the early samples, the amorphous silica was observed as opaque agglomerates. After 69 hours of reaction time, these agglomerates were no longer present, and so the reaction was stopped, and the crystallisation deemed to be complete.

When cool, the crystalline solid was separated from the mother liquor by filtration on a Buchner funnel, and the solid was washed with distilled water until the
washings were bromide free (silver nitrate test). The solid was then dried on filter paper in an oven at 383K.

The preparation of BH3 was similar except that a 1000 cm$^3$ capacity autoclave, also built by Baskerville and Lindsay Ltd., was used and so double the quantity of the initial gel was prepared. The reaction mixture had to be stirred at 200 rpm as, for mechanical reasons, it could not be stirred continuously at 300 rpm.

The large autoclave did not have sampling facilities, and so the reaction was stopped after 69 hours, the crystallisation period for BH2. No amorphous silica was observed by optical microscopy. Separation and after treatment was as for BH2.

Unless otherwise stated, samples of both BH2 and BH3 were calcined by heating in a furnace at 823K in air for 18 hours to give (Na,H)-EU-1.

Ion exchange of samples to make H-EU-1 was carried out by slurrying 1g of the zeolite in 10 cm$^3$ 1N hydrochloric acid (BDH, Aristar), in a sealed plastic bottle, which was rotated in a water bath at 298K for 2 hours. The exchanged solid was filtered, washed with distilled water until chloride free (silver nitrate test), and dried on filter paper in an oven at 383K.

4.1.3 Characterisation

4.1.3.1 X-Ray Diffraction

The X-ray diffraction patterns for the as synthesised and calcined BH2 and BH3 samples are given in Figures 4.1 and 4.2. The diffraction pattern for ICIEU1 is also shown.
Figure 4.1 X-ray diffraction patterns for as synthesised EU-1

a) \((Na, HEX) - EU-1\) (BH2)

b) \((Na, HEX) - EU-1\) (BH3)
Figure 4.2 X-ray diffraction patterns for calcined EU-1
<table>
<thead>
<tr>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity ( I/I_0 )</th>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity ( I/I_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.008</td>
<td>vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.112</td>
<td>m</td>
<td>1.112</td>
<td>vs</td>
</tr>
<tr>
<td>1.011</td>
<td>m</td>
<td>1.011</td>
<td>vs</td>
</tr>
<tr>
<td>0.977</td>
<td>sh</td>
<td></td>
<td>sh</td>
</tr>
<tr>
<td>0.766</td>
<td>vw</td>
<td>0.760</td>
<td>vw</td>
</tr>
<tr>
<td>0.684</td>
<td>vs</td>
<td>0.622</td>
<td>vs</td>
</tr>
<tr>
<td>0.575</td>
<td>vw</td>
<td>0.575</td>
<td>w</td>
</tr>
<tr>
<td>0.561</td>
<td>vVw</td>
<td>0.561</td>
<td>vVw</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.547</td>
<td>vVw</td>
</tr>
<tr>
<td>0.487</td>
<td>vw</td>
<td>0.487</td>
<td>vVw</td>
</tr>
<tr>
<td>0.466</td>
<td>m</td>
<td>0.462</td>
<td>s</td>
</tr>
<tr>
<td>0.432</td>
<td>vs</td>
<td>0.432</td>
<td>vs</td>
</tr>
<tr>
<td>0.420</td>
<td>T ( ^h )</td>
<td>0.416</td>
<td>T</td>
</tr>
<tr>
<td>0.401</td>
<td>m</td>
<td>0.399</td>
<td>s</td>
</tr>
<tr>
<td>0.390</td>
<td>T</td>
<td>0.383</td>
<td>T</td>
</tr>
<tr>
<td>0.383</td>
<td>m</td>
<td>0.380</td>
<td>m</td>
</tr>
<tr>
<td>0.371</td>
<td>m</td>
<td>0.371</td>
<td>m</td>
</tr>
<tr>
<td>0.365</td>
<td>vVw</td>
<td>0.363</td>
<td>vVw</td>
</tr>
<tr>
<td>0.343</td>
<td>w</td>
<td>0.343</td>
<td>w</td>
</tr>
<tr>
<td>0.336</td>
<td>w</td>
<td>0.334</td>
<td>m</td>
</tr>
<tr>
<td>0.327</td>
<td>m</td>
<td>0.327</td>
<td>vs</td>
</tr>
<tr>
<td>0.316</td>
<td>vVw</td>
<td>0.314</td>
<td>vVw</td>
</tr>
<tr>
<td>0.309</td>
<td>vVw</td>
<td>0.307</td>
<td>vVw</td>
</tr>
<tr>
<td>0.295</td>
<td>vVw</td>
<td>0.294</td>
<td>vVw</td>
</tr>
<tr>
<td>0.270</td>
<td>vVw</td>
<td>0.269</td>
<td>vVw</td>
</tr>
<tr>
<td>0.262</td>
<td>vVw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.257</td>
<td>vVw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.254</td>
<td>vVw</td>
<td>0.252</td>
<td>vVw</td>
</tr>
<tr>
<td>0.247</td>
<td>vVw</td>
<td>0.246</td>
<td>vVw</td>
</tr>
<tr>
<td>0.240</td>
<td>vVw</td>
<td>0.240</td>
<td>vVw</td>
</tr>
<tr>
<td>0.232</td>
<td>vVw</td>
<td>0.232</td>
<td>vVw</td>
</tr>
<tr>
<td>0.230</td>
<td>vVw</td>
<td>0.229</td>
<td>vVw</td>
</tr>
</tbody>
</table>

\( a \) relative intensity (%) 
\( b \) T is tridymite

vs 60-100
s 40-60
m 20-40
w 10-20
vVw <10
sh shoulder

Table 4.1 Interplanar spacings for the EU-1 sample BH2

158
<table>
<thead>
<tr>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity&lt;sup&gt;a&lt;/sup&gt;</th>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>as synthesised</td>
<td>calcined</td>
<td>as synthesised</td>
<td>calcined</td>
</tr>
<tr>
<td>2.055 vw</td>
<td>2.008 vw</td>
<td>1.112 m</td>
<td>1.105 vs</td>
</tr>
<tr>
<td>1.112 m</td>
<td>1.016 m</td>
<td>0.988 sh</td>
<td>0.977 sh</td>
</tr>
<tr>
<td>0.977 sh</td>
<td>0.769 vw</td>
<td>0.763 vw</td>
<td>0.686 w</td>
</tr>
<tr>
<td>0.763 vw</td>
<td>0.624 vw</td>
<td>0.622 vw</td>
<td>0.579 vw</td>
</tr>
<tr>
<td>0.622 vw</td>
<td>0.579 vw</td>
<td>0.561 vw</td>
<td>0.561 vw</td>
</tr>
<tr>
<td>0.561 vw</td>
<td>0.487 vw</td>
<td>0.487 vw</td>
<td>0.466 m</td>
</tr>
<tr>
<td>0.487 vw</td>
<td>0.466 m</td>
<td>0.461 s</td>
<td>0.432 vs</td>
</tr>
<tr>
<td>0.461 s</td>
<td>0.432 vs</td>
<td>0.401 m</td>
<td>0.399 s</td>
</tr>
<tr>
<td>0.401 m</td>
<td>0.399 s</td>
<td>0.371 w</td>
<td>0.379 m</td>
</tr>
<tr>
<td>0.371 w</td>
<td>0.379 m</td>
<td>0.365 vw</td>
<td>0.363 vw</td>
</tr>
<tr>
<td>0.365 vw</td>
<td>0.363 vw</td>
<td>0.343 w</td>
<td>0.341 m</td>
</tr>
<tr>
<td>0.343 w</td>
<td>0.341 m</td>
<td>0.336 m</td>
<td>0.333 m</td>
</tr>
<tr>
<td>0.336 m</td>
<td>0.333 m</td>
<td>0.328 s</td>
<td>0.327 vs</td>
</tr>
<tr>
<td>0.328 s</td>
<td>0.327 vs</td>
<td>0.315 vw</td>
<td>0.315 w</td>
</tr>
<tr>
<td>0.315 vw</td>
<td>0.315 w</td>
<td>0.309 vw</td>
<td>0.307 w</td>
</tr>
<tr>
<td>0.309 vw</td>
<td>0.307 w</td>
<td>0.295 vw</td>
<td>0.294 w</td>
</tr>
<tr>
<td>0.295 vw</td>
<td>0.294 w</td>
<td>0.270 vw</td>
<td>0.269 vw</td>
</tr>
<tr>
<td>0.270 vw</td>
<td>0.269 vw</td>
<td>0.262 vw</td>
<td>0.262 vw</td>
</tr>
<tr>
<td>0.262 vw</td>
<td>0.262 vw</td>
<td>0.257 vw</td>
<td>0.257 vw</td>
</tr>
<tr>
<td>0.257 vw</td>
<td>0.257 vw</td>
<td>0.254 vw</td>
<td>0.252 vw</td>
</tr>
<tr>
<td>0.254 vw</td>
<td>0.252 vw</td>
<td>0.247 vw</td>
<td>0.246 vw</td>
</tr>
<tr>
<td>0.247 vw</td>
<td>0.246 vw</td>
<td>0.240 vw</td>
<td>0.240 vw</td>
</tr>
<tr>
<td>0.240 vw</td>
<td>0.240 vw</td>
<td>0.235 vw</td>
<td>0.232 vw</td>
</tr>
<tr>
<td>0.235 vw</td>
<td>0.232 vw</td>
<td>0.232 vw</td>
<td>0.229 vw</td>
</tr>
<tr>
<td>0.232 vw</td>
<td>0.229 vw</td>
<td>0.230 vw</td>
<td>0.229 vw</td>
</tr>
</tbody>
</table>

<sup>a</sup> see Table 4.1

Table 4.2 Interplanar spacings for the EU-1 sample BH3
<table>
<thead>
<tr>
<th>Interplanar Spacing (d) /nm</th>
<th>Relative Peak Intensity ( I/I_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.008</td>
<td>vw</td>
</tr>
<tr>
<td>1.112</td>
<td>vs</td>
</tr>
<tr>
<td>1.011</td>
<td>vs</td>
</tr>
<tr>
<td>0.983</td>
<td>sh</td>
</tr>
<tr>
<td>0.763</td>
<td>w</td>
</tr>
<tr>
<td>0.684</td>
<td>w</td>
</tr>
<tr>
<td>0.622</td>
<td>vw</td>
</tr>
<tr>
<td>0.575</td>
<td>w</td>
</tr>
<tr>
<td>0.561</td>
<td>vw</td>
</tr>
<tr>
<td>0.550</td>
<td>vw</td>
</tr>
<tr>
<td>0.507</td>
<td>vw</td>
</tr>
<tr>
<td>0.487</td>
<td>vw</td>
</tr>
<tr>
<td>0.462</td>
<td>s</td>
</tr>
<tr>
<td>0.432</td>
<td>vs</td>
</tr>
<tr>
<td>0.399</td>
<td>s</td>
</tr>
<tr>
<td>0.379</td>
<td>m</td>
</tr>
<tr>
<td>0.371</td>
<td>m</td>
</tr>
<tr>
<td>0.363</td>
<td>vw</td>
</tr>
<tr>
<td>0.342</td>
<td>w</td>
</tr>
<tr>
<td>0.334</td>
<td>m</td>
</tr>
<tr>
<td>0.327</td>
<td>vs</td>
</tr>
<tr>
<td>0.315</td>
<td>w</td>
</tr>
<tr>
<td>0.308</td>
<td>w</td>
</tr>
<tr>
<td>0.294</td>
<td>w</td>
</tr>
<tr>
<td>0.289</td>
<td>vw</td>
</tr>
<tr>
<td>0.270</td>
<td>vw</td>
</tr>
<tr>
<td>0.261</td>
<td>vw</td>
</tr>
<tr>
<td>0.258</td>
<td>vw</td>
</tr>
<tr>
<td>0.252</td>
<td>vw</td>
</tr>
<tr>
<td>0.246</td>
<td>vw</td>
</tr>
<tr>
<td>0.240</td>
<td>vw</td>
</tr>
<tr>
<td>0.232</td>
<td>vw</td>
</tr>
<tr>
<td>0.229</td>
<td>vw</td>
</tr>
</tbody>
</table>

*See Table 4.1

Table 4.3 Interplanar spacings for the H-EU-1 sample ICIEU1
The interplanar (d) spacings (Tables 4.1, 4.2, and 4.3) agree with the literature values very well (Section 2.1.2), whilst the intensities for the calcined samples gave better agreement with the literature values than do those of the as synthesised materials.

It can be seen that a small amount of a second phase is present in the BH2 sample; this was determined to be tridymite, a dense phase of silica. This indicates that the reaction has to some extent 'overrun', i.e. the metastable phase EU-i formed and then began to recrystallise. Casci reported that an increase in stirring rate decreased the crystallisation period, especially in the 200-300rpm range [1]. This could explain why BH3 did not overrun even though the same crystallisation period and reaction temperature were used.

Comparison of the calcined with the uncalcined samples (Figure 4.1 and 4.2) shows an increase in intensity for the low angle peaks relative to those at higher angles upon removal of the occluded organic material. This was also observed by Casci et al. [1]. It can also be seen that the peak at d=0.432nm, which is used to compare relative sample crystallinity, also decreases on calcination. From Table 4.4, it can be seen that the intensity of this peak for both BH2 and BH3 decreases by approximately the same amount, 27% and 29% respectively, for the calcined sample relative to its as made form. It would, therefore seem to be a function of template removal rather than a collapse of the structure. Similar variations in peak intensities have been observed upon calcination of other molecular sieves.
<table>
<thead>
<tr>
<th>sample</th>
<th>relative intensities of peak at d=0.432nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na,HEX)-EU-1 (BH2)</td>
<td>77</td>
</tr>
<tr>
<td>(Na,H)-EU-1 (BH2)</td>
<td>56</td>
</tr>
<tr>
<td>(Na,HEX)-EU-1 (BH3)</td>
<td>100</td>
</tr>
<tr>
<td>(Na,H)-EU-1 (BH3)</td>
<td>71</td>
</tr>
<tr>
<td>H-EU-1 (ICIEU1)</td>
<td>68</td>
</tr>
</tbody>
</table>

Table 4.4 Relative peak intensities for different samples of EU-1

4.1.3.2 Thermal Analysis

The thermal analysis traces of BH2 and BH3 are shown in Figures 4.3 to 4.6, and further information is given in Tables 4.5 and 4.6.

The traces of the uncalcined material are similar to that observed by Casci et al. [1]. Low temperature weight losses are due to loss of water located on the external surfaces of the crystallites, and in the pores where the process is not impeded by the organic molecule. The main weight loss starts at around 493K in both cases, and is over by 873K for BH2 and 838K for BH3. This is due mainly to the oxidative degradation of the hexamethonium cation, indicated by the exotherms in the DTA, and the release of any trapped water. The %w/w weight losses obtained from the TGA are similar to those observed by Casci, and are indicative of the space filling role of the occluded molecules [1].
Figure 4.3 Thermal analysis of (Na,HEX)-EU-1 (BH2)
Figure 4.4 Thermal analysis of (Na,H)-EU-1 (BH2)
Figure 4.5 Thermal analysis of (Na,HEX)-EU-1 (BH3)
Figure 4.6 Thermal analysis of (Na,H)-EU-1 (BH3)
The DTA indicates that the occluded organic species degrades in four stages for BH2, and three stages for BH3 (although the TGA shows four weight losses, suggesting that the associated DTA peak was probably very small and obscured). This splitting of peaks has been observed in the TPA-ZSM-5 system and attributed to the tetrapropylammonium cation being associated with framework aluminium sites or
broken siloxane bonds, and hence the decomposition processes occur at different temperatures [2,3]. However Franklin and Lowe have reported that the peak splitting observed in the TPA-silicalite-1 system, can be due to oxygen starvation, the splitting of peaks being greater for large sample sizes and faster heating rates [4]. In the present case it seems most likely that the peaks represent separate decomposition processes, possibly associated with different environments for the hexamethonium cation.

The calcined samples, which had been allowed to equilibrate under identical conditions, both showed losses associated with water only (Table 4.6). In the previous section, it was reported that the X-ray powder diffraction pattern for the sample BH2 contained a peak associated with the dense phase tridymite. It can be seen from Table 4.6 that the water content for calcined BH2 is higher than that for calcined BH3, an indication that there is only a trace amount of the dense phase present.

4.1.3.3 X-Ray Fluorescence Analysis

From Table 4.7, the unit cell of the dry, calcined samples of BH2 and BH3 can be calculated as

\[ \text{BH2: } \text{Na}_{0.89} \text{H}_{4.06} \left( \text{Si}_{107.05} \text{Al}_{4.95} \right) \text{O}_{224} \]

\[ \text{BH3: } \text{Na}_{2.84} \text{H}_{2.06} \left( \text{Si}_{107.10} \text{Al}_{4.90} \right) \text{O}_{224} \]

assuming no extraframework silicon or aluminium species are present, and that the amount of the dense phase material tridymite in the sample BH2 was negligible (Sections 4.1.3.2 and 4.1.3.4). The two samples have approximately the same SiO$_2$/Al$_2$O$_3$ ratio, however the sodium
Table 4.7 X-ray fluorescence analysis of samples of EU-1 before and after ion exchange with 1M HCl

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Al</th>
<th>No. of Si atoms uc⁻¹</th>
<th>No. of Al atoms uc⁻¹</th>
<th>No. of Na atoms uc⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na,H)-EU-1 (BH2)</td>
<td>21.61</td>
<td>107.05</td>
<td>4.95</td>
<td>0.89</td>
</tr>
<tr>
<td>H-EU-1 (BH2)</td>
<td>21.74</td>
<td>107.07</td>
<td>4.93</td>
<td>0.24</td>
</tr>
<tr>
<td>(Na,H)-EU-1 (BH3)</td>
<td>21.88</td>
<td>107.10</td>
<td>4.90</td>
<td>2.84</td>
</tr>
<tr>
<td>H-EU-1 (BH3)</td>
<td>22.77</td>
<td>107.29</td>
<td>4.71</td>
<td>0.25</td>
</tr>
<tr>
<td>H-EU-1 (ICIEU1)</td>
<td>17.60</td>
<td>105.99</td>
<td>6.01</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The drop in sodium content after ion exchange indicates that this treatment is successful. Comparison of the SiO₂/Al₂O₃ ratios for the calcined and ion exchanged samples shows the resistance to attack from mineral acids that the framework possesses, typical of high silica zeolites.

In the previous section, it was shown that the amount of organic material in the framework was approximately the same for the two samples. From the above unit cell compositions, and the thermal analysis results, the number of molecules of hexamethonium per unit cell for BH2 and BH3 are 4.59 and 5.49 respectively. The associated excess charge of +5.12uc⁻¹ and +8.92uc⁻¹ must be balanced by hydroxyl anions or broken siloxane bonds. An excess of cations is found with most high silica zeolites. Casci [1] observed that the ratio (SiO₂+Al₂O₃)/(Na₂O+HEXO) for samples...
of EU-I was constant at around 22.24, and concluded that the cation content was determined by the available void space within the framework. In this work, a value of 21.8 was obtained for the sample BH2, in good agreement with Casci. However, a value of 15.85 was obtained for BH3, indicating that for this material there was either a difference in the packing of the cations, or that there were extra present in another location, e.g. the external surface of the crystallites.

4.1.3.4 Scanning Electron Microscopy

The BH3 and ICIEU1 batches crystallised in the ellipsoidal habit typical of EU-I (Plate 4.1). The range of crystallite dimensions for BH3 and ICIEU1 are (<0.5-4µm) x (<0.5-1.5µm) and (<0.5-9µm) x (<0.5-3µm) respectively. In contrast BH2 consists of very small crystallites of <0.5µm (Plate 4.1).

BH2 was synthesised at a faster stirring rate than BH3 which would explain the difference in crystal size. It must also be noted that no tridymite crystals were observed in the SEM of BH2, again indicating that there was only a trace amount of this dense phase material present in the sample.

4.1.3.5 Nitrogen Adsorption

The isotherms for the uptake of nitrogen (Figures 4.7 and 4.8) are of Type I, typical for microporous solids. The saturated pore volumes (Table 4.8), calculated from the Langmuir equation, are in good agreement with each other,
Plate 4.1 Scanning electron micrographs of EU-1
Figure 4.7 Adsorption of nitrogen on calcined EU-1

Volume $N_2$ adsorbed (STP) / $10^{-4}$ m$^3$ g$^{-1}$

$P/P_0$

- $\diamond$ H-EU-1 (ICIEU1)
- $\square$ (Na, H) -EU-1 (BH2)
- $\triangle$ (Na, H) -EU-1 (BH3)
Figure 4.8 Comparison of adsorption of nitrogen on calcined and $H^+$ ion exchanged EU-1 (BH3)
and fall within the range reported for other microporous molecular sieves [5]. The values are slightly higher than that of \( \frac{14 \text{cm}^3}{\text{g}} \) obtained by Casci, using n-hexane [6], which could be indicative of a more efficient packing of nitrogen within the void space.

The pore volume of BH3 is unaffected by ion exchange (Figure 4.8, Table 4.8), a further indication of the resistance of the framework to attack by mineral acid.

There is some variation in the values for \( B \), the Langmuir constant, between the samples. As \( B \) decreases, a greater pressure is required to give the same surface coverage, thus the value of \( B \) can be regarded as a relative measure of the attraction between adsorbate and adsorbent. From Table 4.8, the attractive forces decrease in the order

\[
\text{ICIEU1} > \text{Na,H-BH3} > \text{Na,H-BH2} > \text{H-BH3}
\]

A decrease in the Si/Al ratio can increase the surface attraction forces (Section 1.2.4). This could explain why ICIEU1 has a larger value for \( B \) than the other samples, the latter having similar Si/Al ratios. The values of \( B \) for

\[
\begin{array}{|c|c|c|c|}
\hline
\text{sample} & \text{maximum weight uptake} & \text{pore volume} & 10^3B \\
& \text{10/g} & \text{10/cm}^3 \text{g}^{-1} & \text{/m}^2 \text{N}^{-1} \\
\hline
\text{H-EU-1 (ICIEU1)} & 1.36\pm0.01 & 1.68\pm0.01 & 12.0\pm0.6 \\
\text{(Na,H)-EU-1 (BH2)} & 1.21\pm0.01 & 1.50\pm0.01 & 5.39\pm0.04 \\
\text{(Na,H)-EU-1 (BH3)} & 1.29\pm0.01 & 1.60\pm0.01 & 7.42\pm0.05 \\
\text{H-EU-1 (BH3)} & 1.27\pm0.01 & 1.56\pm0.01 & 2.97\pm0.02 \\
\hline
\end{array}
\]

Table 4.8 Nitrogen adsorption by samples of EU-1
these three samples decrease as the sodium content decreases (Table 4.7), and hence it seems that the sodium cations have a greater influence on the adsorbate/adsorbent attractions than the protons that replace them.

4.2 Aluminophosphate AlPO$_4$-5

4.2.1 Introduction

Attempts to synthesise a pure AlPO$_4$-5 phase following the procedures given in the patent literature were unsuccessful [7]. However, it was found that an increase in organic reagent concentration gave good products. Further investigations revealed that a pure AlPO$_4$-5 phase could also be obtained from an initial gel which contained two different organic reagents, and went through an aging process.

The catalytic activity of the different preparations was compared, and it was found that the samples produced from the dual template synthesis were more active than expected [8]. Further information on this work is given in Section 7.3.

This section deals with the synthesis and characterisation of various samples of AlPO$_4$-5 which were prepared to investigate the relationship between synthesis procedure, physico-chemical properties, and catalytic activity. They were prepared with various templates, and aging times, and had varying degrees of crystallinity, as obtained from the synthesis series. The products ranged from 'nucleation precursors' to aluminophosphate dense
phases.

4.2.2.1 Synthesis Procedure (AlPO\textsubscript{4}-5)

All of the dual template samples were synthesised from an initial gel of molar composition

\[ R \quad TPABr \quad P_2O_5 \quad Al_2O_3 \quad 40H_2O \]

where R is either triethylamine (Et\textsubscript{3}N) or tripropylamine (Pr\textsubscript{3}N), and TPABr is tetrapropylammonium bromide.

The gel was prepared from instructions provided by Dr. C.D. Williams. 46.1g of orthophosphoric acid (85% w/w, BDH Analar) was added to 118.6g of distilled water. To this was added 28.6g of pseudoboehmite (Kaiser alumina, ICI). The mixture was stirred to a homogeneous paste with a Braun Multiprac hand blender, into which 53.3g of TPABr (Fluka, purum) was thoroughly stirred. This mixture was allowed to age at room temperature for a predetermined time. After this period, either 20.2g of Et\textsubscript{3}N (Fluka, puriss) or 28.7g of Pr\textsubscript{3}N (Fluka, purum) was thoroughly stirred in.

The hydrothermal crystallisation was carried out statically in pressure vessels. These vessels were manufactured 'in house' and consisted of a steel casing with a removable polytetrafluoroethylene (PTFE) lining. The steel cap, which contained a PTFE seal, was screwed securely to the main body. A hole drilled through the cap to the PTFE seal acted as a safety device. The bombs had a total capacity of about 20cm\textsuperscript{3}. To allow for the expansion of the reaction mixture on heating, the reaction vessels were never filled more than two thirds full.

The bombs were charged with gel and placed in an oven...
at either 423K or 453K. The reaction was stopped by cooling the reaction vessel to room temperature, and the progress of crystallisation was monitored by measuring the pH of the cold gel (Section 3.2.9).

Three series were synthesised (abridged code ET/a/T/t). They were prepared from an initial gel in which the first stage was allowed to age for 24 hours, and the second organic reagent added was triethylamine. The samples from each series were prepared in individual reaction vessels.

Series 1 was crystallised at 453K. Six samples were removed at reaction times from 1 hour to 42 hours. The samples from this series were coded ET/1/180/t, where E and T represent Et$_3$N and TPABr respectively, 1 represents the aging time of 1 day, 180 is the temperature of the reaction in °C, and t is the reaction time in hours.

Series 2 was carried out at 423K. Nine samples were removed at reaction times from 1 hour to 7 hours. The samples were coded ET/1/150-1/t where 150-1 represents the first series at 150°C.

Series 3 was also carried out at 423K. Five samples were removed at reaction times from 1 hour to 2 hours. The samples from this series were coded ET/1/150-2/t.

In all cases, the solid phase was separated from the mother liquor by centrifuging, and washed four times by suspension of the solid in distilled water followed by centrifuging. The solids were dried at 383K.

Further samples were supplied by Dr. C.D. Williams. These were as follows.
A series in which the first stage of the gel was allowed to age for varying periods of time (0, 1, 2, 4, and 10 days) and the second organic reagent added was triethylamine. The reactions were carried out at 423K for 24 hours in static bombs. The samples were coded ET/a, where a is the aging time in days.

(2) A series similar to (1) except that the second organic reagent added was tripropylamine. The samples were coded PT/a.

(3) A batch was made from the gel of molar composition

\[ 2\text{Et}_3\text{N} \quad \text{P}_2\text{O}_5 \quad \text{Al}_2\text{O}_3 \quad 40\text{H}_2\text{O} \]

All of the Et\(_3\)N was added at once instead of the TPABr, and no aging was involved. The reaction was carried out as in (1). The batch was coded 2E/0 where 2E represents 2 moles of Et\(_3\)N.

(4) A batch similar to (3) except Pr\(_3\)N replaced Et\(_3\)N. The sample was coded 2P/0.

Unless otherwise stated, the samples were heated when needed in a furnace at 823K in air for eighteen hours to remove the organic material.

4.2.2.2 Synthesis Procedure (Dense Phases)

The hydrothermal crystallisation of a gel of molar composition

\[ \text{P}_2\text{O}_5 \quad \text{Al}_2\text{O}_3 \quad 40\text{H}_2\text{O} \]

is known to produce AlPO\(_4\) dense phases [9].

The gel was prepared following the procedure given in the previous section, up to the addition of the first organic reagent. The crystallisation reaction was carried
out in a PTFE lined acid digestion bomb (Parr, model 4749).

The first batch was synthesised at 423K for five days, and was coded DP1.

The second batch was divided between two bombs and placed in an oven at 458K. One of the bombs, DP2, was periodically removed from the oven, cooled, and the contents studied with a Vickers model M41 optical microscope. After 10 days, no further visible change was observed, and so the reaction in the other bomb, DP3, was stopped.

The final batch was also synthesised at 458K, this time for 24 days, and was coded DP4.

In all cases, the solid was separated from the mother liquor by filtration, washed four times, and dried.

4.2.3 Characterisation

4.2.3.1 X-Ray Diffraction

4.2.3.1.1 Aluminophosphate AlPO₄-5

The X-ray powder diffraction patterns for an as synthesised and a calcined sample of AlPO₄-5 are shown in Figure 4.9. The peak positions and intensities (Table 4.9) are in very good agreement with those given in the literature (Table 2.6).

It can be seen that there is a change in certain peak intensities and a shift in some of the positions upon removal of the occluded organic material, as occurs with zeolites. The most notable change is the reversal in intensity of the two lines corresponding to interplanar spacings of 0.689nm (2θ=12.85) and 0.595nm (2θ=14.90).
Figure 4.9 X-ray diffraction patterns for AlPO₄-5

(ET/1/180/42)
Table 4.9 Interplanar spacings for AlPO₄-5 (ET/1/180/42)

The formation of the crystalline material from the amorphous gel can be followed in Figure 4.10. Initially, there is a reduction in intensity of the peaks due to the pseudoboehmite, which is accompanied by the appearance of a very broad, low intensity hump from 2θ=19-35 (d=0.467-0.256nm). Upon calcination of ET/1/150-2/1, the lines due to the pseudoboehmite collapse, but the broad hump remains. Interestingly, deviations from the baseline

<table>
<thead>
<tr>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity a (I/I₀)</th>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.195</td>
<td>vs</td>
<td>1.195</td>
<td>vs</td>
</tr>
<tr>
<td>0.689</td>
<td>w</td>
<td>0.686</td>
<td>m</td>
</tr>
<tr>
<td>0.595</td>
<td>w</td>
<td>0.595</td>
<td>vw</td>
</tr>
<tr>
<td>0.450</td>
<td>s</td>
<td>0.450</td>
<td>s</td>
</tr>
<tr>
<td>0.426</td>
<td>vs</td>
<td>0.422</td>
<td>s</td>
</tr>
<tr>
<td>0.397</td>
<td>vw</td>
<td>0.397</td>
<td>vs</td>
</tr>
<tr>
<td>0.362</td>
<td>m</td>
<td>0.358</td>
<td>w</td>
</tr>
<tr>
<td>0.342</td>
<td>m</td>
<td>0.343</td>
<td>s</td>
</tr>
<tr>
<td>0.308</td>
<td>w</td>
<td>0.307</td>
<td>w</td>
</tr>
<tr>
<td>0.296</td>
<td>w</td>
<td>0.298</td>
<td>m</td>
</tr>
<tr>
<td>0.267</td>
<td>vw</td>
<td>0.266</td>
<td>w</td>
</tr>
<tr>
<td>0.259</td>
<td>w</td>
<td>0.259</td>
<td>m</td>
</tr>
<tr>
<td>0.243</td>
<td>vw</td>
<td>0.243</td>
<td>vw</td>
</tr>
<tr>
<td>0.240</td>
<td>w</td>
<td>0.238</td>
<td>w</td>
</tr>
</tbody>
</table>

a relative intensity (%)

vs 60-100
s 40-60
m 20-40
w 10-20
vw <10
sh shoulder
Figure 4.10 X-ray diffraction patterns to show increase in AlPO$_4$-5 crystallinity during hydrothermal crystallisation of the aluminophosphate gel

$\text{Et}_3N\text{ TPABr P}_2\text{O}_5\text{ Al}_2\text{O}_3 40H_2O$

182
over this region can be observed in the X-ray diffraction patterns of all the AlPO₄-5 samples, including those published by other groups [10,11,12,13]. This suggests that it is difficult to prepare the AlPO₄-5 phase as a pure crystalline material by the synthesis routes used.

Figure 4.10 also shows that the formation of AlPO₄-5 is accompanied by the formation and subsequent collapse of AlPO₄-H₃, a hydrate phase with a unit cell composition AlPO₄·1.67H₂O. This phase was first reported by d'Yvoire [14]. It is the same as the AlPO₄·1.5H₂O phase reported by Pluth and Smith [15]. It is built up from alternating layers of 6.6.6 2D nets of Al(O)₄(OH₂O)₂ octahedra and PO₄ tetrahedra, and 4.8.8 2D nets of Al(O)₂ and PO₄ tetrahedra, connected by up and down linkages.

The crystallisation of the gel follows an S shaped growth curve, typical of molecular sieve synthesis (Figures 4.11 and 4.12). As expected, the gel crystallises at a faster rate at a higher reaction temperature. From Figure 4.11, it can be seen that there is a prenucleation period of up to 1 hour. As there was no means of measuring the temperature of the gel, t=0 was taken as the time when the reaction vessels were placed in the oven, so the prenucleation period includes the time taken for the gel to reach the reaction temperature.

A different picture is obtained if the change in amorphous material that is formed, as observed by the low intensity hump, is monitored during the crystallisation. The amount of amorphous material was determined by measuring the deviation of the pattern from the baseline at
Figure 4.11 Increase in AlPO₄-5 crystallinity as a function of reaction time at 423K
Figure 4.12 Increase in AlPO₄-5 crystallinity as a function of reaction time at 453K (ET/1/180/t)
2θ=27.0 (d=0.330nm) relative to the greatest deviation. This is plotted as a function of reaction time (Figure 4.13). The initial rise followed by the gradual decrease indicates that the amorphous material is a precursor of the AlPO₄-5 phase, and that the precursor does not become fully transformed indicated by the levelling off of the curve. This is further substantiated by the faster decrease in amorphous material content at the higher temperature.

There seems to be no clear relationship between the crystallinity of the final product and the tertiary amine used in the crystallisation (Table 4.10). However, in both cases there is a general reduction in sample crystallinity as the gel aging time is increased (Table 4.10). The relative crystallinities are generally much lower than those for the final products from the first two series (ET/a/T/t, Figures 4.11 and 4.12). On calcination the samples from the ET/a and PT/a series gave products with a fairly narrow range of crystallinities. All of these samples originated from the same first stage gel batch; this seems to suggest that the degree of crystallinity is dependant upon the gel preparation procedure.

Investigation of the amorphous content of these samples reveals that there is no relationship between the aging time and the amount of amorphous material present (Figure 4.14). However, there is less amorphous material in the PT/a than the ET/a samples. The content of the latter is similar to that in the ET/a/T/t synthesis series (Figure 4.13). Upon calcination, the amorphous content of
Figure 4.13 Change in relative amorphous content as a function of reaction time.
<table>
<thead>
<tr>
<th>a (gel aging time)</th>
<th>as synthesised</th>
<th>calcined</th>
<th>percent AlPO₄-tridymite content PT/a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ET/a /%</td>
<td>PT/a /%</td>
<td>ET/a /%</td>
</tr>
<tr>
<td>0</td>
<td>62.6</td>
<td>64.9</td>
<td>44.8</td>
</tr>
<tr>
<td>1</td>
<td>68.0</td>
<td>61.8</td>
<td>47.1</td>
</tr>
<tr>
<td>2</td>
<td>54.1</td>
<td>68.4</td>
<td>44.1</td>
</tr>
<tr>
<td>4</td>
<td>72.5</td>
<td>56.6</td>
<td>55.8</td>
</tr>
<tr>
<td>10</td>
<td>53.8</td>
<td>47.0</td>
<td>46.3</td>
</tr>
</tbody>
</table>

a percent of calcined crystalline material in PT/a that is AlPO₄-tridymite

Table 4.10(a) Relative crystallinities of AlPO₄-5 samples prepared from aged gels

<table>
<thead>
<tr>
<th></th>
<th>as synthesised</th>
<th>calcined</th>
<th>percent AlPO₄-tridymite content PT/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>2E/0</td>
<td>82.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2P/0</td>
<td>88.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2E/0</td>
<td>70.4</td>
<td>70.8</td>
<td></td>
</tr>
<tr>
<td>2P/0</td>
<td></td>
<td></td>
<td>8.7</td>
</tr>
</tbody>
</table>

a see Table 4.10(a)

Table 4.10(b) Relative crystallinities for AlPO₄-5 samples prepared from gels with a single template
Figure 4.14 Relative amorphous content of the aged samples as a function of aging period
the ET/a series increased slightly, but the increase was much larger for the PT/a series, and in consequence the final products had similar amorphous contents. This suggests that the amorphous content in the AlPO₄-5 phase is primarily dependant upon the initial gel.

All of the as-synthesised samples made with Pr₃N (single and dual organic preparations) contain a small amount of the dense phase AlPO₄-tridymite. The percentage of the sample that is tridymite is given in Table 4.10. As none of the samples synthesised with Et₃N contain this material, it would suggest that the AlPO₄-5 phase is not as stable during the synthesis with Pr₃N. Choudhary observed the formation of tridymite with a Pr₃N system at this reaction temperature [12]. Wilson observed it but only at higher reaction temperatures [9].

4.2.3.1.2 Dense Phases

In agreement with other workers (Section 2.2.3), the hydrothermal crystallisation of an aluminophosphate gel that does not contain an organic amine or quaternary ammonium salt resulted in the formation of aluminophosphate hydrate and dense phases (Figure 4.15, Tables 4.11-14).

The relative amounts of each phase in the samples were estimated, from the X-ray powder diffraction patterns, to be

<table>
<thead>
<tr>
<th></th>
<th>AlPO₄-H4</th>
<th>berlinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP1</td>
<td>50.6%</td>
<td>49.4%</td>
</tr>
<tr>
<td>DP2</td>
<td>81.7%</td>
<td>18.3%</td>
</tr>
<tr>
<td>DP3</td>
<td>64.1%</td>
<td>35.9%</td>
</tr>
<tr>
<td>DP4</td>
<td>96.7%</td>
<td>3.3%</td>
</tr>
</tbody>
</table>
Figure 4.15 X-ray diffraction patterns for samples produced in AlPO₄ dense phase syntheses
<table>
<thead>
<tr>
<th>inter planar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
<th>phase</th>
<th>inter planar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.723</td>
<td>vw</td>
<td>H4</td>
<td>0.728</td>
<td>s</td>
</tr>
<tr>
<td>0.496</td>
<td>sh</td>
<td>U</td>
<td>0.490</td>
<td>vs</td>
</tr>
<tr>
<td>0.487</td>
<td>m</td>
<td>H4</td>
<td>0.458</td>
<td>m</td>
</tr>
<tr>
<td>0.455</td>
<td>vw</td>
<td>H4</td>
<td>0.436</td>
<td>m</td>
</tr>
<tr>
<td>0.426</td>
<td>vs</td>
<td>B</td>
<td>0.428</td>
<td>s</td>
</tr>
<tr>
<td>0.390</td>
<td>vs</td>
<td>H4</td>
<td>0.392</td>
<td>vs</td>
</tr>
<tr>
<td>0.368</td>
<td>s</td>
<td>H4</td>
<td>0.369</td>
<td>—</td>
</tr>
<tr>
<td>0.362</td>
<td>vw</td>
<td>U</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.351</td>
<td>vw</td>
<td>H4</td>
<td>0.345</td>
<td>s</td>
</tr>
<tr>
<td>0.343</td>
<td>vw</td>
<td>U</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.336</td>
<td>m</td>
<td>H4</td>
<td>0.339</td>
<td>s</td>
</tr>
<tr>
<td>0.318</td>
<td>vw</td>
<td>H4</td>
<td>0.319</td>
<td>m</td>
</tr>
<tr>
<td>0.310</td>
<td>vw</td>
<td>H4</td>
<td>0.311</td>
<td>m</td>
</tr>
<tr>
<td>0.298</td>
<td>vw</td>
<td>H4</td>
<td>0.300</td>
<td>s</td>
</tr>
<tr>
<td>0.285</td>
<td>w</td>
<td>H4</td>
<td>0.286</td>
<td>vs</td>
</tr>
<tr>
<td>0.279</td>
<td>vw</td>
<td>H4</td>
<td>0.280</td>
<td>w</td>
</tr>
<tr>
<td>0.275</td>
<td>w</td>
<td>H4</td>
<td>0.276</td>
<td>w</td>
</tr>
<tr>
<td>0.264</td>
<td>vw</td>
<td>H4</td>
<td>0.265</td>
<td>w</td>
</tr>
<tr>
<td>0.251</td>
<td>m</td>
<td>H4</td>
<td>0.251</td>
<td>vs</td>
</tr>
<tr>
<td>0.247</td>
<td>vw</td>
<td>B</td>
<td>0.247</td>
<td>w</td>
</tr>
<tr>
<td>0.244</td>
<td>vw</td>
<td>H4</td>
<td>0.245</td>
<td>m</td>
</tr>
<tr>
<td>0.242</td>
<td>vw</td>
<td>H4</td>
<td>0.242</td>
<td>w</td>
</tr>
<tr>
<td>0.235</td>
<td>vw</td>
<td>B</td>
<td>0.231</td>
<td>w</td>
</tr>
</tbody>
</table>

- **a** relative intensity (%)  
- **b** H4 = AlPO₄-H4  
- **vs** 60-100  
- **s** 40-60  
- **m** 20-40  
- **w** 10-20  
- **vw** <10  
- **sh** shoulder  
- **Peaks for phases identified using Powder Diffraction File produced by JCPDS International Centre for Diffraction Data**

**Table 4.11** Identification of peaks for X-ray diffraction pattern of DP1
### Table 4.12 Identification of peaks for X-ray diffraction pattern of DP2

| inter | relative | phase | inter | relative |
| planar | peak | peak | planar | intensity | spacing | spacing |
| spacing | intensity | | spacing | intensity | (d) | (I/I₀) | (d) | (I/I₀) |
| (nm) | (I/I₀) | | (nm) | (I/I₀) | | | | |
| 0.435 | vs | T | 0.437 | vs |
| 0.427 | sh | B | 0.428 | m |
| 0.413 | vs | T | 0.413 | vs |
| 0.387 | m | T | 0.386 | vs |
| 0.338 | w | {T | 0.337 | w |
| 0.322 | vw | T | 0.328 | m |
| 0.300 | vw | T | 0.300 | m |
| 0.289 | vw | T | 0.288 | m |
| 0.282 | vw | U | | |
| 0.252 | m | T | 0.255 | s |
| 0.244 | vw | B | 0.247 | w |
| 0.242 | vw | T | 0.241 | m |
| 0.233 | vw | T | 0.233 | s |
| 0.231 | vw | B | 0.231 | w |

**Notes:**

* a, b, c see Table 4.11
### Table 4.13 Identification of peaks for X-ray diffraction pattern of DP3

<table>
<thead>
<tr>
<th>inter planar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
<th>phase</th>
<th>inter planar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.435</td>
<td>m</td>
<td>T</td>
<td>0.437</td>
<td>vs</td>
</tr>
<tr>
<td>0.427</td>
<td>vs</td>
<td>B</td>
<td>0.428</td>
<td>m</td>
</tr>
<tr>
<td>0.412</td>
<td>m</td>
<td>T</td>
<td>0.413</td>
<td>vs</td>
</tr>
<tr>
<td>0.398</td>
<td>vw</td>
<td>B</td>
<td>0.398</td>
<td>vw</td>
</tr>
<tr>
<td>0.387</td>
<td>w</td>
<td>T</td>
<td>0.387</td>
<td>vs</td>
</tr>
<tr>
<td>0.338</td>
<td>vs</td>
<td>T</td>
<td>0.337</td>
<td>w</td>
</tr>
<tr>
<td>0.328</td>
<td>vw</td>
<td>T</td>
<td>0.328</td>
<td>m</td>
</tr>
<tr>
<td>0.300</td>
<td>vw</td>
<td>T</td>
<td>0.300</td>
<td>m</td>
</tr>
<tr>
<td>0.288</td>
<td>vw</td>
<td>T</td>
<td>0.288</td>
<td>m</td>
</tr>
<tr>
<td>0.252</td>
<td>vw</td>
<td>T</td>
<td>0.255</td>
<td>s</td>
</tr>
<tr>
<td>0.247</td>
<td>w</td>
<td>B</td>
<td>0.247</td>
<td>w</td>
</tr>
<tr>
<td>0.242</td>
<td>vw</td>
<td>T</td>
<td>0.241</td>
<td>m</td>
</tr>
<tr>
<td>0.233</td>
<td>vw</td>
<td>T</td>
<td>0.233</td>
<td>s</td>
</tr>
<tr>
<td>0.231</td>
<td>vw</td>
<td>B</td>
<td>0.231</td>
<td>w</td>
</tr>
</tbody>
</table>

* a, b, c see Table 4.11

### Table 4.14 Identification of peaks for X-ray diffraction pattern of DP4

<table>
<thead>
<tr>
<th>inter planar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
<th>phase</th>
<th>inter planar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.433</td>
<td>vw</td>
<td>T</td>
<td>0.437</td>
<td>vs</td>
</tr>
<tr>
<td>0.427</td>
<td>vs</td>
<td>B</td>
<td>0.428</td>
<td>m</td>
</tr>
<tr>
<td>0.398</td>
<td>vw</td>
<td>B</td>
<td>0.398</td>
<td>vw</td>
</tr>
<tr>
<td>0.342</td>
<td>sh</td>
<td>T</td>
<td>0.337</td>
<td>w</td>
</tr>
<tr>
<td>0.339</td>
<td>vs</td>
<td>B</td>
<td>0.337</td>
<td>vs</td>
</tr>
<tr>
<td>0.336</td>
<td>vs</td>
<td>B</td>
<td>0.247</td>
<td>w</td>
</tr>
<tr>
<td>0.247</td>
<td>m</td>
<td>B</td>
<td>0.231</td>
<td>w</td>
</tr>
</tbody>
</table>

* a, b, c see Table 4.11
The transformation of the phases occurred in the order
\[ \text{AlPO}_4 \cdot \text{H}_4 \rightarrow \text{AlPO}_4 \text{-tridymite} \rightarrow \text{berlinite (AlPO}_4 \text{-quartz)} \]
reflecting the order of stability and density of each phase.

\( \text{AlPO}_4 \cdot \text{H}_4 \) is an aluminophosphate hydrate (\( \text{AlPO}_4 \cdot 1 \cdot 2\text{H}_2\text{O} \))
first reported by d'Yvoire [14]. It contains aluminium in
an octahedral environment only. This phase was also
observed by Wilson et al. [9] in their investigation of the
effects of template concentration on \( \text{AlPO}_4 \cdot 5 \) synthesis.

4.2.3.2 pH Measurements

The change in pH of the synthesis gel as the reaction
proceeds follows an S shaped curve, typical of molecular
sieve synthesis (Figures 4.16 and 4.17). The final pH for
the ET/1/180 series is similar to that observed by Wilson
et al. [9], whilst that for the ET/1/150-1 series is lower,
but might have risen to the higher value if the reaction
had been allowed to continue.

The overall rise in pH is due to the equimolar
consumption of Al and P from the mother liquor [9],
increasing the ratio of free amine/P\(_2\)O\(_5\), and hence the pH.

The initial drop in pH can be explained by the theory
put forward by Jahn et al. based on their investigations of
the initial gel [16] (see Section 2.2.3). They postulate
that the amine molecules are bound via the phosphate
tetrahedra to the initial species built up from AlO\(_4\) and PO\(_4\)
tetrahedra, and in this way the Al tetrahedral coordination
is stabilised. Heating the reaction mixture increases the
rate of formation of the prenucleation species, causing a
Figure 4.16 Change in pH of the aluminophosphate gel as a function of reaction time at 423K

![Graph showing pH change over time]
Figure 4.17 Change in pH of the aluminophosphate gel as a function of reaction time at 453K

(ET/1/180/t)
decrease in the free amine/P\textsubscript{2}O\textsubscript{5} ratio, and hence a decrease in the pH.

4.2.3.3 Thermal Analysis

The thermal analysis of the final products of the syntheses give traces similar to those shown in Figures 4.18-4.20, which are typical for molecular sieves containing organic material. Three weight losses occur for the samples containing one organic reagent e.g. 2P/0, whilst there are four weight losses for the samples synthesised from the dual system e.g ET/1 and PT/1.

<table>
<thead>
<tr>
<th>Temperature Range /K</th>
<th>( I^a )</th>
<th>TGA /% w/w</th>
<th>DTA</th>
<th>TGA /% w/w</th>
<th>DTA ( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient - 398</td>
<td>( \alpha_1 )</td>
<td>7.2</td>
<td>—</td>
<td>6.6</td>
<td>endo</td>
</tr>
<tr>
<td>398 - 488</td>
<td>( \alpha_2 )</td>
<td>2.2</td>
<td>—</td>
<td>5.4</td>
<td>endo</td>
</tr>
<tr>
<td>488 - 873</td>
<td>( \gamma )</td>
<td>7.6</td>
<td>—</td>
<td>6.8</td>
<td>endo</td>
</tr>
<tr>
<td>Total % weight loss</td>
<td></td>
<td>17.0</td>
<td></td>
<td>18.8</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Weight change identifier 
\( b \) exo = exothermic 
endo = endothermic

Table 4.15 Thermal analysis of AlPO\textsubscript{4}-5 samples synthesised with a single organic template

The weight losses observed in Figure 4.18 and Table 4.15 can be attributed to the following. The first endothermic weight loss (\( \alpha_1 \)) is due to the removal of water. The second weight loss (\( \alpha_2 \)), also endothermic, is probably caused by the outward diffusion of unrestricted
Figure 4.18 Thermal analysis of AlPO₄-5 containing tripropylamine (2P/0)
Figure 4.19 Thermal analysis of AlPO$_4$-5 containing tripropylamine and tetrapropylammonium cations (PT/1)
Figure 4.20 Thermal analysis of AlPO$_4$-5 containing triethylamine and tetrapropylammonium cations (ET/1)
tripropylamine i.e. from the external surface and close to the pore mouth. The boiling point for Pr₃N, 429K, falls within the temperature range for this loss. The final weight loss (γ), which is exothermic, can be attributed to the oxidative degradation of the remaining Pr₃N. Choudhary observed two exothermic weight losses during the calcination of AlPO₄-5 containing tripropylamine (Figure 2.9). As mentioned in Section 4.1.3.2, large sample weights can cause oxygen starvation during calcination and so produce multiple exothermic peaks when only one is expected. Choudhary used 50mg sample weight whereas 10mg was used in this work.

Although the DTA trace indicates four major thermal events in Figures 4.19 and 4.20, the second endotherm (β) and the first exotherm (γ) are encompassed by one continuous weight loss. Details of the weight losses for the ET/a and PT/a samples are given in Table 4.16.

The first endothermic weight loss (α) is due to the removal of water and the outward diffusion of the respective tertiary amine. There is no sharp endotherm in Figure 4.19 for the outward diffusion of Pr₃N as observed in Figure 4.18, and the α weight loss ends at 448K, indicating that there is little unrestricted Pr₃N in this sample. However, the samples indicated in Table 4.16 do have a sharp weight loss circa 428K.

As the second endotherm (β) is not present for 2P/0, it is probably due to the loss of the tetrapropylammonium cation. It has been reported [17] that TPA species present
**Table 4.16(a) Thermal analysis of AlPO₄-5 samples PT/a**

<table>
<thead>
<tr>
<th>temperature range /K</th>
<th>I&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TGA /% w/w</th>
<th>DTAn&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>ambient - 448</td>
<td>α</td>
<td>3.8</td>
<td>4.8</td>
</tr>
<tr>
<td>448 - 533</td>
<td>β</td>
<td>2.4</td>
<td>3.6</td>
</tr>
<tr>
<td>533 - 723</td>
<td>γ</td>
<td>7.2</td>
<td>7.5</td>
</tr>
<tr>
<td>723 - 873</td>
<td>δ</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>total % weight loss</td>
<td></td>
<td>15.7</td>
<td>18.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> weight change identifier  
<sup>b</sup> exo = exothermic  
endo = endothermic

**Table 4.16(b) Thermal analysis of AlPO₄-5 samples ET/a**

<table>
<thead>
<tr>
<th>temperature range /K</th>
<th>I&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TGA /% w/w</th>
<th>DTAn&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>ambient - 423</td>
<td>α</td>
<td>6.9</td>
<td>7.4</td>
</tr>
<tr>
<td>423 - 543</td>
<td>β</td>
<td>13.9</td>
<td>12.4</td>
</tr>
<tr>
<td>543 - 718</td>
<td>γ</td>
<td>5.6</td>
<td>5.0</td>
</tr>
<tr>
<td>718 - 873</td>
<td>δ</td>
<td>2.2</td>
<td>1.1</td>
</tr>
<tr>
<td>total % weight loss</td>
<td></td>
<td>28.6</td>
<td>25.9</td>
</tr>
</tbody>
</table>

<sup>a</sup> weight change identifier  
<sup>b</sup> exo = exothermic  
endo = endothermic
in an amorphous aluminosilicate gel break down by a Hoffmann elimination reaction in the temperature range 503K to 573K, a range which encompasses the temperature of the $\beta$ weight losses. The degradation of TPAOH by a Hoffmann elimination reaction occurs thus

$$(\text{C}_3\text{H}_7)_4\text{N}^+\text{OH}^- \rightarrow (\text{C}_3\text{H}_7)_3\text{N} + \text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{O}$$

The reaction temperature is greater than the boiling points of the products and so they immediately diffuse away.

If degradation of TPA'/aluminophosphate gel species occurred, then a large $\beta$ weight loss would be expected in the ET/1/150-2/t series, but such is not observed (Figure 4.21, Table 4.17a). The pronounced weight loss only occurred for the ET/a samples (Table 4.16(b)) and not the ET/a/T/t series (Tables 4.17 and 4.18). The high $\beta$ weight loss may well be a consequence of the gel preparation.

The first exothermic weight loss, $\gamma$ (Figures 4.19 and 4.20, Table 4.16), is due to the oxidative degradation of the respective tertiary amine, and the second exothermic weight loss, $\delta$, is due to the oxidative degradation of the remaining TPA cations.

Comparison of the weight losses with aging time reveals no correlation for the ET/a series (Table 4.16(b)). For the PT/a samples (Table 4.16(a)), as the aging time increases, there is a general increase in occluded molecules lost by endothermic processes, and a general decrease in those lost through exothermic processes. There seems to be no correlation between the weight losses of either series with sample crystallinity or with amorphous content.
Figure 4.21 Thermal analysis of AlPO₄-5 series ET/1/150-2/t to show change in water/organic content of solid phase during hydrothermal crystallisation
<table>
<thead>
<tr>
<th>Temperature range /K</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>ambient - 408</td>
<td>α</td>
<td>13.9</td>
<td>10.8</td>
<td>9.8</td>
<td>9.3</td>
</tr>
<tr>
<td>408 - 533</td>
<td>β</td>
<td>2.3</td>
<td>1.7</td>
<td>3.5</td>
<td>3.8</td>
</tr>
<tr>
<td>533 - 703</td>
<td>γ</td>
<td>4.3</td>
<td>4.2</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>703 - 873</td>
<td>δ</td>
<td>4.7</td>
<td>2.2</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Total % weight loss</td>
<td></td>
<td>25.2</td>
<td>18.9</td>
<td>17.0</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Table 4.17(a) Thermal analysis of AlPO₄-5 samples

ET/1/150-1/t

<table>
<thead>
<tr>
<th>Temperature range /K</th>
<th>1</th>
<th>1.25</th>
<th>1.5</th>
<th>1.75</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ambient - 418</td>
<td>α</td>
<td>12.7</td>
<td>13.2</td>
<td>12.6</td>
<td>12.2</td>
</tr>
<tr>
<td>418 - 623</td>
<td>β</td>
<td>3.9</td>
<td>3.8</td>
<td>4.0</td>
<td>3.9</td>
</tr>
<tr>
<td>623 - 1123</td>
<td>δ</td>
<td>6.2</td>
<td>6.0</td>
<td>3.9</td>
<td>4.2</td>
</tr>
<tr>
<td>Total % weight loss</td>
<td></td>
<td>22.8</td>
<td>23.0</td>
<td>20.5</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Table 4.17(b) Thermal analysis of AlPO₄-5 samples

ET/1/150-2/t
For the ET/1/150-1/t and ET/1/180/t series (Tables 4.17a and 4.18), distinct trends are observed. As the reaction time increases, there is a decrease in the α, γ, and δ weight losses, and an increase in the β weight loss. The trend is more significant for the lower temperature series, whereas in the higher temperature series, the change in these values has steadied for the longer reaction times. This suggests that the organic molecules inside and outside of the crystallites approached equilibrium concentrations in the lower temperature reaction, and had almost reached equilibrium in the higher temperature reaction.

For the samples prepared in the ET/a and PT/a series (Table 4.16), the differences in individual organic contents could be a result of the crystalline material/mother liquor being at different stages of attaining the above mentioned equilibrium. This would be
caused by temperature fluctuations during the crystallisation reaction, and the length of the heating period not being exactly the same for each sample.

Figure 4.21 shows how the crystallisation of the gel traps the organic reagents. Initially there are just two major weight losses. The low temperature one, which becomes the α loss, is due to water complexed to the prenucleation species. The other, which becomes the β weight loss, is due to the organic molecules bonded to the prenucleation species. As mentioned earlier, no large weight loss associated with the Hoffmann elimination reaction was observed.

As the reaction time increases, the first weight loss becomes sharper and is complete at an increasingly lower temperature as the hydrate phase AlPO₄·H₃ (Section 4.2.3.1.1) replaces the prenucleation species which subsequently collapses. The completion temperature for the second weight loss increases as the TPA species becomes trapped and so needs a higher temperature to be degraded. This is accompanied by a loss in the actual amount of the reagent present, indicated by a lower weight loss, and also the appearance of the γ weight loss as the triethylamine becomes trapped. This probably encompasses the β loss as well.

The total number of organic molecules per unit cell for the samples in Figures 4.18 to 4.20 can be calculated using the data in Tables 4.15 and 4.16. The following assumptions were made;
(i) for the sample 2P/0, the weight losses α2 and γ are due to loss of Pr₃N only;
(ii) for the sample PT/1, the weight losses β and δ are for TPAOH, and γ is for Pr₃N;
(iii) for the sample ET/1, the weight losses β and δ are for TPAOH, and γ is for Et₃N; and
(iv) for all the samples, the first weight loss is water only and so is taken from the total sample weight to give the dry sample weight.

The number of molecules of each organic reagent per unit cell (uc⁻¹) of AlPO₄⁻5 sample obtained were;

(i) 2P/0: - 1.5 Pr₃N uc⁻¹;
(ii) PT/1: - 0.5 TPAOH + 0.9 Pr₃N uc⁻¹; and
(iii) ET/1: - 1.3 TPAOH + 1.0 Et₃N uc⁻¹.

These values are higher than those expected (Table 2.7) and suggests that there is an excess of organic material.

4.2.3.4 Elemental Analysis

The aluminium/phosphorus ratios for a typical cross section of the AlPO₄⁻5 samples used (Table 4.19) all fall within the framework structure composition range of Al₂O₃:1±0.2P₂O₅ reported in the patent literature [18].

Any deviation from the idealised AlPO₄⁻5 structure with Al/P=1 is indicative of the presence of impurities or crystal defects. It has already been shown that there is amorphous material present in the various samples (Section 4.2.3.1), however there seems to be no direct correlation between the Al/P ratio and the amount of
Table 4.19 Aluminium/phosphorus ratios for AlPO₄-5 samples

<table>
<thead>
<tr>
<th>sample</th>
<th>Al/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>2P/0</td>
<td>0.97±0.04</td>
</tr>
<tr>
<td>PT/0</td>
<td>1.07±0.05</td>
</tr>
<tr>
<td>ET/0</td>
<td>1.16±0.05</td>
</tr>
<tr>
<td>PT/2</td>
<td>1.05±0.05</td>
</tr>
<tr>
<td>ET/2</td>
<td>1.12±0.05</td>
</tr>
<tr>
<td>PT/4</td>
<td>1.00±0.05</td>
</tr>
<tr>
<td>ET/4</td>
<td>0.93±0.05</td>
</tr>
</tbody>
</table>

amorphous material present, or the sample crystallinity. This suggests that the amorphous material could have a variable composition.

The Al/P ratio does, however, decrease within each series as the aging time increases, indicating that the aging process does play some role in the formation of the AlPO₄-5 structure. Further investigation of the aged gel would be needed to identify this role.

4.2.3.5 Scanning Electron Microscopy

4.2.3.5.1 Aluminophosphate AlPO₄-5

The AlPO₄-5 phases crystallised into one of two distinct morphologies.

The batches crystallised from gels containing a single amine formed hexagonal barrel shaped crystal aggregates (Plate 4.2). This is the morphology normally associated with the AlPO₄-5 phase. As can be seen from the micrographs, the barrels consist of bundles of rods. No single crystals
Plate 4.2 Scanning electron micrographs of the different morphologies of AlPO₄-5

211
were observed. The crystal aggregate sizes fall in the range \((2-10\mu m) \times (0.5-7\mu m)\).

A more interesting morphology results from the hydrothermal crystallisation of the gels containing the two organic reagents. This time, spheres are produced (Plate 4.2). Comparison of the spheres with Kaiser alumina, the aluminium source, suggests that a pseudomorphic transformation has occurred. Both sets of spheres have a small depression with a groove bisecting the sphere.

Closer inspection of the surface and interior of broken \(\text{AlPO}_4\)-5 spheres reveals that they are agglomerates of hexagonal platelets (Plate 4.3). A similar morphology was reported by Tapp and co-workers from their synthesis of \(\text{AlPO}_4\)-11 from pseudoboehmite [19].

The formation of the crystallites can be seen in Plate 4.3. This follows the synthesis of the \(\text{AlPO}_4\)-5 phase by monitoring the transformation of the surface from the amorphous Kaiser alumina to the highly crystalline ET/1/180/42. The relative crystallinities of the samples are shown in Figures 4.11 and 4.12.

The Kaiser surface has no regular features (4.3(a)) and breaks up during the prenucleation period (4.3(b)). The appearance of crystallites in 4.3(c) correlates with the increase in crystallinity indicated by X-ray diffraction. The surface gives the appearance that the crystallites are long and very thin, gathered in bundles. An 'exploded' sphere (4.3(e)) shows that they are edges of thin hexagonal platelets. These crystallites are all orientated in the same direction such that the visible edge runs parallel to
Plate 4.3 Comparison of the surfaces of Kaiser alumina and AlPO₄-5 samples of spherical morphology
the groove in the sphere. The appearance remains unchanged for a slight increase in sample crystallinity. The final transformation is seen in 4.3(d) and 4.3(f) (broken sphere) where the hexagonal platelets have become thicker, accompanied by a high sample crystallinity.

The AlPO₄-5 spheres, on average, appear to be smaller than the Kaiser alumina spheres, although they all have diameters that fall within a range of 5-50µm. As both sets of spheres have the same general appearance, this would suggest a contraction of the spheres upon transformation to the AlPO₄-5 phase, although the reduction in size could also be due to dissolution of the surface, or outer layers of the crystallites falling off.

The pseudomorphic transformation is probably related to the porosity of the pseudoboehmite. The water soluble components of the gel penetrate the Kaiser spheres and so allow crystallisation to occur throughout the sphere. This is more likely to occur in a static system as a concentration of the prenucleation species will build up in and around the alumina spheres, whereas if the system were stirred, the species would be more evenly distributed. Of the crystallisations from the gels that contained two organic reagents, only the PT/10 formed barrel shaped crystals instead of spheres, and it is thought that this might be because the reaction vessel was disturbed during the crystallisation procedure.

Large pseudomorphs could be very industrially useful as they might obviate the need for pelleting. For use in this way it is essential that they are mechanically stable.
and have a high attrition resistance.

4.2.3.5.2 Dense Phases

Plate 4.4 shows the morphology of two of the phases produced.

The hydrate phase (Plate 4.4(a)) crystallised as cubic intergrowths. The clusters of intergrowths appear to be spherical with diameters approximately the same as those for the Kaiser alumina spheres, indicating a pseudomorphic transformation has occurred, as with some of the AlPO₄·5 phases.

Plates 4.4(b) shows berlinite crystals from batch DP4. The size range of the crystals were (10-75μm)x(25-200μm). Intergrown crystals were observed.

4.2.3.6 Nitrogen Adsorption

The adsorption isotherms for nitrogen for both the barrel and pseudomorph type morphologies (Figure 4.22) are of Type I, typical for microporous solids.

The pore volume for ET/l/180/42, the most crystalline sample and which is also a pseudomorph (Table 4.20) is similar to that observed for AlPO₄·5 by other workers. However, the pore volume is slightly less for the 2P/0 sample, which has barrel shaped crystals. This suggests that the pore system is partially blocked in this sample, either by occluded amorphous material or lattice collapse. This could also account for the difference in values for the Langmuir constant B, the blocked areas having more attractive surface properties.
Plate 4.4 Scanning electron micrographs of aluminophosphate dense phases

a) $\text{AlPO}_4\cdot\text{H}_4$ (DP1)

b) berlinite (DP4)
Figure 4.22 Adsorption of nitrogen on AlPO$_4$-5 samples of different morphology
<table>
<thead>
<tr>
<th>sample</th>
<th>maximum weight uptake 10/gg&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>pore volume 10/cm&lt;sup&gt;3&lt;/sup&gt;g&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>10&lt;sup&gt;3&lt;/sup&gt;B/m&lt;sup&gt;2&lt;/sup&gt;N&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>2P/0</td>
<td>0.90±0.01</td>
<td>1.11±0.01</td>
<td>7.58±0.13</td>
</tr>
<tr>
<td>ET/1/180/42</td>
<td>1.16±0.01</td>
<td>1.43±0.01</td>
<td>1.34±0.03</td>
</tr>
<tr>
<td>DP4</td>
<td>0.08</td>
<td>0.10±0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 4.20 Nitrogen adsorption by AlPO<sub>4</sub>-5 samples and berlinite

As expected, the dense phase berlinite has a small surface area.
4.3 References


219
5.0 Introduction

Adsorption techniques have long been used to measure the pore volumes, channel dimensions, and gas/solid phase interactions in molecular sieves (Section 1.2.4). In this Chapter measurement of the uptake of organic molecules, as well as nitrogen, by samples of the zeolite EU-1, and the aluminophosphate AlPO₄-5 is described. The aim of these measurements was to determine how, if at all, the different synthesis procedures affected the adsorption properties of the products. In all cases, the sorbate molecules were smaller than the pore diameters, and hence the molecular sieving properties of the samples were not tested.

The amount of gas \( x \) adsorbed per gram of solid is dependant upon the equilibrium pressure \( P \), the temperature \( T \), and the nature of the gas and the solid. Hence

\[
x = f(P, T, \text{gas, solid})
\]  (5.1)

For a given gas on a given solid at a constant temperature below the critical temperature for the gas, equation (5.1) can be simplified to

\[
x = f\left(\frac{P}{P_0}\right)_T, \text{gas, solid}
\]  (5.2)

Plotting \( x \) against \( P/P_0 \) results in the adsorption isotherms shown in Figure 1.6. The adsorption of gases by microporous solids usually result in Type I isotherms. The Langmuir equation is normally found to give a good description of this isotherm type, and hence a good description of
sorption in zeolites.

The Langmuir equation is based on a theoretical treatment which assumes monolayer coverage on a homogeneous sorbent surface over which the potential field is constant. However, zeolite adsorption sites are not all of the same type and thus the Langmuir model cannot be expected to give perfect agreement.

When a molecule strikes the surface of a solid inelastically, it will stay for a period of time before returning to the gas phase. During the time between the condensation \((n_1)\) and subsequent evaporation \((n_2)\) of the molecule, it is said to be adsorbed.

Langmuir derived an equation for the condensation process as follows [1,2]. Consider one wall of a box of unit volume. Half of the molecules are moving towards the wall, the other half are moving away. If \(\rho\) is the density of the gas, then the mass of gas moving towards the wall within this unit volume is \(\frac{1}{2}\rho\). If \(\bar{u}\) is the average velocity of all the molecules, then the average velocity of the molecules heading towards the wall is \(\frac{1}{2}\bar{u}\). Hence the mass \(m'\) which strikes unit surface every second is

\[
m' = \frac{1}{2}\rho \bar{u} \tag{5.3}
\]

\(\bar{u}\) can be determined from

\[
\bar{u} = \int_{u=0}^{u_{\text{max}}} u \frac{dN}{N} \tag{5.4}
\]

where \(dN/N\) is the fraction of the number of molecules over which the velocities \(u\) are averaged. Calculation of the distribution of molecular velocities [3] and its subsequent substitution into equation (5.4) gives
\[ \bar{u} = 4\pi \sqrt{\frac{m}{2\pi kT}} \int_{u=0}^{u_{\infty}} u^3 e^{-\frac{kmv^2}{kT}} \, du \]  

(5.5)

This is integrated to

\[ \bar{u} = \sqrt{\frac{8kT}{\pi m}} \]  

(5.6)

where \( k \) is the Boltzmann constant and \( m \) is the mass of the molecule. This can be rewritten as

\[ \bar{u} = \sqrt{\frac{8RT}{\pi M}} \]  

(5.7)

where \( R \) is the gas constant, \( T \) is the temperature, and \( M \) is the molecular mass.

The equation of state for an ideal gas

\[ PV = RT \]  

(5.8)

can be rewritten

\[ \rho = \frac{PM}{RT} \]  

(5.9)

Substitution of equations (5.9) and (5.7) into (5.3) and rearranging gives

\[ m' = \sqrt{\frac{M}{2\pi RT}} \rho \]  

(5.10)

the mass of molecules arriving per second from the gas phase per unit of freely exposed surface. The number of molecules is given by

\[ n = \frac{N}{\sqrt{(2\pi MRT)}} \rho \]  

(5.11)

If \( \theta_0 \) is the fraction of bare surface available for adsorption, then the rate of condensation can be written as

\[ n_1 = \frac{N}{\sqrt{(2\pi MRT)}} \rho a_1 \theta_0 \]  

(5.12)

where \( a_1 \) is the condensation coefficient and allows for the possibility that only some of the incident molecules will
condense on an empty site.

For the molecule to leave the surface (evaporate) it needs sufficient energy \( E \) per mole to overcome the attractive forces holding it to the surface. If \( v_1 \) is the frequency of oscillation of the molecule normal to the solid surface, and \( e^{-E/RT} \) is the probability that a molecule will evaporate on reaching the extreme of its vibration, the number of molecules evaporating from a given site per second can be given by \( v_1 e^{-E/RT} \). Hence the rate of evaporation from the surface can be written as

\[
n_i = z_m \theta_1 v_1 e^{-E/RT}
\]  
(5.13)

where \( \theta_1 \) is the fraction of the surface covered, and \( z_m \) is the number of molecules in a complete monolayer.

At equilibrium, the rate of evaporation is equal to the rate of condensation, i.e.

\[
\frac{N}{\sqrt{(2\pi MRT)} P \alpha_i \theta_0} = z_m \theta_1 v_1 e^{-E/RT}
\]  
(5.14)

Since \( \theta_0 = (1-\theta_1) \), and assuming that all the incident molecules that strike the surface will stick, i.e. \( \alpha_i = 1 \), equation (5.14) gives

\[
k_e P (1-\theta_1) = k_s \theta_1
\]  
(5.15)

where

\[
k_e = \frac{N}{\sqrt{(2\pi MRT)}}
\]  
(5.16)

which is constant for a given gas at constant temperature, and

\[
k_s = z_m v_1 e^{-E/RT}
\]  
(5.17)

which is constant for a given solid at constant temperature.
Equation (5.15) can be rearranged to give

$$\theta_i = \frac{k_e P}{k_c + k_e P} \quad (5.18)$$

which can be rewritten as

$$\frac{x}{x_m} = \frac{BP}{1 + BP} \quad (5.19)$$

where $x$ is the amount of gas adsorbed, $x_m$ is the maximum amount of gas that can be adsorbed, and $B$ is the Langmuir constant, or adsorption coefficient, given by $k_e/k_c$. From equations (5.16) and (5.17), it can be seen that $B$ is constant at a constant temperature for a given adsorbent/adsorbate system. If, say, $k_e$ increases, i.e. there is an increase in the probability for the molecules to evaporate from the site, the value for $B$ decreases.

Equation (5.19) can be rearranged to the form

$$\frac{P}{x} = \frac{P}{x_m} + \frac{1}{Bx_m} \quad (5.20)$$

If the adsorption follows Langmuir theory, then a plot of $P/x$ against $P$ produces a straight line of slope $1/x_m$ and intercept $1/Bx_m$.

Knowledge of the density of the adsorbate at the temperature of investigation allows the calculation of the pore volume of the adsorbent

$$\text{pore vol} = \frac{x_m}{\rho} \quad (5.21)$$

The surface areas of the samples were not calculated, again for the reasons given in Section 1.2.4.
5.1 Butene Sorption using Constant Volume Apparatus

5.1.1 Introduction

An investigation of the sorption of the three isomers but-1-ene, cis but-2-ene, and trans but-2-ene was used to determine their accessibility to the internal surfaces of the molecular sieves, and hence to obtain an indication of the amount of sample surface involved in the catalytic isomerisation reaction. The equipment and technique used was that described in Section 3.2.6.2.

5.1.2.1 Zeolite EU-1

The isotherms for the sorption of the three butene isomers on H-BH3 are shown in Figure 5.1. It is immediately noticeable that straightforward adsorption/desorption did not take place. There is very substantial hysteresis, and furthermore the loops appear to remain open. Such behaviour is unusual and not normally observed for sorption at such low relative pressures.

An explanation for this type of behaviour can be provided by consideration of the diffusion of the molecule through the channel system [4]. If the kinetic diameter of the molecule is close to the diameter of the pore, then the rate of diffusion will be slower than for a molecule of smaller kinetic diameter and so the system will take longer to equilibrate. Upon desorption, this will be shown as a hysteresis loop at low pressures that does not appear to close.

If this were the case for the butene sorption however, then the curves shown in Figure 5.1 would be different. The
Figure 5.1 Adsorption of but-n-ene on H-EU-1 (BH3) at ambient temperature
kinetic diameters of but-1-ene, *trans* but-2-ene, and *cis* but-2-ene are 0.495nm, 0.495nm, and 0.558nm respectively, giving relative rates of diffusion in the order

\[
\text{but-1-ene} = \text{trans but-2-ene} > \text{cis but-2-ene}
\]

This would result in the desorption isotherm for the *cis* isomer being significantly different from the other two if equilibrium has not been established. The fact that the desorption isotherms are virtually identical suggests that the hysteresis arises from a different effect.

Henderson [5] measured the rate of uptake of the butene isomers on EU-1 and showed that equilibrium seemed to be established in less than ten minutes after contact. In this work, this system was allowed to equilibrate for at least thirty minutes, and was monitored for pressure changes from fifteen minutes after a change in volume. The maximum volume uptakes (Equation 5.21) obtained from the isotherms (Table 5.1) are similar to those obtained by Henderson, which are also similar to those measured by nitrogen adsorption (Table 4.8). The combination of these again suggests that the hysteresis loop results from an effect other than diffusion.

Similar isotherms to those in Figure 5.1 were observed by MacIver and co-workers [6] for the adsorption of but-1-ene on silica-alumina catalysts at temperatures as low as 195K. They attributed the behaviour to the chemisorption of the but-1-ene. The hysteresis did not close at essentially zero relative pressure, and polymerisation was also thought to have occurred.
Infrared studies of the sorption of but-1-ene on deammoniated zeolite Y at 273K has revealed the presence of an irreversibly bound species [7]. Initially, C=C stretching frequencies for but-1-ene and cis but-2-ene were observed, indicating that isomerisation had taken place (the corresponding vibration for trans but-2-ene is infrared inactive). These bands then disappeared and were replaced by C-H stretching and bending frequencies for a saturated surface hydrocarbon species that could not be physically desorbed at room temperature. This was accompanied by a decrease in the intensity of the band due to the acidic hydroxyl groups, and it was thought that saturated species were forming on these sites.

Chemisorption of the butenes is probably the most likely explanation for the shape of the isotherms obtained.
in this investigation. Diffusional effects cannot, however, be entirely ruled out. As the channel system is monodimensional, the diffusional paths can become restricted or even blocked by the chemisorbed butene molecules, which may result in an increase in the size of the hysteresis loop.

The adsorption coefficients (Table 5.1) show an increase in affinity in the order

but-1-ene < cis but-2-ene < trans but-2-ene

Weeks [7] and Jacobs [8] both reported that zeolite Y had a stronger affinity for the but-2-ene isomers than for but-1-ene, and that the saturated surface species was formed from the but-2-ene isomers.

Further investigation of the system with infrared spectroscopic techniques would be required to help substantiate these explanations.

Figure 5.2 shows the voidage made inaccessible by the strongly bound species. The void volume was initially measured with nitrogen and found to be 0.185 cm$^3$ g$^{-1}$. The EU-1 sample was then contacted with but-1-ene at room temperature for eight hours, and subsequently outgassed under vacuum at room temperature for eighteen hours. After this treatment, the pore volume was remeasured with nitrogen, and the voidage was reduced to 54% of its original value (Table 5.2), indicating that some of the hydrocarbon was still in the channel system. As the channel system is monodimensional, space between two blockages may be inaccessible to the nitrogen molecules, so there is probably less hydrocarbon in the channel system than is
Figure 5.2 Adsorption of nitrogen on H-EU-1 (BH3) with and without preadsorbed but-1-ene

- before adsorbing but-1-ene
- after pumping off but-1-ene at room temperature
- after calcining in oxygen at 723K and pumping under vacuum
<table>
<thead>
<tr>
<th>adsorption stage</th>
<th>pore volume $^{a}$</th>
<th>$10^3B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen sorption before but-1-ene adsorbed</td>
<td>$1.85\pm0.01$</td>
<td>$2.50\pm0.23$</td>
</tr>
<tr>
<td>nitrogen sorption after treatment with but-1-ene and subsequent pumping</td>
<td>0.99</td>
<td>$2.81\times10^{-3}$</td>
</tr>
<tr>
<td>nitrogen sorption after removal of but-1-ene by heating in oxygen</td>
<td>$1.83\pm0.01$</td>
<td>$3.01\pm0.27$</td>
</tr>
</tbody>
</table>

$a$ density nitrogen $0.808g\ cm^{-3}$

Table 5.2 Adsorption of nitrogen on EU-1 (BH3)

suggested by the data. The sample was then pumped under vacuum and calcined in situ in an atmosphere of pure oxygen ($55kN\ \text{m}^{-2}, 723K$). The void volume was subsequently measured to be $0.183\text{cm}^3\text{g}^{-1}$, i.e. restored to its original value.

5.1.2.2 Aluminophosphate AlPO$_4$-5

Butene adsorption and desorption on a sample of AlPO$_4$-5 (ET/1/180/42) showed rather similar behaviour to that observed for H-EU-1 (Figure 5.3). The hysteresis loop was not as large as that obtained for EU-1 and the desorption isotherm did not show the same plateau effect. This suggests that the butene was not as firmly bound in this system, probably due to the lack of strong acid sites in AlPO$_4$-5. However, the presence of the hysteresis loops indicate that some irreversible adsorption had taken place.

There are two possible sites for this chemisorption. The first is the terminal hydroxyl groups, which have been detected by infrared spectroscopy (Section 1.3.5).
Figure 5.3 Adsorption of but-n-ene on AlPO₄-5 (ET/1/180/42) at ambient temperature.

- but-1-ene
- cis but-2-ene
- trans but-2-ene

Open symbols: adsorption
Closed symbols: desorption

Vol but-n-ene adsorbed (STP) / 10⁻³ m³ g⁻¹

P/P₀

0.00 0.02 0.04 0.06 0.08 0.10 0.12
Chemisorption on these groups at the pore mouths may restrict the access to the channel. In addition, as this sample is a sphere of tiny crystallites, there will be many more terminal hydroxyl groups present on the external surface than there is with the barrel shaped crystals.

The second possible site could be on that part of the AlPO₄-5 sample that is indicated as being amorphous by the X-ray diffraction pattern (Section 4.2.3.1.1). Elemental analysis of a selection of the samples (Section 4.2.3.4) showed Al/P ratios greater than unity. The excess aluminium atoms probably have associated acidic hydroxyl groups. Again, further investigation of the system by infrared spectroscopy may give more information as to the nature of the irreversible adsorption.

The maximum volume uptake of the butenes by the AlPO₄-5 sample (Table 5.3) was similar to the pore volume measured with nitrogen, hence all the voidage in the main 12 T-atom channel must be available to the alkenes.

As with the butene/EU-1 system, there seemed to be greater affinity for the but-2-ene isomers than for but-1-ene, as indicated by the adsorption coefficients (Table 5.3), although the order had changed slightly

\[
\text{but-1-ene} \prec \text{trans but-2-ene} \prec \text{cis but-2-ene}
\]

Not all of the adsorbed but-1-ene could be removed by outgassing the sample under vacuum at room temperature (Figure 5.4, Table 5.4). The void volume of the clean sample was measured with nitrogen and found to be 0.148 cm³ g⁻¹. The sample was then contacted with but-1-ene for eight hours, and subsequently outgassed under vacuum for
<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Adsorption</th>
<th></th>
<th>Desorption</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum volume uptake $^a$</td>
<td>$10^3B$ /m$^2$N$^{-1}$</td>
<td>Maximum volume uptake $^a$</td>
<td>$10^3B$ /m$^2$N$^{-1}$</td>
</tr>
<tr>
<td>but-1-ene</td>
<td>1.19±0.03</td>
<td>0.58±0.01</td>
<td>1.14±0.01</td>
<td>1.37±0.03</td>
</tr>
<tr>
<td>cis but-2-ene</td>
<td>1.23±0.02</td>
<td>0.94±0.01</td>
<td>1.20±0.01</td>
<td>1.76±0.03</td>
</tr>
<tr>
<td>trans but-2-ene</td>
<td>1.21±0.01</td>
<td>0.76±0.01</td>
<td>1.18±0.02</td>
<td>1.22±0.02</td>
</tr>
</tbody>
</table>

$^a$ densities used: but-1-ene 0.595g cm$^{-3}$
 cis but-2-ene 0.621g cm$^{-3}$
 trans but-2-ene 0.604g cm$^{-3}$

**Table 5.3** Adsorption and desorption of n-butenes on AlPO$_4$-5 (ET/1/180/42)

<table>
<thead>
<tr>
<th>Adsorption stage</th>
<th>Pore volume $^a$</th>
<th>$10^3B$ /m$^2$N$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen sorption before but-1-ene adsorbed</td>
<td>1.48±0.02</td>
<td>0.88±0.02</td>
</tr>
<tr>
<td>nitrogen sorption after treatment with but-1-ene and subsequent pumping</td>
<td>0.48±0.01</td>
<td>0.06</td>
</tr>
<tr>
<td>nitrogen sorption after removal of but-1-ene by heating in oxygen</td>
<td>1.45±0.02</td>
<td>0.96±0.02</td>
</tr>
</tbody>
</table>

$^a$ density nitrogen 0.808g cm$^{-3}$

**Table 5.4** Adsorption of nitrogen on AlPO$_4$-5 (ET/1/180/42)
Figure 5.4 Adsorption of nitrogen on AlPO$_4$-5 (ET/1/180/42) with and without preadsorbed but-1-ene.

Before adsorbing but-1-ene

Blocks after pumping off but-1-ene at room temperature

Diamonds after calcining in oxygen at 723K and pumping under vacuum

Volume N$_2$ adsorbed (STP) / 10$^{-5}$ m$^3$ g$^{-1}$

0.0 0.2 0.4 0.6

$P/P_O$
eighteen hours. After this treatment, the pore volume was remeasured with nitrogen, and the voidage was reduced to 32% of the original value. The sample was then pumped under vacuum, and calcined in situ in an atmosphere of pure oxygen (55 kN m$^{-2}$, 723K). The void volume was subsequently measured to be 0.145 cm$^3$ g$^{-1}$ by nitrogen adsorption, its original value.

As the channel system in AlPO$_4$-5 is unidimensional, voidage between two chemisorbed species in the channel may be inaccessible to the nitrogen, hence there could be less hydrocarbon irreversibly adsorbed than is suggested by the data. Indeed, the values in Table 5.4 indicate that the sample still contained 5.95% w/w of hydrocarbon, whereas the thermal analysis of the sample treated under identical conditions showed that only 4.35% w/w was still bound (Figure 5.5).

Comparison of the EU-1 and the AlPO$_4$-5 isotherms suggests that the chemisorption/polymerisation effect is strongest for EU-1. Hence it would be expected that the pore volume taken up by the butene would be greater with EU-1 than AlPO$_4$-5, but in fact it is the reverse. The channel structure of EU-1 is such that polymerisation is more likely to occur in the large side pockets leaving the main channels still free, whereas as mentioned above, polymerisation in the channels would block off unfilled space.

Figure 5.6 shows the sorption of but-1-ene on a sample of AlPO$_4$-5 (ET/1/180/42) at room temperature as a function of time. Plot (a) shows adsorption onto the clean sample,
Figure 5.5  Thermal analysis of AlPO₄-5 (ET/1/180/42) after vacuum desorption of but-1-ene at ambient temperature.
Figure 5.6 Rate of uptake of but-1-ene on AlPO₄-5 (ET/1/180/42) at various pressures and ambient temperature
plot (b) is adsorption at an increased pressure achieved by decreasing the volume of the system, and plot (c) is the desorption upon returning the system to its original volume.

It would seem that after the very rapid initial uptake, there was a slow diffusion of but-1-ene into the channel system. However, upon desorption, the outward diffusion appeared to be instantaneous, i.e. there was an immediate drop in uptake from $3.11 \times 10^{-5} \text{m}^3 \text{g}^{-1}$ to $2.85 \times 10^{-5} \text{m}^3 \text{g}^{-1}$. If the molecules had constrictions to overcome when diffusing into the channels, then it would be expected that they would have to overcome the same obstacles upon outward diffusion. This would result in plot (c) showing a gradually decreasing slope which was not observed.

The gradual increase for adsorption (plots (a) and (b)) could be due to a slow polymerisation of the alkene on the surface of the crystallites. This would explain why the desorption line is level, the outward diffusion of the butene molecules being rapid, leaving the polymer residue on the surface.

As mentioned in the previous section, it was thought that the saturated species was formed from but-2-ene. Analysis of the but-1-ene gas before and after contact with the AlPO$_4$-5 sample for twenty four hours showed that some skeletal isomerisation to the but-2-enes had taken place (Table 5.5), giving some support to the above explanation. As but-2-enes were observed, it can be assumed that the isomerisation reaction took place at a faster rate than the polymerisation.
Table 5.5 Extent of but-1-ene isomerisation after contact with AlPO<sub>4</sub>-5 (ET/1/180/42) at room temperature for 24 hours.

<table>
<thead>
<tr>
<th>n-butene isomer</th>
<th>isomer content /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>but-1-ene</td>
<td>93.4</td>
</tr>
<tr>
<td>cis but-2-ene</td>
<td>2.4</td>
</tr>
<tr>
<td>trans but-2-ene</td>
<td>4.2</td>
</tr>
</tbody>
</table>

5.2 Hydrocarbon Sorption using a Cahn Microbalance

5.2.1 Introduction

The adsorption of selected hydrocarbons onto samples of AlPO<sub>4</sub>-5 was carried out gravimetrically using a Cahn Electrobalance. The apparatus and experimental procedure has been previously described (Section 3.2.6.3). The Langmuir equation was used in the analysis of the raw data obtained from the investigations (Section 5.1.1). The maximum hydrocarbon uptake, and Langmuir constants that were calculated give an indication of the sorbent/sorbate interactions. As the adsorption apparatus continuously measures the change in weight of the sample on a chart recorder, the uptake rates were also monitored.

5.2.2 Aluminophosphate AlPO<sub>4</sub>-5

The isotherms for the adsorption of various hydrocarbons on the AlPO<sub>4</sub>-5 sample 2P/0 are shown in Figure 5.7. A deviation from the Type I isotherm was observed in all cases at a relative pressure above P/P<sub>0</sub>=0.45. The data for each isotherm below this relative
Figure 5.7 Adsorption of organic vapours on AlPO₄-5 (2P/0) at ambient temperature
pressure fitted the Langmuir equation quite well.

The deviations at $P/P_0 > 0.45$ are thought to be due to the occurrence of capillary condensation. The scanning electron micrographs (Plate 4.2) revealed gaps between the rods that formed the barrel crystals; condensation may occur in such regions.

The maximum uptakes and adsorption coefficients for each system, calculated from the data that conformed to the Langmuir equation, are given in Table 5.6.

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>maximum volume uptake $\times 10^3$/cm$^3$</th>
<th>$10^3B$ m$^3$/N$^{-1}$</th>
<th>maximum weight uptake $\times 10^2$/gg$^{-1}$</th>
<th>number of molecules adsorbed per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>$1.32 \pm 0.02$</td>
<td>$3.52 \pm 0.37$</td>
<td>$10.5 \pm 0.2$</td>
<td>$4.7$</td>
</tr>
<tr>
<td>n-hexane</td>
<td>$1.08 \pm 0.04$</td>
<td>$1.46 \pm 0.31$</td>
<td>$7.13 \pm 0.03$</td>
<td>$1.2$</td>
</tr>
<tr>
<td>ortho-xylene</td>
<td>$1.28 \pm 0.02$</td>
<td>$132 \pm 37$</td>
<td>$11.3 \pm 0.2$</td>
<td>$1.6$</td>
</tr>
<tr>
<td>meta-xylene</td>
<td>$1.13 \pm 0.02$</td>
<td>$57.1 \pm 1.6$</td>
<td>$9.72 \pm 0.02$</td>
<td>$1.3$</td>
</tr>
<tr>
<td>para-xylene</td>
<td>$1.02 \pm 0.02$</td>
<td>$35 \pm 3.5$</td>
<td>$8.80 \pm 0.02$</td>
<td>$1.2$</td>
</tr>
</tbody>
</table>

a densities used: methanol 0.791 g cm$^{-3}$
n-hexane 0.660 g cm$^{-3}$
ortho-xylene 0.880 g cm$^{-3}$
meta-xylene 0.864 g cm$^{-3}$
para-xylene 0.861 g cm$^{-3}$

Table 5.6 Adsorption of various organic compounds on AlPO$_4$-5 (2P/0)
A range of uptakes was obtained, all of which were not greater than that determined for nitrogen adsorption (0.148 cm$^3$ g$^{-1}$). The values show that the void space accessible to nitrogen could also be accessed by the organic molecules. However, that there is a significant variance in the uptakes indicates that the Gurvitsch pore filling rule (Section 1.2.4) was not obeyed.

This can be attributed to a number of factors that stem from the packing of the molecules within the channels. The main consequence of these factors is that the resultant density of the adsorbed molecules is different from that of the density of the liquid hydrocarbon at the temperature of adsorption, which is used in the calculation of the uptake volume.

With the exception of methanol, the hydrocarbons studied all had critical diameters greater than the radius of the AlPO$_4$-5 channel, so only one molecule should be present per cross-sectional area of the channel. Consider n-hexane. It is a long, narrow molecule, so, when it is sorbed within the AlPO$_4$-5 framework, a lot of space around the molecule is not occupied, whereas ortho-xylene, a short, wide molecule, fills the space more completely. These features are reflected in the calculated uptakes for the various sorbed organic molecules. With methanol, the critical diameter of 0.385 nm allows for two molecules per cross-sectional area of the channels, which is reflected in the larger uptake.

The number of molecules sorbed per unit cell was also calculated (Table 5.6), with the assumption of an ideal
AlPO₄-5 unit cell. Although the aluminium and phosphorus content has previously been determined by elemental analysis (Section 4.2.3.4), how the deviation from the ideal Al/P ratio affects the structure is not known. The values obtained for the number of molecules per unit cell, although higher than expected, support the above explanation for molecular packing.

If the molecules were positioned head to tail, then para-xylene, for example, with a molecular length of approximately 0.99nm would give a value of 0.85uc⁻¹. The higher experimental value can result from two possible causes. The first is that although only the data that fitted the Langmuir isotherm were used to calculate the maximum uptake of sorbate, intercrystalline adsorption may already have started. The calculation assumes only intracrystalline adsorption. The second factor is that the molecules may have skewed orientation within the channel, so the individual molecules overlap.

The adsorption coefficients for each system (Table 5.6) reflect the nature of the molecules. The xylenes had the largest B values, probably as a result of the interaction of the π-electrons with the aluminophosphate surface. The dipole moments for the three isomers decrease in the order

\[ \text{ortho} > \text{meta} > \text{para} \]

which is also reflected by their B values. N-hexane, with no dipole moment, had the smallest adsorption coefficient, a reflection of the weakest sorbent/sorbate interaction for the systems studied.
Figure 5.8 shows the uptake of the sorbates as a function of time. The xylene isomers showed similar rates of uptake, with equilibrium being established in 70 minutes, whereas n-hexane had a much more rapid uptake due to its smaller kinetic diameter, with equilibrium being established within 10 minutes. Similar observations were obtained by Lohse et al [9]. It may also be noted that para-xylene reached equilibrium in a shorter time period than the other two isomers, which can be explained by the former having a smaller kinetic diameter.

The uptake for methanol was slower than expected, considering its smaller molecular size. A possible explanation is that when one methanol molecule is adsorbed onto the surface, the effective diameter of the channel is reduced, restricting the diffusion of the molecules. Indeed, a very rapid initial uptake was observed (Figure 5.8).

The adsorption of selected hydrocarbons onto AlPO_4-5 samples synthesised via different routes, i.e. single template and aged dual template procedures, were compared. The results are shown in Figures 5.9 (n-hexane) and 5.10 (para-xylene), and Table 5.7.

For both n-hexane and para-xylene adsorption, there was an increase in the adsorption coefficients in the order

$$2P/0 < PT/4 < ET/4$$

As the adsorbate is the same for each set of isotherms, the change in the B values suggests that the adsorbing surfaces of the AlPO_4-5 samples studied have an increased attractive force in the above order. Further investigation of the
Figure 5.8 Rate of uptake of organic vapours adsorbed on AlPO$_4$-5 (2P/0) at ambient temperature.
Figure 5.9 Adsorption of n-hexane on AlPO₄-5 samples of different morphologies at ambient temperature.

\[ \text{weight uptake (g/g)} \]

\[ \frac{P}{P_0} \]

\[ \nabla \text{2P/0} \]
\[ \nabla \text{PT/4} \]
\[ \nabla \text{ET/4} \]

--- deviation from Langmuir isotherm
Figure 5.10 Adsorption of para-xylene on AlPO₄-5 samples of different morphologies at ambient temperature.
Table 5.7 Adsorption of selected hydrocarbons on samples of AlPO₄-5 systems would be required to determine whether this is a function of, for example, aging time, organic template, sample crystallinity, or a combination of factors.

Deviations from the Langmuir isotherm were seen to take place at lower P/P₀ for the para-xylene/pseudomorph (ET/4, PT/4) systems than for para-xylene/2P/0, whereas there was little difference in the n-hexane systems investigated. This may be accounted for by the variation in adsorption coefficients. The pseudomorphic samples (dual template) have a greater external surface area than the barrel shaped crystals, resulting from the tiny crystallites, which may allow more multilayer adsorption to take place in the intercrystalline voids. Whereas the increased attractive force of the surface will have only a small effect on the adsorbent/adsorbate interaction with non-polar molecules, e.g. n-hexane, there will be a greater

| AlPO₄-5 sample | n-hexane | | para-xylene |
|----------------|-----------|-------------------------------|
|                | maximum   | 10²B                          | maximum     | 10²B                      |
|                | volume    | /m²N⁻¹                        | volume      | /m²N⁻¹                    |
|                | uptake²   | 10/cm³g⁻¹                     | uptake²     | 10/cm³g⁻¹                 |
| 2P/0           | 1.08±0.04 | 1.46±0.31                     | 1.02±0.02   | 35.0±3.5                  |
| PT/4           | 1.10±0.05 | 3.09±0.11                     | 1.15±0.02   | 46.8±3.0                  |
| ET/4           | 1.12±0.05 | 3.24±0.17                     | 1.16±0.02   | 47.6±2.7                  |

a densities used: n-hexane 0.660g cm⁻³
para-xylene 0.861g cm⁻³

Table 5.7 Adsorption of selected hydrocarbons on samples of AlPO₄-5 systems would be required to determine whether this is a function of, for example, aging time, organic template, sample crystallinity, or a combination of factors.

Deviations from the Langmuir isotherm were seen to take place at lower P/P₀ for the para-xylene/pseudomorph (ET/4, PT/4) systems than for para-xylene/2P/0, whereas there was little difference in the n-hexane systems investigated. This may be accounted for by the variation in adsorption coefficients. The pseudomorphic samples (dual template) have a greater external surface area than the barrel shaped crystals, resulting from the tiny crystallites, which may allow more multilayer adsorption to take place in the intercrystalline voids. Whereas the increased attractive force of the surface will have only a small effect on the adsorbent/adsorbate interaction with non-polar molecules, e.g. n-hexane, there will be a greater
interaction with the electron ring of the para-xylene molecule. This in turn could lead to stronger molecular interactions in the building up of multilayers.

It may also be that this is the reason that the dual template samples showed a larger apparent uptake volume when measured with para-xylene than n-hexane, in that multilayer adsorption had already started to take place in the lower pressure (Langmuir isotherm) region.

5.3 Pyridine Desorption

5.3.1 Introduction

The adsorption of bases such as pyridine is one of the many techniques that has been used to determine the number and strength of acid sites present in solid acid catalysts (Section 1.2.5). In this section, thermal analysis was used to desorb the pyridine from samples of EU-1 and AlPO₄-5. The temperature of desorption is an indication of the relative site strength, whilst the weight loss for each desorption range can be used as a measure of the number of sites present.

5.3.2 Experimental

The following procedure was carried out in the investigation of the EU-1 and the AlPO₄-5 samples. A small amount of the calcined, and, for EU-1, ion exchanged, sample (circa 0.1g) was heated in a furnace in air at 723K for eighteen hours. This was then transferred quickly to an open glass bottle, whilst still hot, and immediately placed on a tray in a vacuum desiccator, which contained pyridine
(Fisons, AR) that had been dried with zeolite 4A (BDH). The desiccator was evacuated using a rotary vacuum pump, and left at ambient temperature for 48 hours to allow the contents to equilibrate. During this period, the base of the desiccator was kept cooler than the surrounding air temperature by standing it in ice. This method was used to minimise the amount of capillary condensation that may occur in the intercrystalline spaces of the molecular sieve during the adsorption process.

Desorption of the pyridine from the samples was carried out on a Stanton Redcroft TG 750/770 Thermal Balance for the AlPO₄-5 samples, and a Stanton Redcroft STA 780 Thermal Analyser in the case of EU-1. Details for the operation of the apparatus has been given in Section 3.2.2. The samples were heated in an inert atmosphere of nitrogen so that the pyridine molecules were removed from the sorbent by desorption rather than oxidative degradation. By this method, the amount of pyridine adsorbed, and the temperature ranges for the subsequent desorption were obtained.

5.3.3.1 Zeolite EU-1

The desorption of pyridine from the three batches of H-EU-1 (ICIEU1, BH2, and BH3) are shown in Figure 5.11 as the weight loss from the preadsorbed samples as a function of the temperature. A summary is given in Table 5.8. The differential thermal analysis traces that were recorded simultaneously were found to be of little value due to operational difficulties.
Figure 5.11 Thermal desorption of pyridine from samples of H-EU-1
It can be seen from Figure 5.11 that there were two significant weight losses, which occurred in approximately the same temperature ranges for all the pyridine/EU-1 systems investigated. This procedure can only show the distribution of acid site strengths, it does not identify Lewis or Brönsted acidity. This could be done by infrared spectroscopy [10].

The first weight loss can be attributed to unbound pyridine, the boiling point of which is 388K, and physisorbed pyridine. There may also be a small amount of air and water. The high temperature weight loss can be attributed to pyridine molecules which were chemisorbed onto acidic sites.

Pyridine desorption from a sample of H-ZSM-5 was observed over similar temperature ranges by Parker et al. [11]. They obtained a good agreement between the number of molecules of pyridine chemisorbed with the number of aluminium atoms present per unit cell. Table 5.9 gives the
number of pyridine molecules chemisorbed per aluminium atom for each sample. The deviation from the expected value of 1 pyridine molecule per aluminium indicates that some of the aluminium sites were inaccessible to the pyridine molecules. This could arise if one of the EU-i side pockets contained two acid sites. It is just possible to fit two pyridine molecules, which have dimensions similar to that for benzene (0.585nm x 0.34nm [12]), side by side in one of the pockets, but whether this would occur will depend on the relative locations of the aluminium atoms. Adsorption of a smaller basic molecule such as ammonia may result in a one to one relationship between the sorbed molecules and the aluminium atoms.

5.3.3.2 Aluminophosphate AlPO₄-5

The desorption of pyridine from three batches of AlPO₄-5 (2P/0, ET/2, and PT/2) is shown in Figure 5.12 as the weight loss from the preadsorbed samples as a function of time.
Figure 5.12 Thermal desorption of pyridine from samples of AlPO₄-5
Table 5.10 Thermal analysis data of AlPO₄-5 samples loaded with pyridine

<table>
<thead>
<tr>
<th>temperature range /K</th>
<th>2P/0</th>
<th>PT/2</th>
<th>ET/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>298-353</td>
<td>4.12</td>
<td>4.02</td>
<td>5.11</td>
</tr>
<tr>
<td>353-728</td>
<td>9.60</td>
<td>10.49</td>
<td>9.87</td>
</tr>
<tr>
<td>total % weight loss</td>
<td>13.72</td>
<td>14.51</td>
<td>14.98</td>
</tr>
</tbody>
</table>

It can be seen that the behaviour is unlike that of H-EU-1 samples and only a low temperature weight loss was observed. This must be due to unbound and physisorbed pyridine. It was preceded by a small weight loss, probably due to the removal of adventitious water vapour.

A low temperature weight loss, covering the boiling point of the adsorbed base, is the expected result for a sample that does not have any strong acid sites. The results obtained are in agreement with the observations by Xu Quinha et al. [13] and Hedge et al. [14] in their work on the temperature programmed desorption of ammonia from samples of AlPO₄-5. Both groups reported a single desorption peak.

The greater amount of pyridine adsorbed in the samples PT/2 and ET/2, both spherical crystal agglomerates, was probably due to the larger external surface area offered by the mass of tiny crystallites, compared to the bundles of
larger rods that form the barrel shaped crystals of 2P/O (Section 4.2.3.5). Further adsorption studies on samples of the two morphologies would be required to confirm this.

The results in Figure 5.12 are consistent with the strictly alternating aluminium and phosphorus framework of the aluminophosphate molecular sieves, which does not allow for the formation of the strong acid sites that are present in aluminosilicate molecular sieves. They also indicate that the part of the sample that gives rise to the deviation from the baseline in the X-ray diffraction patterns, and is thought to be amorphous (Section 4.2.3.1.1), does not make a significant contribution to the acidic properties of the samples. These AlPO₄-5 samples are therefore expected to show little or no activity in the isomerisation of n-butenes, in comparison to the H-EU-1 samples.

These pyridine desorption results are also consistent with the butene desorption investigation, in that in both cases, adsorbate interaction was weaker with AlPO₄-5 than with EU-1. However no further light has been thrown on the location of the butene polymerisation, although it seems unlikely that it occurs on strong acid sites on the amorphous component.
5.4 References


[4] Reference 2, Chapter 4


CHAPTER 6
Degradation of Aluminophosphate Molecular Sieves by Aqueous Salt Solutions

6.1 Introduction

An investigation into the acidic nature of the aluminophosphate A1PO₄-5 using an ion-exchange procedure [1] revealed an interesting effect. This procedure involved making a slurry of a sample of A1PO₄-5 in an aqueous solution of sodium chloride, filtering the slurry after 24 hours, and then determining the acidity of the mother liquor by potentiometric titration against a standard solution of sodium hydroxide.

The pH of the mother liquor after filtration was 2.65. The titration required 0.68 mmol NaOH g⁻¹ A1PO₄-5 to give an endpoint at pH 6.1. This quantity of NaOH was much greater than expected, given that the neutral aluminophosphate framework should not exhibit significant acidity, and is in line with values reported for acid catalysts. For example, Gordon [2] measured strong acid endpoints of 0.60 mmol NaOH g⁻¹ H-ZSM-5, 0.89 mmol NaOH g⁻¹ H-mordenite, 0.87 mmol NaOH g⁻¹ H-ferrierite, and 0.29 mmol NaOH g⁻¹ H-EU-1. Skeels and Flank [3] recorded a range of total acidity titrated endpoints between <0.015 and 0.57 mmol NaOH g⁻¹ ZSM-5, the result being dependant upon the procedure for formation of the hydrogen form.

The X-ray powder diffraction pattern of the dry A1PO₄-5 after filtration revealed that the crystallinity of the sample had been reduced in comparison to that for the
sample before ion exchange, and also that the dense phase AlPO₄-tridymite had formed.

The instability of the AlPO₄-5 structure to hydrothermal treatment and extremes of pH [4] has already been illustrated in Section 2.2.4.1. The X-ray diffraction result suggests that the AlPO₄-5 structure is also unstable in aqueous solutions of NaCl. In this chapter, work on the effect of other aqueous salt solutions on the crystallinity of AlPO₄-5, AlPO₄-11, and AlPO₄-25 will be described. These investigations were pursued because of their possible implication for aluminophosphate synthesis, and also as a basis for future sorption studies, particularly the imbibition of salts from aqueous salt solutions [5]. Although aluminophosphate molecular sieves can be synthesised from reaction mixtures that can contain simple inorganic anions (Cl⁻, Br⁻, etc), their presence offers few advantages and tends to produce dense phases [6,7]. It is noteworthy that aqueous salt solutions were found to be "inappropriate" for the removal of tripropylamine from as-synthesised AlPO₄-5 [8]; (no further details were given).

The practical work in this chapter was carried out jointly with Dr. C.D. Williams.

6.2 Experimental
6.2.1 Synthesis of Aluminophosphates

AlPO₄-5 was crystallised at 423K from a gel of composition

\[ 2\text{Pr}_3\text{N} \quad \text{P}_2\text{O}_5 \quad \text{Al}_2\text{O}_3 \quad 40\text{H}_2\text{O} \]

in a stirred one litre autoclave. The preparative procedure
was the same as that described in Section 4.2.2.1. No gel aging was involved. The product obtained after 24 hours was washed, dried, and calcined for 16 hours at 823K. A second preparation was carried out by an identical procedure from a gel of composition

$$1.2\text{Pr}_3\text{N} \ 0.8\text{Pr}_4\text{NBr} \ \text{P}_2\text{O}_5 \ \text{Al}_2\text{O}_3 \ 40\text{H}_2\text{O}$$

It must be noted that these samples were not the same as those described in Chapter 4, and so, to avoid confusion, the sample prepared with a single template will be referred to as $\text{AlPO}_4\cdot5(\text{S})$, and that with the mixed template as $\text{AlPO}_4\cdot5(\text{M})$.

In both cases, X-ray powder diffraction showed the products to be good samples of $\text{AlPO}_4\cdot5$ with only slight contamination by other crystalline materials, and little evidence of amorphous impurities. Scanning electron micrographs showed that the products were mixtures of hexagonal barrel-shaped aggregates ($11 \times 8.6\mu\text{m}$) and $4.7 \times 1.4\mu\text{m}$ rod-shaped single crystals. The $\text{AlPO}_4\cdot5(\text{M})$ sample did not have the spherical aggregate habit as observed for other mixed template $\text{AlPO}_4\cdot5$ samples (Section 4.2.3.5.1). This was thought to be because the mixture was stirred during crystallisation. A small amount of amorphous material was also observed.

$\text{AlPO}_4\cdot11$ was crystallised from the composition

$$[(\text{CH}_3)_2\text{CH}]_2\text{NH} \ \text{P}_2\text{O}_5 \ \text{Al}_2\text{O}_3 \ 40\text{H}_2\text{O}$$
in a static PTFE-lined $125\text{cm}^3$ bomb for 72 hours at 473K [9]. The X-ray powder diffraction pattern was in good agreement with that for $\text{AlPO}_4\cdot11$ [9]. A scanning electron micrograph showed that the material was made of bundles of rod-like
crystals, approximately 3μm long.

AlPO₄-21 was crystallised from the composition

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \quad \text{P}_2\text{O}_5 \quad \text{Al}_2\text{O}_3 \quad 4\text{OH}_2\text{O} \]

in a stirred PTFE-lined bomb for 8 days at 473K and converted to AlPO₄-25 by calcination at 723K for 16 hours [9]. The material was shown to be free from crystalline impurities by X-ray powder diffraction and found by scanning electron microscopy to consist of broken lath-like crystals, 5-30μm long, in disordered aggregates.

All of the aluminophosphates were prepared from pseudoboehmite and Analar phosphoric acid. Tripropylamine (>99%), n-propylamine (>99%), and tetrapropylammonium bromide (>99%) were from Fluka. Di-isopropylamine (99%) was from Aldrich.

6.2.2 Treatment with Salt Solutions

The salts were Analar grade materials from BDH Ltd. Solutions were prepared with distilled water and mixed with the aluminophosphates in polypropylene bottles. In some cases, the bottles were tumbled in a thermostat bath at 298K, and in others, the mixtures were stirred at room temperature. Thereafter, the solid phase was separated by filtration, washed on the filter with distilled water, dried at 383K, equilibrated with atmospheric water vapour, and then examined by X-ray powder diffraction (Section 3.2) and scanning electron microscopy (Section 3.4). It was found to be difficult to remove all the salts from the materials treated with concentrated solutions, and it is believed that the salt ions imbibed by the molecular sieves
leached out slowly after the solid phase had been washed with distilled water.

6.3 Effects of Treatment with Aqueous Salt Solutions

6.3.1 Action of Aqueous Salt Solutions

For these experiments, 0.5g of calcined AlPO₄-5 was mixed with 25cm³ of aqueous chloride solution (0.1, 1.0, 5.0mol dm⁻³) and tumbled at 298K for 18 hours. Typical X-ray diffraction patterns of the material before and after treatment are shown in Figures 6.1 and 6.2. It can be seen that the predominant effect is a marked decrease in the peak heights; this corresponds to a breakdown of the crystal structure and the formation of amorphous material. For calcined AlPO₄-5(S) with 0.1mol dm⁻³ NaCl, there was a 43% reduction in the height of the peak at 2θ=12.9°, whereas with distilled water [1000cm³ + 1g calcined AlPO₄-5(S)], there was only an 18% reduction. The extent of the structural degradation increased with the salt concentration, but was relatively insensitive to the nature of the alkali metal cation (Na⁺ or K⁺).

In all cases, the pH of the solution phase dropped from ~5.5 to ~3.0, the largest change being observed for the highest chloride ion concentration. The pH changes suggest that phosphoric acid is released to the solution phase, and this was confirmed by positive tests for phosphate.

It can be seen by comparison of Figures 6.1 and 6.2 that the attack with 1.0mol dm⁻³ KCl was more marked for AlPO₄-5(M) than for AlPO₄-5(S), although in other
Figure 6.1 Treatment of calcined AlPO₄-5(S) with aqueous salts
Figure 6.2 Treatment of calcined AlPO₄-5(M) with aqueous salts
experiments, the reverse was observed. Scanning electron micrographs showed that the treated materials were extensively damaged and that much amorphous debris was formed. However, in the case of the AlPO₄-5(M), the original hexagonal aggregates could still be clearly discerned after treatment with 5.0mol dm⁻³ NaCl, whereas the treated AlPO₄-5(S) was in the form of amorphous-looking aggregates with sizes of up to 25μm. On subsequent calcination at 723K, the structure of the AlPO₄-5(M) was partially retained and some AlPO₄-tridymite was formed (Figure 6.2), whereas with AlPO₄-5(S), complete conversion to AlPO₄-tridymite occurred (Figure 6.1).

When the treatment with chloride solutions was repeated with uncalcined AlPO₄-5(S) and AlPO₄-5(M), there was virtually no effect on their X-ray diffraction patterns. It is not possible to tell whether the organic template stabilises the lattice against degradation or merely slows down the process by preventing access of the chloride ions to the channel system.

To test the effect of other anions, 0.5g samples of calcined AlPO₄-5(S) were mixed with 50cm³ of 5.0mol dm⁻³ solutions of NaI, NaBr, and Na₂S₂O₃ and a 1.0mol dm⁻³ solution of Na₂SO₄ and tumbled at 298K for 18 hours. All the salts had some effect on the AlPO₄-5, but the range of behaviour was quite wide. The percentage crystallinities based on the height of the peak at 2θ=12.9° are given in Table 6.1. A similar experiment with a saturated solution of Na₂CO₃ completely destroyed the AlPO₄-5(S); in this case,
### Table 6.1 Percentage crystallinities of AlPO$_4$-5(S) samples after treatment with aqueous salt solutions

<table>
<thead>
<tr>
<th>anion</th>
<th>% crystallinity$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$^-$</td>
<td>8</td>
</tr>
<tr>
<td>S$_2$O$_3^-$</td>
<td>9</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>19</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>48</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ based on peak at 2θ=12.9°

### Table 6.2 Percentage crystallinities of AlPO$_4$-11 samples after treatment with aqueous sodium salt solutions

<table>
<thead>
<tr>
<th>anion</th>
<th>% crystallinity$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$^-$</td>
<td>11</td>
</tr>
<tr>
<td>S$_2$O$_3^-$</td>
<td>30</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>47</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>70</td>
</tr>
</tbody>
</table>

$^a$ based on peak at 2θ=16.1°

Table 6.1 and Table 6.2 provide the percentage crystallinities of AlPO$_4$-5(S) and AlPO$_4$-11 samples, respectively, after treatment with aqueous salt solutions. The crystallinity values are determined based on characteristic peaks at 2θ=12.9° and 2θ=16.1°, respectively.
it is probable that the active anion was not CO$_3^{2-}$ but OH$^-$. This experiment and a similar one in which the contact time was increased to 3 days showed that the order of lattice attack is

$$\text{OH}^- > \text{I}^- > \text{S}_2\text{O}_3^{2-} > \text{Br}^- > \text{Cl}^-$$

Similar 18 hour treatments of AlPO$_4$-11 and AlPO$_4$-25 showed the same order of attack, but the effect was less than for AlPO$_4$-5 and least for the narrow pore AlPO$_4$-25. The percentage crystallinities for AlPO$_4$-11 based on the diffraction line at $2\theta=16.1^\circ$ are given in Table 6.2, and for AlPO$_4$-25 based on the line at $2\theta=15.1^\circ$ are in Table 6.3.

### Table 6.3 Percentage crystallinities of AlPO$_4$-25 samples after treatment with aqueous sodium salt solutions

<table>
<thead>
<tr>
<th>anion</th>
<th>% crystallinity$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{I}^-$</td>
<td>40</td>
</tr>
<tr>
<td>$\text{S}_2\text{O}_3^{2-}$</td>
<td>74</td>
</tr>
<tr>
<td>$\text{Br}^-$</td>
<td>91</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>91</td>
</tr>
</tbody>
</table>

$^a$ based on peak at $2\theta=15.1^\circ$

6.3.2 Action of Aqueous Acids

Treatment of calcined AlPO$_4$-5(S) with 1.0 mol dm$^{-3}$ HNO$_3$ acid by tumbling for 1 day at 298K had a much smaller effect than that produced by 1.0 mol dm$^{-3}$ KCl (percent
crystallinities KCl (56%), HNO₃ (72%), and it appears that the marked effect observed with HCl [4] was due primarily to the chloride ion. Uncalcined AlPO₄-5(S) was not attacked by 1.0 mol dm⁻³ HNO₃. Treatment of calcined AlPO₄-5(S) with 1.0 mol dm⁻³ H₃PO₄ at 298K had very little effect on the X-ray diffraction pattern; the height of the major peak at 2θ=22.4° remained unchanged, whereas that at 2θ=19.7° showed a slight decrease in intensity.

6.3.3 Damp Materials

It was observed that samples of calcined AlPO₄-5 that had been stored at room temperature for seven months showed changes in their X-ray diffraction patterns. A new line appeared at 2θ=21.6°, and there was a 44% reduction in crystallinity (based on the diffraction line at 2θ=12.9°). It seemed possible that these changes could have been promoted by the presence of small quantities of water.

To simulate and speed up this process, calcined AlPO₄-5(S) (0.5g) was mixed with water (2g) and held in a sealed container at 368K for 18 hours, 2 days, and 7 days. No new peaks were observed in the X-ray powder diffraction pattern, but there was a decrease in the crystallinity of the sample; the percent crystallinities based on the peak at 2θ=12.9° were 83%, 76%, and 53%, respectively (Figure 6.3).

In a corresponding experiment with uncalcined AlPO₄-5(S), no effect on the X-ray powder diffraction pattern was observed. When calcined AlPO₄-5(S) was held at 368K without the addition of water, the X-ray powder diffraction pattern remained unchanged after 2 days, but
Figure 6.3 Treatment of AlPO₄-5(S) with water at 368K
new peaks due to AlPO₄-tridymite appeared after 7 days and there was a 21% decrease in the crystallinity AlPO₄-5. When the original experiment with calcined AlPO₄-5(S) was repeated with 5.0 mol dm⁻³ aqueous NaCl, a total collapse of the AlPO₄-5 structure was observed at 368K.

When calcined AlPO₄-11 (0.5 g) was treated with water (2 g) at 368K, there was a significant decrease in crystallinity (Figure 6.4). In contrast, calcined AlPO₄-25 in an identical experiment remained unchanged after 2 days at 368K (Figure 6.5), although a slight increase in amorphous content was observed after 7 days. It seems likely that most microporous aluminophosphates will be susceptible to attack by water and that the rate of reaction will be markedly dependent on the framework structure.

6.4 Conclusion

These effects follow a clear general pattern of behaviour. The aluminophosphate molecular sieves are attacked by water especially when in their calcined form, and even prolonged contact at room temperature can have a deleterious effect. The rate of degradation and transformation becomes accelerated in the presence of soluble salts, and although the exact mechanism was not determined, it would suggest that their action was likely to be catalytic in nature. Although the extent of action for the different anions is varied and may be related to the ease in which they can enter the channels, the potency of the thiosulphate anion suggests that the mechanism may
Figure 6.4 Treatment of AlPO₄-11 with water at 368K
untreated calcined AlPO$_4$-25

after treatment for 2 days

Figure 6.5 Treatment of AlPO$_4$-25 with water at 368K
involve nucleophilic attack.

Although it is believed that anions are primarily responsible for the rapid aqueous degradation of the aluminophosphates, it is clear that cations must also have some effect. In some cases, it appears that the potency of the anion can be mitigated by organic cations. Hence AlPO₄-5 can be synthesised in the presence of bromide ions, and the imbibition of tetrapropylammonium bromide from aqueous solutions by AlPO₄-5 can be studied with only slight lattice damage [5].

The microporous aluminophosphates are much more reactive than are the crystalline microporous silicas, and it is apparent that a whole range of structural changes and dissolution processes are possible when they are contacted with water or with aqueous salt solutions. This reactivity must be taken into account when they are used, and when they are stored for a long period of time. It seems likely that the kinetics of degradation will be dependent upon the quality of the as-made crystals, but without further work it is not possible to assess the variability of the process. In any case it would seem sensible to keep the aluminophosphate molecular sieves dry, and to store them in their as-made form.
6.5 References


7.1 Introduction

7.1.1 The Mechanism of the \textit{n}-butene Isomerisation Reaction

The interconversion of the \textit{n}-butenes is a reaction of great interest. The selective nature and the kinetics of the reaction, whilst not requiring extreme conditions, has helped in the investigation of many catalysts.

If \textit{but-1-ene} and \textit{cis} and \textit{trans} \textit{but-2-ene} are the only compounds observed throughout the reaction, then it can be assumed that the interconversion follows the triangular reaction scheme shown in Figure 7.1 [1]. This fits in with many of the proposed mechanisms for the reaction over various catalysts; however if there is no observed interconversion between two of the isomers, then the relevant individual rate constant can be assumed to be zero. Obviously the product ratios are linked with the individual rate constants, and thus Haag and Pines [1] were able to formulate a method to determine the relative values for $k_1-k_6$.

The \textit{but-1-ene} isomerisation reaction over various types of catalysts produces different product ratios, which has been explained through the various reaction mechanisms.

Over basic catalysts, high \textit{cis/trans} ratios were observed from \textit{but-1-ene} [1-3]. Extraction of a proton from \textit{C}_3 of \textit{but-1-ene} results in the formation of a $\pi$-allylic species. There are two conformers of this species that can occur; a \textit{cis} and a \textit{trans} form. Interconversion between the
Figure 7.1 Relationship between individual rate constants for the reversible parallel reactions in the interconversion of the but-1-ene isomers [1]
two is very difficult due to restricted rotation around the C$_2$-C$_3$ bond. The cis allylic species is more stable on the catalyst surface, hence a high initial cis/trans ratio is observed.

Initial cis/trans ratios of less than 1 are observed over catalysts with a metal function [4-6]. The reaction mechanisms over such catalysts are thought to proceed through a secondary butyl radical intermediate [4]. Free rotation about all the bonds is possible, so both positional and geometric isomerisation can occur. The radical adsorbed onto the catalyst surface exists in different conformers; that which results solely in cis but-2-ene requiring the highest energy. Thus a low cis/trans ratio is observed, which increases as the temperature of the reaction increases.

Various mechanisms have been proposed for the reaction over acidic catalysts. Turkevich and Smith [7] suggested that there was a transfer of hydrogens between the molecule and the catalyst, known as the "hydrogen switch" mechanism, that resulted in a double bond shift. However, this does not allow for direct cis to trans interconversion.

Lucchesi et al. [8] observed predominantly cis but-2-ene at low but-1-ene conversions. They proposed a mechanism in which the isomerisation was

\[ \text{but-1-ene} \rightarrow \text{cis but-2-ene} \rightarrow \text{trans but-2-ene} \]

A proton $\pi$ complexes to the double bond of the but-1-ene molecule, and C$_3$ donates a proton to the catalyst. Restricted rotation means that only the cis isomer is formed directly. The cis form is converted to the trans one.
through a π complex of the cis molecule which results in geometric isomerisation.

Haag and Pines [9] also observed a high initial cis/trans ratio from but-1-ene, with cis/but-1-ene > 1 from the trans isomer, and trans/but-1-ene = 1 from cis but-2-ene. They proposed that a proton was added to the n-butene to form a common intermediate in the secondary butyl carbonium ion, and that the proton was eliminated via a slow rearrangement to one of three π complexes, with subsequent loss of the proton. The relative energies of the three π transition states, one for each of the n-butene isomers, is in the order

\[
\text{cis but-2-ene} < \text{trans but-2-ene} \approx \text{but-1-ene}
\]

explaining the product ratios.

Hightower and Hall [10] observed that, for but-1-ene over SiO₂-Al₂O₃, the initial cis/trans ratio was relatively insensitive to the source of the catalyst, the silica-alumina ratio, the degree of catalyst poisoning, and the reaction temperature. They proposed that the mechanism must involve a common intermediate, thus allowing a direct pathway between all the isomers. The proposed intermediate was the secondary butyl carbonium ion, shown in Figure 7.2. The carbons C₁, C₂, and C₃ all lie in the same plane, whereas the C₄ methyl group extends away from the catalyst surface. Rotation about the C₂-C₃ bond can be limited by steric hindrance, and also by restriction if the reaction takes place in narrow channels. The secondary carbonium ion is formed from but-1-ene by the addition of a proton to C₁, and the but-2-ene isomer formed when a proton is removed from
Figure 7.2 The secondary butyl carbonium ion intermediate formed during the but-\textit{n-ene} isomerisation reaction on acidic catalysts
C₃. Loss of Hₐ (Figure 7.2) forms cis but-2-ene, whilst loss of H₉ results in the trans isomer. Though these two hydrogens are geometrically different, they are energetically the same, hence there is an equal chance of either removal and temperature independent initial cis/trans ratios close to unity should be observed.

The formation of but-1-ene from the secondary butyl carbonium ion involves the loss of one of the three C₁ hydrogens, and thus an initial but-1-ene/but-2-ene of greater than unity would be expected starting from a but-2-ene isomer. However, the strength of a C-H bond on a primary carbon is greater than on a secondary carbon, which results in but-1-ene/but-2-ene ratios of less than unity. Hightower and Hall [11] calculated a but-1-ene/but-2-ene ratio of 0.75 for cis but-2-ene isomerisation over a silica-alumina catalyst, and obtained experimental results of 0.43 to 1.0

Thus the product ratio can be used as a guide to the type of catalyst and the mechanism. However it cannot be relied upon as the sole determinant.

The acid-base nature of catalysts can be characterised from the shape of the reaction profiles of the n-butene isomerisation reaction over said catalysts [12,13]. The reaction profiles are drawn as triangular composition diagrams, using data from reactions in which the initial reactant gas contains various percentage compositions of two of the isomers. Three shapes of profiles are obtained; the trans-convex, the cis-convex, and the rake, which respectively classify acid catalysts, basic catalysts, and
catalysts which show predominantly acidic characteristics.

7.1.2 Interpretation of Catalytic Data

The apparatus used and the experimental procedure has been described in Section 3.2.5.

The raw data from the butene isomerisation experiments was obtained in the form of integrals of the peaks generated from the detection of the butenes by the gas chromatograph (GC). The area of each peak is proportional to the amount of hydrocarbon that passes through the flame ionisation detector (FID). The FID is capable of detecting most organic compounds, but has different sensitivities for each hydrocarbon. Hence it is necessary to determine the sensitivity factors for the hydrocarbons of interest.

The sensitivity factors were calculated by the following method. A known pressure of the pure butene was sampled through the GC three or more times, and the average of the peak areas calculated. This was carried out for a range of pressures, and in the present case was repeated for each butene. The peak area, A, is directly proportional to the pressure, P, according to the relationship

\[ A = kP \]  

(7.1)

Hence a plot of area against pressure produces a straight line of slope k for each alkene (Figure 7.3).

The total pressure in the system, \( P_{\text{tot}} \), is

\[ P_{\text{tot}} = P_B + P_C + P_T \]  

(7.2)

where the subscripts represent but-1-ene, cis but-2-ene, and trans but-2-ene respectively. The concentration of each alkene can be represented as a fraction of the total.
Figure 7.3 Relative sensitivities of the GC FID to the but-n-ene isomers
concentration, and hence, from equation 7.2, the concentration of but-1-ene, $x_b$, is

$$x_b = \frac{P_B}{P_{tot}}$$  \hspace{1cm} (7.3)

Using equation (7.1)

$$x_b = \frac{\frac{A_B}{k_B}}{\frac{A_B}{k_B} + \frac{A_C}{k_C} + \frac{A_T}{k_T}}$$  \hspace{1cm} (7.4)

which rearranges to

$$x_b = \frac{A_B}{A_B + \frac{k_B}{k_C}A_C + \frac{k_B}{k_T}A_T}$$  \hspace{1cm} (7.5)

From this, it can be seen that the sensitivity factor for but-1-ene, the reactant, is assumed to be unity, and the sensitivities for the products are calculated relative to this. The sensitivities determined for the equipment used in this work for the cis and trans isomers were 0.97 and 0.94 respectively.

The corrected peak areas are converted to relative concentrations as percentages of the total peak area, i.e. total butene concentration. This is done so that the errors caused by small variations in the sample size, and also by the small amount of electron drift are avoided. Such errors become apparent when individual concentrations are determined, e.g. when sampling for the sensitivity factor, and are in the region of ±3%.

From these relative concentrations, the cis/trans (product) ratios can be calculated. By plotting these against time, a product profile can be obtained.
Extrapolation of this back to \( t=0 \) gives the initial product ratio \((\text{cis}/\text{trans})_0\).

The rate constant for the reaction is calculated as the disappearance of \( \text{but-1-ene} \). The reaction is reversible and can be written as

\[
\begin{align*}
\text{But-1-ene} & \xrightleftharpoons[k_{-1}]{k} \text{But-2-ene} \\
\text{At } t=0 & \quad [\text{But-1-ene}]_0 = a \quad [\text{But-2-ene}]_0 = 0 \\
\text{At } t=t & \quad [\text{But-1-ene}]_t = x \quad [\text{But-2-ene}]_t = a-x
\end{align*}
\]
as the amount of \( \text{but-1-ene} \) is being directly measured.

At \( t=\infty \) \( [\text{But-1-ene}]_\infty = x_e \quad [\text{But-2-ene}]_\infty = a-x_e \)

The rate of disappearance of \( \text{but-1-ene} \), \( -\frac{dx}{dt} \), is

\[
-\frac{dx}{dt} = kx - k_{-1}(a-x) \quad (7.6)
\]

At equilibrium

\[
0 = kx_e - k_{-1}(a-x_e) \quad (7.7)
\]

which rearranges to

\[
k_{-1} = \frac{kx_e}{(a-x_e)} \quad (7.8)
\]

Substituting (7.8) into (7.6) gives

\[
\frac{dx}{dt} = kx - k_{-1}\frac{x_e}{a-x_e}(a-x) = \frac{ka(x-x_e)}{(a-x_e)} \quad (7.9)
\]

This is rearranged and integrated.

\[
(a-x_e) \int \frac{dx}{(a-x_e)} = -ka \int dt \\
(a-x_e) \ln(x-x_e) = -kat + \text{constant} \quad (7.10)
\]

287
At \( t=0, x=a, \) which, in equation 7.10 gives
\[
(a-x_e) \ln(a-x_e) = \text{constant} \quad (7.11)
\]
Substituting (7.11) in (7.10) and rearranging gives
\[
\ln(x-x_e) = \frac{k_a t}{(a-x_e)} + \ln(a-x_e) \quad (7.12)
\]
A plot of \( \ln(x-x_e) \) against time gives a straight line, from the slope of which a value for \( k \) is obtained. Division of this value by the mass of catalyst, in grams, used gives the apparent rate constant, \( k \), for the reaction per gram of catalyst, in units of time\(^{-1}\).

Values for \( x_e \) are obtained using a computer program based on the method of Kalló and Schay \([14,15]\). The equilibrium constants \( K_{te} \) and \( K_{ti} \) are calculated for the temperature range 298K to 523K, and from these the equilibrium concentrations are obtained by solving the set of simultaneous equations
\[
K_{te} = \frac{c}{t} \quad (7.13)
\]
\[
K_{ti} = \frac{b}{t} \quad (7.14)
\]
\[
b + c + t = 1 \quad (7.15)
\]
where \( b, c, \) and \( t \) are the relative equilibrium concentrations of the butenes.

Evaluation of the rate constant, \( k \), at different reaction temperatures, \( T \), can be used to obtain the apparent activation energy, \( E_a \), for the reaction from the Arrhenius equation
\[
\frac{E_a}{RT} = k = A e \quad (7.16)
\]
where \( R \) is the gas constant, and \( A \) is the frequency factor.
for the reaction. This can be rearranged to a more convenient form

$$\ln k = \ln A - \frac{E_a}{RT} \quad (7.17)$$

By plotting $\ln k$ against $1/T$ gives a line, from the slope of which the apparent activation energy, $E_a$, can be evaluated.

Butenes can become irreversibly bound to the zeolite surface (Section 5.1.2.1, [16,17]) which may lead to the deactivation of the catalyst. An insight into how the various factors investigated affect the polymerisation is gained by subjecting the final samples to thermal analysis to determine the hydrocarbon content as a weight percent.

7.1.3 General Characteristics of the Isomerisation Reaction

The aim of this section is to explain and show in graphical form the general characteristics that were observed for the isomerisation reaction.

A typical reaction mixture composition for the isomerisation of but-1-ene over H-EU-1 is shown in Figure 7.4. In all of the experiments carried out with but-1-ene, cis and trans but-2-ene were the only products observed; the cis/trans ratio is shown as a function of the reactant converted for a typical reaction in Figure 7.5. As mentioned in Section 7.1.1, the initial product ratio, $(c/t)_0$, can be used in the interpretation of the reaction mechanism. This value is obtained by the extrapolation of the product ratio curve to zero conversion. An example of this is shown in Figure 7.5, which gives a value for $(c/t)_0$. 289
Figure 7.4 Relative composition of recirculating gas during a typical but-1-ene isomerisation reaction on H-EU-1
Figure 7.5  cis/trans product ratio for a typical but-1-ene isomerisation reaction on H-EU-1
of ~1.1.

The plot given by Equation 7.12 to determine the first order rate constant is shown in Figure 7.6. A straight line was not obtained, contrary to expectation, and this was the case for the majority of the experiments. As only but-2-enes were the observed products, and $d[\ln(x-x_e)]/dt$ (Figure 7.6) rarely appeared to be constant, it would suggest that

(i) from the very outset of the reaction, the active sites were being deactivated/poisoned;

(ii) but-1-ene was being converted to another product which was not observed in the gaseous phase.

The most probable explanation is that polymerisation of the n-butenes occurs on the zeolite surface, forming products which cannot desorb into the gas phase. Consequently, this will restrict the passage of the butene molecules through the channel system. The formation of a saturated surface species has been observed [16,17], by IR spectroscopy, during the isomerisation of but-1-ene on zeolite Y (Section 5.1.2.1). This was accompanied by a decrease in the hydroxyl stretching band at 3640 cm$^{-1}$, the strong acid site in zeolite Y. If similar behaviour occurred in the current investigation, then of the two suggestions above, (i) would occur as a result of (ii).

Further evidence of a strongly adsorbed species is given in Figure 7.7. This shows the thermal analysis of a sample of H-EU-1 after an isomerisation reaction. After the first endothermic weight loss of water, there follows two exothermic weight losses which are probably due to strongly
Figure 7.6 Typical reaction rate plot for but-1-ene isomerisation on H-EU-1
Figure 7.7 Typical thermal analysis trace of a sample of H-EU-1 after a but-1-ene isomerisation reaction.
adsorbed organic material. The second weight loss could be due to carbonaceous material bound directly to the acid sites, whilst the first loss may result from material breaking off from the oligomer more than one carbon from the binding carbon. That a temperature of 670K was needed to remove all of the organic material indicates that the surface/adsorbate interaction was very strong indeed.

Further investigation of the contaminated samples using infrared spectroscopy would help to clarify the nature and location of this carbonaceous residue.

Although the catalysts seemed to be being deactivated from the outset, the initial conversion must take place on relatively unpoisoned sites, and so the initial rate constant was calculated over the first thirty seconds of the reaction, and is denoted throughout as $k_{30}$.

7.2 Zeolite EU-1
7.2.1 Assessment of System Reliability and Activation Optimisation

In order to determine that the results obtained from the reaction were a function of the difference in samples, or a predefined change in the operational parameters, but-1-ene isomerisation reactions were carried out over samples from the same batch of EU-1 under identical pretreatment and reaction conditions.

Figures 7.8 and 7.9 show the results of the reaction carried out over H-EU-1 (ICIEU1) at 366K. It can be seen that there was good agreement between the results of these runs, indicating that system was capable of producing
Figure 7.8 Reproducibility of the reaction rate for but-1-ene isomerisation on H-EU-1 (ICIEU1)
Figure 7.9 Reproducibility of the product ratio for but-1-ene isomerisation on H-EU-1 (ICIEU1)
reliable results.

The total pressure of the butenes within the system must govern the percentage of the surface area of the catalyst covered, in accordance with the respective adsorption isotherm. Ballivet et al. [18] showed that an increase in initial reaction pressure over silica-alumina catalysts was accompanied by an increase in the rate of product formation.

<table>
<thead>
<tr>
<th>run number</th>
<th>reactant pressure /Nm⁻²</th>
<th>10²k₃₀/s⁻¹</th>
<th>(C₀/t₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38120 (normal)</td>
<td>1.39</td>
<td>0.76</td>
</tr>
<tr>
<td>2</td>
<td>54860 (increased)</td>
<td>1.64</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 7.1 Rate constants and initial product ratios for but-1-ene isomerisation over H-EU-1 (BH3) at different reactant pressures

Table 7.1 and Figure 7.10 compare the results obtained from experiments in which different initial pressures of but-1-ene were used in the reaction at 323K over samples of H-EU-1 (BH3). All other pretreatment and reaction conditions were identical. It can be seen that the reaction at lower pressure had a lower k₃₀ value than that at the higher pressure (Table 7.1), although the difference observed was very small.

The high silica (dealuminated) samples used by Ballivet [18] showed reaction rates that had a Langmuir
Figure 7.10 Effect of increased initial reactant concentration on the product ratios for but-1-ene isomerisation on H-EU-1 (BH3)
type dependence upon the initial reaction pressure; hence the higher the pressure, the smaller the increase in reaction rate. It may be that a Langmuir type dependence is operational in this system, and the pressures used in these experiments are close to the plateau region. This would explain the small difference in rates for a 44% increase in reaction pressure. Indeed, the pressures used in this study were higher than those in Ballivet's work. Further experiments at lower pressures would be needed to verify if there was a Langmuir dependence in this system. Ballivet suggests that, as the rate of isomerisation is proportional to the surface coverage, then the reaction in the adsorbed state is a slower step than reactant adsorption or product desorption.

Figure 7.10 shows a good agreement between the product ratios as the reaction progresses, an indication that in this case it was a function of but-1-ene conversion, and not of the reactant pressure.

A low initial product ratio which rises during the reaction, as observed here, has previously been explained [19] by the slower diffusion of the bulkier cis isomer (0.55nm) than the trans isomer (0.48nm), with subsequent secondary isomerisation of the cis molecule to the more thermodynamically stable trans form. Indeed, comparison of the critical diameter of the main EU-1 channel, 0.58nm, with the diameters of the two molecules supports this.

The higher pressure did not seem to increase the oligomerisation on the surface as may have been expected (Table 7.2). The results showed a similar amount of residue
Table 7.2 Thermal analysis of H-EU-1 (BH3) after but-1-ene isomerisation at different reactant pressures

<table>
<thead>
<tr>
<th>run number</th>
<th>1st weight loss</th>
<th>2nd weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/°C</td>
<td>/% w/w</td>
</tr>
<tr>
<td>1</td>
<td>193</td>
<td>4.9</td>
</tr>
<tr>
<td>2</td>
<td>192</td>
<td>4.7</td>
</tr>
</tbody>
</table>

A temperature at which weight loss starts
remained on the catalyst after each reaction. The second weight loss is thought to arise from carbon residue bound directly to the acid sites (Section 7.1.3). As the samples used were of the same synthesis batch, then they should have the same number of acid sites, which is reflected in the similarity of the second weight losses.

Samples of the EU-1 batch BH2 were tested at the three stages of activation in order to determine the catalytic activity of the sample at each particular stage. The values obtained for $k_{30}$ (Table 7.3) increased with the acidity of the catalyst as expected. No significant reaction was observed with the 'as-synthesised' sample, an indication of the lack of acid sites on the external surface of the crystallites. The ratio of $k_{30}$ values for the calcined and ion-exchanged samples was similar to the ratio of H+ content.
Table 7.3 Rate constants and initial product ratios for but-1-ene isomerisation over EU-1 (BH2) at various stages of activation

<table>
<thead>
<tr>
<th>sample</th>
<th>$10^2k_{30}$/s$^{-1}$</th>
<th>$\frac{c}{t_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na, HEX)-EU-1</td>
<td>no reaction</td>
<td></td>
</tr>
<tr>
<td>(Na, H)-EU-1</td>
<td>3.21</td>
<td>0.63</td>
</tr>
<tr>
<td>H-EU-1</td>
<td>4.04</td>
<td>0.62</td>
</tr>
</tbody>
</table>

in these samples (Table 4.7).

A comparison of the initial reaction rates in Tables 7.1 (BH3) and 7.3 (BH2) shows that BH2 seems to be more active than BH3. The Si/Al ratio for the two batches was near identical (Table 4.7), and so cannot be the basis for the increased activity. The most likely cause is the difference in the average crystallite dimensions in the samples. BH2 was shown to have a much smaller range than BH3 (Section 4.1.3.4). Harrison et al. [19] observed an increase in activity for but-1-ene isomerisation over Nu-10 on reduction of average crystal size. Smaller crystals give an increased apparent surface area, with a greater possibility of acid sites on the external surface, and also shorter diffusion paths to the internal catalytic sites. This latter point would result in an increased rate of reaction, as was observed here, for those reactions in which diffusion is the rate limiting step.

This explanation is at variance with that used earlier.
to explain the pressure dependence of the results. An alternative explanation is that, in the reactions at different but-1-ene pressures, the higher pressure produced an increased initial rate of diffusion, the result of which was a greater initial reaction rate, i.e. diffusion was the rate limiting step. Further studies in which the pressure of reactant is varied over samples of different average crystal size would help clarify this.

Although the initial product ratios were similar for the reaction over the samples of calcined and ion-exchanged EU-1 (Table 7.3), there was a small divergence in their paths as the reaction proceeded (Figure 7.11), the (Na,H)-EU-1 sample having the higher cis isomer content. Differences in cis/trans ratios may be caused by

(i) different reaction mechanisms;

(ii) the selective adsorption of one of the isomers;

(iii) diffusional constraints; or

(iv) restricted transition state selectivity in favour of one of the isomers.

As the only difference between the samples was the replacement of Na' with H', (i) can be ruled out, as the rate constants (Table 7.3) implied that only the protonated sites were active, and hence (iv) must also be discounted as the mechanisms appear to be the same.

Results in Section 4.1.3.5 showed that a sample of BH3 containing Na' had a larger Langmuir constant than an H' ion-exchanged sample, i.e. it had a stronger adsorbent/adsorbate interaction (Section 5.1.1). In addition, as shown in Figure 5.1, EU-1 has a greater
Figure 7.11 Product ratios for but-1-ene isomerisation on EU-1 (BH2) at various stages of activation.
affinity for *trans* but-2-ene than for the *cis* isomer. A combination of these two factors may explain why (Na,H)-EU-1 gives a product with a lower *trans* content than H-EU-1.

<table>
<thead>
<tr>
<th>sample</th>
<th>1st weight loss</th>
<th>2nd weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na,HEX)-EU-1</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(Na,H)-EU-1</td>
<td>180 5.2</td>
<td>342 1.4</td>
</tr>
<tr>
<td>H-EU-1</td>
<td>200 4.2</td>
<td>345 1.3</td>
</tr>
</tbody>
</table>

a temperature at which weight loss starts

*Table 7.4* Thermal analysis of EU-1 (BH2) after but-1-ene isomerisation at various stages of activation

Further evidence for this may be seen in *Table 7.4*, in that the (Na,H)-EU-1 sample contained more of the less strongly bound residue, removal of which began at a lower temperature than observed previously. This suggests that there was an organic species present other than usually seen, possibly the *trans* isomer.

Figure 7.12 and Tables 7.5 and 7.6 show the results for samples of calcined EU-1 (BH3) exchanged with equal quantities of hydrochloric acid solutions with different molarities (10cm³ HCl g⁻¹ zeolite for two hours in a rotating waterbath at 298K).
Figure 7.12 Effect of ion exchange procedure on the catalytic behaviour of EU-1 (BH3) to 
the but-1-ene isomerisation reaction

- Calcined only
- 0.01M HCl
- 0.1M HCl
- 1.0M HCl
<table>
<thead>
<tr>
<th>HCl conc</th>
<th>$10^2 k_{30} / s^{-1}$</th>
<th>$\frac{c}{T}$</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>no exchange</td>
<td>1.23</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>0.01M</td>
<td>1.49</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>0.1M</td>
<td>1.71</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>1.0M</td>
<td>1.76</td>
<td>0.58</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.5 Rate constants and initial product ratios for but-1-ene isomerisation over EU-1 (BH3) ion-exchanged with different concentrations of hydrochloric acid

<table>
<thead>
<tr>
<th>HCl conc</th>
<th>1st weight loss</th>
<th>2nd weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T /°C</td>
<td>/% w/w</td>
</tr>
<tr>
<td>no exchange</td>
<td>190</td>
<td>4.9</td>
</tr>
<tr>
<td>0.01M</td>
<td>192</td>
<td>4.5</td>
</tr>
<tr>
<td>0.1M</td>
<td>190</td>
<td>4.7</td>
</tr>
<tr>
<td>1.0M</td>
<td>190</td>
<td>4.5</td>
</tr>
</tbody>
</table>

a temperature at which weight loss starts

Table 7.6 Thermal analysis of ion-exchanged EU-1 (BH3) after but-1-ene isomerisation

It can be see that an increase in acid strength gave rise to a higher value for $k_{30}$ (Table 7.5), for concentrations up to 0.1M. This indicates that the ion-exchange treatment with this solution was sufficient to effect the full acidic strength of the catalyst.
Figure 7.12 shows that, in the main, the product ratio was dependant upon the amount of but-1-ene converted. One noticeable feature was that \((c/t)\) for the non-exchanged sample was higher than for the others, but its \(c/t\) values merged with these at higher conversions. This contradicts the earlier observation for BH2 (Figure 7.11). If the reaction over the non-exchanged sample had been allowed to go further, then it would probably be seen that the \(c/t\) ratio had levelled out, i.e. that it was already close to its maximum. The higher product ratio appearing earlier in the course of the reaction than observed with BH2 may be caused by the high Na' content in the calcined BH3 samples (Section 4.1.3.3) which results in a greater adsorption of the trans isomer, as discussed earlier. Table 7.6 shows that the (Na,H)-EU-1 did have slightly more of the weaker bound organic species than the acid exchanged samples, although the difference was not as pronounced as that reported in Table 7.4.

It was decided that, in view of the similarity in the results for the samples exchanged with 0.1M and 1M hydrochloric acid solution, combined with the earlier evidence that the use of 1M HCl had an insignificant effect upon the Si/Al ratio of the EU-1 samples (Section 2.1.4.1 and 4.1.3.3), this strength acid should be continued to be used in the ion-exchange procedure in accordance with the procedure described in Section 4.1.2, to ensure the maximum removal of Na' ions.
7.2.2 Determination of the Activation Energy

The but-1-ene isomerisation reaction was carried out over fresh samples of two of the EU-1 catalysts, ICIEU1 and BH2, at various temperatures in order to determine the activation energy ($E_a$) for these systems (see Section 7.1.2).

<table>
<thead>
<tr>
<th>reaction temperature /K</th>
<th>$10^3k_0$/s$^{-1}$</th>
<th>$(C)/t_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>389</td>
<td>4.19</td>
<td>1.20</td>
</tr>
<tr>
<td>367</td>
<td>3.10</td>
<td>0.92</td>
</tr>
<tr>
<td>334</td>
<td>1.61</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table 7.7 Rate constants and initial product ratios for but-1-ene isomerisation over H-EU-1 (ICIEU1)

<table>
<thead>
<tr>
<th>reaction temperature /K</th>
<th>$10^2k_0$/s$^{-1}$</th>
<th>$(C)/t_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>365</td>
<td>9.78</td>
<td>0.70</td>
</tr>
<tr>
<td>323</td>
<td>4.04</td>
<td>0.60</td>
</tr>
<tr>
<td>314</td>
<td>3.19</td>
<td>0.56</td>
</tr>
<tr>
<td>294</td>
<td>1.73</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 7.8 Rate constants and initial product ratios for but-1-ene isomerisation over H-EU-1 (BH2)

The Arrhenius plot in Figure 7.13, constructed from the data in Table 7.7 yielded $E_a=19.0\pm1.0$kJ mol$^{-1}$ for ICIEU1. Likewise, $E_a=21.7\pm0.6$kJ mol$^{-1}$ was obtained for BH2.
Figure 7.13 Arrhenius plot for the but-1-ene isomerisation reaction on H-EU-1 (ICIEU1)
Figure 7.14 Arrhenius plot for the but-1-ene isomerisation reaction over H-EU-1 (BH2)
(Figure 7.14, Table 7.8). The similarity of these values suggests that the mechanism for the reaction was the same over both catalysts.

The value for the activation energy of the reaction over EU-1 was lower than those obtained by other workers for various solid catalysts including zeolites [5,6,19-23], an indication that the reaction is more favourable over EU-1. However, this "super activity" may also result in the increase in the rate of deactivation due to strong adsorption and subsequent polymerisation.

One further piece of information obtainable from the Arrhenius plots is the pre-exponential factor, or frequency number (A, equation 7.17), an indication of the activity of the catalytic sites. For ICIEU1 and BH2, values of 15.2±2.0s⁻¹ and 127.2±6.0s⁻¹ respectively were obtained. The large difference in frequency may be due to the much smaller average crystal size of the BH2 sample. This allows easier access of the molecules to the active sites through shorter diffusion paths, i.e. further indication that the reaction is diffusion controlled.

Figures 7.15 and 7.16 show the dependency of the product selectivity on the reaction temperature. In both cases, the reaction was more selective towards the cis isomer as the temperature was reduced. This was also observed by Henderson [24] for EU-1 and ZSM-23 samples, and by Harrison [23] for samples of ZSM-5, ZSM-11, and ferrierite.

This may be accounted for by a number of reasons. In Section 5.1.2.1, it was shown that the trans isomer was
Figure 7.15 Product ratios for the isomerisation of but-1-ene on H-EU-1 (ICIEU1) at different reaction temperatures.
Figure 7.16 Product ratios for the isomerisation of but-1-ene on H-EU-1 (BH2) at different reaction temperatures.
adsorbed in preference to the other isomers. As the temperature for the butene isomerisation reaction was increased, less trans but-2-ene was being adsorbed, manifested in the lower observed cis/trans ratios. The second explanation, which may be coupled with the first, is that the differing product ratios are a result of the increased diffusivities of the molecules caused by the higher reaction temperatures. In all the samples mentioned above, the effective pore diameter of the zeolite was close to the kinetic diameter of cis but-2-ene isomer, and so the diffusivity of this molecule was less than that of the trans form. Although the higher temperature will increase the rate of diffusion for all the isomers, the less restricted molecule, i.e. the trans isomer, should have a lower activation energy of diffusion [25] and hence the ratio of cis/trans diffusion will be lower at higher temperatures, as observed here.

For both samples, with the exception of the highest reaction temperature, the values for \((c/t)_0\) were essentially independent of the reaction temperature, as would be expected from a carbonium ion reaction mechanism [11]. The values of \((c/t)_0\) depend on the extrapolation of the values at higher conversions to zero conversion. For the highest reaction temperature, the extent of this extrapolation makes these values of \((c/t)_0\) relatively unreliable.

The amount of organic residue within each set of samples was found to be independent of the reaction temperature (Tables 7.9 and 7.10). These results indicate that the amount of oligomerisation was restricted by the
sample, i.e. by pore volume and number of sites for oligomerisation, and that the oligomerisation was rapid, occurring early in the reaction. Studies of this reaction system at these temperatures by infrared spectroscopy may help verify this explanation.

<table>
<thead>
<tr>
<th>Reaction temperature /K</th>
<th>1st weight loss</th>
<th>2nd weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/Kₐ¹</td>
<td>% w/w</td>
</tr>
<tr>
<td>389</td>
<td>209</td>
<td>3.0</td>
</tr>
<tr>
<td>367</td>
<td>205</td>
<td>3.1</td>
</tr>
<tr>
<td>334</td>
<td>211</td>
<td>3.0</td>
</tr>
</tbody>
</table>

A temperature at which weight loss starts

Table 7.9 Thermal analysis of H-EU-1 (ICIEU1) after but-1-ene isomerisation

<table>
<thead>
<tr>
<th>Reaction temperature /K</th>
<th>1st weight loss</th>
<th>2nd weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/Kₐ¹</td>
<td>% w/w</td>
</tr>
<tr>
<td>365</td>
<td>185</td>
<td>4.3</td>
</tr>
<tr>
<td>323</td>
<td>190</td>
<td>4.5</td>
</tr>
<tr>
<td>314</td>
<td>192</td>
<td>4.5</td>
</tr>
<tr>
<td>294</td>
<td>193</td>
<td>4.5</td>
</tr>
</tbody>
</table>

A temperature at which weight loss starts

Table 7.10 Thermal analysis of H-EU-1 (BH2) after but-1-ene isomerisation
7.2.3 Comparison of the Isomerisation of the Three n-butene Isomers

Reactions starting with 100% of the three n-butenes were carried out on H-EU-1 (BH3), at a temperature of 373K. Figure 7.17 shows the profiles obtained for each of the three reactions. Comparison of this graph with those produced by Tsuchiya et al. [12] for n-butene mixtures over various types of catalyst indicate that this profile is most like the rake type, characteristic of an acid catalyst.

The rates of conversion for the cis and trans isomers were found to decrease in the same manner as observed for but-1-ene. The deactivation was much more rapid for the but-2-enes, as can be seen in Figure 7.17 by the smaller spacings between successive points. On this basis the rate of deactivation is in the order

\[ \text{trans but-2-ene} > \text{cis but-2-ene} > \text{but-1-ene} \]

This is consistent with the theory of deactivation by polymerisation after adsorption of but-2-enes (Section 7.1.3) [16,17], in that the deactivation was quicker when a higher concentration of the but-2-enes was present.

The but-1-ene/but-2-ene product ratios \((1/c)_0\) and \((1/t)_0\) (Table 7.11) were always less than unity, hence geometrical isomerisation (cis to trans interconversion) was taking place in preference to a double bond shift (but-2-ene to but-1-ene isomerisation). These values (Table 7.11) fall within the range of those compiled by Jacobs [26] for zeolite catalysts of increasing acidity,
Figure 7.17 Gas phase composition for but-n-ene isomerisation over H-EU-1 (BH3) at 374K
butene isomer | \(10^2k_{30}/\text{s}^{-1}\) | product ratio
---|---|---
but-1-ene | 5.21 | \(\frac{c}{t}_0 = 1.28\)
cis but-2-ene | 1.81 | \(\frac{1}{c}_0 = 0.83\)
trans but-2-ene | 1.99 | \(\frac{1}{c}_0 = 0.70\)

Table 7.11 Rate constants and initial product ratios for n-butene isomerisation over H-EU-1 (BH₃) at 373K and are consistent with the carbonium ion mechanism [11] (Section 7.1.1).

The fact that preferential geometric isomerisation was observed indicates that there was no restriction of rotation about the C₂–C₃ bond of the secondary carbonium ion which is necessary for cis-trans isomerisation. This suggests that the reaction takes place in the side pockets off the main channels.

The simultaneous formation of the two other n-butene isomers from the reactant indicates that there was a direct interconversion between all three isomers in accordance with the triangular reaction scheme in Figure 7.1. In this scheme, the rate ratios, and therefore the initial product ratios, are correlated by the equation [9]

\[
\frac{k_1k_3k_4}{k_5k_2k_6} = 1
\]

(7.18)

i.e. the forward reaction is equal to the reverse reaction.
From Figure 7.1, it can be seen that

\[
\frac{k_1}{k_3} = \left(\frac{t}{c}\right)_0, \quad \frac{k_5}{k_2} = \left(\frac{c}{l}\right)_0, \quad \frac{k_4}{k_6} = \left(\frac{1}{t}\right)_0
\]

where 1 is but-1-ene, t is trans but-2-ene, and c is cis but-2-ene, and so equation 7.18 can be rewritten as

\[
\left(\frac{t}{c}\right)_0 \times \left(\frac{c}{l}\right)_0 \times \left(\frac{1}{t}\right)_0 = 1
\]  

(7.19)

From the initial product ratios in Table 7.11, a value of 0.93 was obtained for \(k_1k_3/k_3k_2k_6\). In view of the extrapolation procedure used to determine the initial product ratios, this is an acceptable value.

The individual relative rate constants for the reaction scheme were determined in accordance with the procedure of Haag and Pines [1] and are shown in Figure 7.18. These values show more clearly the preferential products from individual reactants.

Thermal analysis of the catalysts after each reaction gave similar weight losses for all three reaction systems (Table 7.12). This indicates that the amount of oligomerisation was restricted by the catalyst, as observed in the previous section. Although the weight losses determined in these analyses were virtually identical, it cannot be said that the oligomers formed were the same and thus independent of the reactant isomer. Clearly structural information for the organic species within the channels and side pockets is still required.
Figure 7.18 Individual relative rate constants for the interconversion of the but-n-ene isomers over H-EU-1 (BH3) at 374K
Table 7.12 Thermal analysis of H-EU-1 (BH3) after n-butene isomerisation at 373K

<table>
<thead>
<tr>
<th>Butene isomer</th>
<th>1st weight loss</th>
<th>2nd weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/K(^{a})</td>
<td>% w/w</td>
</tr>
<tr>
<td>but-1-ene</td>
<td>172</td>
<td>5.0</td>
</tr>
<tr>
<td>cis but-2-ene</td>
<td>175</td>
<td>4.8</td>
</tr>
<tr>
<td>trans but-2-ene</td>
<td>175</td>
<td>4.8</td>
</tr>
</tbody>
</table>

a temperature at which weight loss begins

7.2.4 Establishment of Procedures for Catalyst Regeneration

One of the most important requirements for the use of zeolites as catalysts and adsorbents is that it should be possible to restore the activity of spent materials. To study this, used catalysts were regenerated in the reaction vessel and their activity redetermined. The regeneration procedures consisted of:-

(i) heating ICIEU1 under vacuum at 723K overnight (Table 7.13, Figure 7.19);
(ii) heating ICIEU1 in air at 723K overnight (Table 7.14, Figure 7.20);
(iii) heating BH2 under vacuum at 723K overnight (Table 7.15, Figure 7.21); and
(iv) heating BH2 in air at 723K overnight (Table 7.16, Figure 7.22).
Figure 7.19 Product ratios for the isomerisation of but-1-ene on H-EU-1 (ICIEU1) regenerated under vacuum overnight at 723K.
Figure 7.20 Product ratios for the isomerisation of but-1-ene on H-EU-1 (ICIEU1) regenerated in air overnight at 723K

![Graph showing product ratios vs. percent but-1-ene converted]

- run 1
- run 2
- run 3
Figure 7.21 Product ratios for the isomerisation of but-1-ene on H-EU-1 (BH2) regenerated under vacuum overnight at 723K

![Graph showing product ratios for the isomerisation of but-1-ene on H-EU-1 (BH2) regenerated under vacuum overnight at 723K. The graph depicts the cis/trans product ratio against percent but-1-ene converted with data points for run 1, run 2, run 3, and run 4.]
Figure 7.22 Product ratios for the isomerisation of but-1-ene on H-EU-1 (BH2) regenerated in air overnight at 723K.

- Run 1
- Run 2
- Run 3

Percent but-1-ene converted

Cis/trans product ratio
### Table 7.13
Rate constants, rate ratios, and initial product ratios for but-1-ene isomerisation over H-EU-1 (ICIEU1) regenerated under vacuum at 723 K for 18 hours

<table>
<thead>
<tr>
<th>run number</th>
<th>$10^2k_{30}/s^{-1}$</th>
<th>$k_f^A/k_i$</th>
<th>$(\frac{c}{t})_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.52</td>
<td></td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td>3.01</td>
<td>1.20</td>
<td>1.04</td>
</tr>
<tr>
<td>3</td>
<td>3.00</td>
<td>1.19</td>
<td>1.04</td>
</tr>
<tr>
<td>4</td>
<td>2.35</td>
<td>0.94</td>
<td>1.01</td>
</tr>
</tbody>
</table>

A ratio of $k_{30}$ for current run to that for run 1 samples.

### Table 7.14
Rate constants, rate ratios, and initial product ratios for but-1-ene isomerisation over H-EU-1 (ICIEU1) regenerated in air at 723 K for 18 hours

<table>
<thead>
<tr>
<th>run number</th>
<th>$10^2k_{30}/s^{-1}$</th>
<th>$k_f^A/k_i$</th>
<th>$(\frac{c}{t})_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.98</td>
<td></td>
<td>0.92</td>
</tr>
<tr>
<td>2</td>
<td>2.71</td>
<td>0.91</td>
<td>0.96</td>
</tr>
<tr>
<td>3</td>
<td>2.53</td>
<td>0.85</td>
<td>1.00</td>
</tr>
</tbody>
</table>

A ratio of $k_{30}$ for current run to that for run 1 samples.
### Table 7.15 Rate constants, rate ratios, and initial product ratios for but-1-ene isomerisation over H-EU-1 (BH2) regenerated under vacuum at 723K for 18 hours

<table>
<thead>
<tr>
<th>run number</th>
<th>$10^2 k_0/s^{-1}$</th>
<th>$k_{2a} / k_1$</th>
<th>$(C/C_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.55</td>
<td></td>
<td>0.68</td>
</tr>
<tr>
<td>2</td>
<td>3.90</td>
<td>1.10</td>
<td>0.76</td>
</tr>
<tr>
<td>3</td>
<td>4.28</td>
<td>1.20</td>
<td>0.71</td>
</tr>
<tr>
<td>4</td>
<td>4.06</td>
<td>1.14</td>
<td>0.72</td>
</tr>
</tbody>
</table>

A ratio of $k_{30}$ for current run to that for run 1 samples.

### Table 7.16 Rate constants, rate ratios, and initial product ratios for but-1-ene isomerisation over H-EU-1 (BH2) regenerated in air at 723K for 18 hours

<table>
<thead>
<tr>
<th>run number</th>
<th>$10^2 k_0/s^{-1}$</th>
<th>$k_{2a} / k_1$</th>
<th>$(C/C_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.95</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>2</td>
<td>4.05</td>
<td>1.05</td>
<td>0.64</td>
</tr>
<tr>
<td>3</td>
<td>3.89</td>
<td>0.99</td>
<td>0.67</td>
</tr>
</tbody>
</table>

A ratio of $k_{30}$ for current run to that for run 1 samples.
It is immediately obvious from the activity ratios that the general trend was for the vacuum regeneration treatment to increase the activity of the sample, whilst regeneration in air did not. In conjunction with this, the samples regenerated under vacuum became increasingly darker in colour, becoming almost black at the end of the series of runs, whereas those regenerated in air remained white.

This observation indicates the trend in catalyst activity may be a result of the presence of coke within the samples. Ozaki and Kiruna [27], Clark and Finch [28], and Hightower and Hall [11] have all reported that the carbonaceous residue may be involved in butene isomerisation by providing acidic catalytic sites. It would seem that, in the current investigation, this was also the case. Although the actual formation of the oligomers has been seen to reduce catalytic activity, it appears that heating the sample to 723K under vacuum modifies the residue such that it provides acidic catalytic sites for the reaction to occur upon.

If this were the case, a change in cis/trans product ratios with repeated regeneration is to be expected. Comparison of the product ratios as a function of the reactant converted for each sample (Figures 7.19 with 7.20, and 7.21 with 7.22) show that, although the (c/t)₀ values were very similar, overall the samples regenerated in air produced more of the cis isomer than when heated under vacuum. If this effect was due solely to the restricted diffusion of the cis isomer as a result of the coke formation then a further decrease in the c/t ratio for each
subsequent regeneration under vacuum as the deposits built up would be expected. This is clearly not the case. It appears that, even following the initial pretreatment under vacuum, the catalyst shows the same product selectivity as for the subsequent reactions after regeneration. As the sample had not become discoloured after the initial treatment, this may rule out the possibility of organic contamination in the fresh samples causing this product ratio.

It must also be noted from Figures 7.19-7.22 that the samples heated under vacuum retained their activity for longer than those regenerated in air.

All these observations can be explained by the following hypothesis. The initial pretreatment of the catalyst by heating under vacuum does not activate the sample as fully as when heated in air, as seen from the lower $k_{30}$ values for the former (Tables 7.13 to 7.16). It could be that the treatment under vacuum caused dehydroxylation of the sample, as a result of which the less active Lewis acid sites were formed. Whereas hydroxyl groups (strong acid sites) both catalyse the reaction and are also the site of oligomerisation [16,17,29] Lewis acid sites are thought to oligomerise the but-2-ene molecules, and use protons from this in the isomerisation reaction [18]. This would mean that the reaction over the vacuum treated samples always took place on an oligomer proton source. This would explain why the product selectivities are similar for each subsequent regeneration. A study of the treatment and the reaction by infrared spectroscopy is
needed to substantiate this theory.

The increase in $k_2/k_1$ ratios for the vacuum treated samples is most likely caused by an increase in the number of proton donor sites on the polymer residue building up within the crystallite, rather than an increase in the activity of individual sites. This could also explain why these samples did not appear to deactivate as rapidly as the air regenerated samples, i.e. there was a greater number of sites to be deactivated.

A series of reactions was carried out in which the sample was initially pretreated under vacuum, followed by vacuum regeneration, then two regenerations in air, and finally two regenerations under vacuum. The results are shown in Table 7.17 and Figure 7.23.

<table>
<thead>
<tr>
<th>run number</th>
<th>pretreatment (regeneration)</th>
<th>$10^2 k_{30}/s^{-1}$</th>
<th>$k_r/k_1$</th>
<th>$\left(\frac{c}{t_0}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>vacuum, 723K, 18h</td>
<td>2.27</td>
<td>--</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>vacuum, 723K, 18h</td>
<td>2.50</td>
<td>1.10</td>
<td>1.01</td>
</tr>
<tr>
<td>3</td>
<td>air, 723K, 18h</td>
<td>1.63</td>
<td>0.72</td>
<td>0.98</td>
</tr>
<tr>
<td>4</td>
<td>air, 723K, 18h</td>
<td>1.13</td>
<td>0.49</td>
<td>1.01</td>
</tr>
<tr>
<td>5</td>
<td>vacuum, 723K, 18h</td>
<td>1.40</td>
<td>0.61</td>
<td>0.98</td>
</tr>
<tr>
<td>6</td>
<td>vacuum, 723K, 18h</td>
<td>1.25</td>
<td>0.55</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*a ratio of $k_{30}$ for current run to that for run 1 samples

Table 7.17 Rate constant, rate ratios, and initial product ratios for but-1-ene isomerisation over H-EU-1 (ICIEU1) regenerated in air and vacuum

331
Figure 7.23 Product ratios for the isomerisation of but-1-ene over H-EU-1 (ICIEU1) regenerated in both air and under vacuum overnight at 723K
Again, regeneration of the sample under vacuum caused discolouration of the catalyst, whilst treatment in air rendered it white, indicating that the oligomer was oxidatively removed.

The ratios of activities (Table 7.17) showed a trend in agreement with the previous four sets of results in that the runs following vacuum treatment had a higher activity than a run on "clean" (air treated) catalyst. However, it is noticeable that the activity of the sample decreased within each type of regeneration, and that the catalyst activity after the first air regeneration was much less than the original activity. A single Brönsted acid site is more active than a single Lewis acid site, and this could account for the lower activity after the initial vacuum treatment in comparison with the air treatment. When the sample was regenerated in air the catalytic activity was reduced. This suggests that the ratio of Brönsted to Lewis sites was less than in the initial state, an effect possibly caused by irreversible dehydroxylation. In addition, the continued cycle of heating and catalytic activity may cause localised framework collapse, preventing access to acid sites.

Table 7.18 shows that regeneration of the sample under vacuum for 90 minutes at the reaction temperature (365K) was insufficient treatment to restore the catalytic activity and probably had little effect on the alteration of the residue. This is evident in that regeneration under normal vacuum conditions after run 2 restored activity to the catalyst (run 3). The similar product ratios for the
I run pretreatment (c
umber (regeneration)
10²k₃₀/s⁻¹ | kᵣ₀/k₁ | (c/₁₀)
---|---|---
1 | vacuum, 723K, 18h | 2.71 | 1.00
2 | vacuum, 365K, 90min | 0.15² | 0.06 | 0.98
3 | vacuum, 723K, 18h | 2.71 | 1.00 | 0.98

Table 7.18 Rate constants, rate ratios, and initial product ratios for but-1-ene isomerisation over H-EU-1 (ICIEU1) regenerated in vacuum

reactions (Figure 7.24) indicate that the reaction occurred on the same sites in all three runs.

From the experiments in this section, it can be seen that activation under vacuum at a high temperature for eighteen hours restored the activity of EU-1. However, there was a change in the catalytic site, the nature of which needs further investigation. Regeneration in air did not decrease the catalyst’s activity significantly, provided that it was not interspersed with vacuum regeneration. Further experiments would ascertain the extent to which these cycles could be carried out before the catalyst was deactivated beyond practical use.

It would seem therefore that the presence of this carbonaceous residue may be used to modify the catalytic attributes of EU-1 by controlling the rate of activity and/or the product ratio.
Figure 7.24 Product ratios for the isomerisation of but-1-ene over H-EU-1 (ICIEU1) regenerated under vacuum in various conditions

- Run 1
- Run 2, 636K, 90 minutes
- Run 3, 723K, 18 hours
7.3 Aluminophosphate AlPO₄-5

7.3.1 To Compare the Activity of AlPO₄-5 (Single and Dual Template) with EU-1

From the information in the open literature on the structure and properties of AlPO₄-5 (Section 2.2) and other aluminophosphate molecular sieves (Section 1.3), AlPO₄-5 is expected to be a poor catalyst for but-1-ene isomerisation. This is indeed found to be the case as illustrated in Figure 7.25 which shows that the AlPO₄-5 sample 2P/0 (see Section 4.2.2.1 for the explanation of AlPO₄-5 sample code designation) had only a fraction of the activity of that displayed by the H-EU-1 sample BH3; both experiments being carried out under identical conditions (Table 7.19).

<table>
<thead>
<tr>
<th>catalyst</th>
<th>mass of catalyst /g</th>
<th>reaction temperature /K</th>
<th>10²k₅₀/s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO₄-5 (2P/0)</td>
<td>0.04</td>
<td>373</td>
<td>0²</td>
</tr>
<tr>
<td>H-EU-1 (BH3)</td>
<td>0.04</td>
<td>373</td>
<td>5.21</td>
</tr>
<tr>
<td>AlPO₄-5 (2E/0)</td>
<td>0.10</td>
<td>473</td>
<td>0.17</td>
</tr>
<tr>
<td>AlPO₄-5 (PT/0)</td>
<td>0.10</td>
<td>473</td>
<td>0.79</td>
</tr>
</tbody>
</table>

a no reaction after 30s

Table 7.19 Comparison of rate constants for but-1-ene isomerisation over H-EU-1 and AlPO₄-5

Obviously, if the reaction temperature and the sample weight are increased, then so will the overall activity. It was for this reason that these were increased from 0.04g and 373K to 0.1g and 473K.
Figure 7.25 To compare the rate of but-1-ene isomerisation on AlPO_4-5 and H-EU-1
Figure 7.26 To compare the rate of but-1-ene isomerisation on AlPO₄-5 samples prepared with single and dual organic templating agents.
Figure 7.26 (Table 7.19) compares the reactivity of a sample synthesised from a gel containing a single organic amine (2E/0) with that from a gel containing two organic compounds (PT/0). It is obvious that the latter was much more active. Indeed, it was observed in early investigations [31] that this was the general rule. Hunt also observed that samples synthesised from gels that had been allowed to age had an even greater activity.

The framework of AlPO₄-5 is electroneutral, so there are no exchangeable cations to allow the introduction of hydrogen ions for acid sites, as is the case for zeolites. However, terminal hydroxyl groups have been observed [31-33], as has low temperature desorption of ammonia [33], so there is the possibility that some acidic sites are present. A limited amount of activity for acid catalysed reactions has also been observed (Section 2.2.4.3). It could be that the terminal hydroxyl groups act as acid sites, and this is the source of the activity observed with AlPO₄-5 (PT/0). In addition, the mixed organic samples were composed of spheres of tiny crystallites, whereas the single organic samples were barrel shaped bundles of long rods (Section 4.2.3.5.1). The spherical agglomerates appear to have the larger external surface area and hence are expected to have more terminal hydroxyl groups.

In Section 4.2.3.4, elemental analysis showed that the Al/P ratio for the AlPO₄-5 samples investigated were close to the theoretical value of 1.00. As suggested in Section 4.2.3.4, the deviation from this value may indicate framework defect sites or it may be due to the amorphous
material that has been observed in the X-ray diffraction patterns (Section 4.2.3.1.1). In both cases, terminal hydroxyl groups may be present, and these could act as catalytic sites.

These framework defect sites may also result from the degradation observed when calcined samples of AlPO₄-5 were allowed to stand in air (Chapter 6). To minimise this effect, small batches of the samples were calcined only when needed, and the calcined samples were kept dry in a desiccator.

There is a further possible explanation for the catalytic activity. Adsorbed butene is thought to produce sites for the isomerisation reaction [11,18,27,28]. The difference in electronegativities of the phosphorus and aluminium atoms causes a delocalisation of the charge between the two atoms which would be expected to act as a strong attractant to the double bond of the butene molecule. Again, the smaller crystallites should have a larger surface area and hence more adsorbed butene for catalysis to take place on. The smaller crystals would also have shorter diffusion paths, which may result in an increase in the catalytic activity of the sample for a diffusion controlled reaction.

In the following Sections, the results for the butene isomerisation reaction over various samples of "mixed organic" AlPO₄-5 (see Section 4.2.2.1 for synthesis details) are described and discussed.
7.3.2 Effect of Reaction Variables

Of the initial pretreatments, the most severe appears to be the calcination of the freshly crystallised AlPO₄-5, to remove the organic molecules from the channel system. Normally, this is carried out at 823K. However there may be fluctuations in the temperature. Too low a temperature will not remove the organic material completely, and too high a temperature may cause annealing of framework defect sites, both of which are expected to reduce the catalytic activity of the sample.

Samples of batch code PT/1 were calcined at temperatures of 773K, 873K, and 973K. The number of possible variables that would affect the temperature was kept to a minimum. Each 2.0g sample was calcined separately, but placed on the same spot in the furnace. Calcination was for eighteen hours.

<table>
<thead>
<tr>
<th>Calcination temperature /K</th>
<th>$10^2 k_{30}/s^{-1}$</th>
<th>$\frac{c}{t/0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>3.02</td>
<td>0.76</td>
</tr>
<tr>
<td>873</td>
<td>2.88</td>
<td>0.78</td>
</tr>
<tr>
<td>973</td>
<td>1.56</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Table 7.20 Rate constants and initial product ratios for but-1-ene isomerisation over AlPO₄-5 (PT/1) calcined at different temperatures

Figure 7.27 (Table 7.20) shows the activity plots for the isomerisation reaction over these samples. It can be seen that the activities were very similar for the samples.
Figure 7.27 To compare the rate of but-1-ene isomerisation on AlPO₄-5 (PT/1) calcined at different temperatures.
calcined at the lowest temperatures, but was significantly lower for the high temperature sample. The product ratios (Figure 7.28, Table 7.20) were the same for each reaction, an indication that all proceeded by the same mechanism and that the reduced activity at high temperature calcination was not due to a change in mechanism.

The AlPO$_4$-5 framework has been shown to be thermally stable at high temperatures [34,35]. Choudhary et al. [35] showed that the activity of AlPO$_4$-5 to the catalysis of ortho-xylene isomerisation and cumene (C$_6$H$_5$CH(CH$_3$)$_2$) cracking decreases at calcination temperatures greater than 773K. These observations suggest that calcination at high temperatures anneals framework defect sites by dehydroxylation, with a resultant decrease in acidic catalytic activity.

From the results in Table 7.20, it would seem that only a very large fluctuation in the furnace temperature would have a significant effect on the catalytic behaviour. To minimise this, samples were calcined singly, on the same spot within the furnace, at a temperature of 823K for 18 hours (as described in Section 4.2.2.1).

The reproducibility of the reaction is shown in Table 7.21 and in Figures 7.29 and 7.30, for the sample ET/1/180/42. It can be seen that runs carried out under identical conditions give essentially identical results. Comparison of these results with those in the previous experiment again shows a difference in activity between different synthesis batches.
Figure 7.28 Product ratios for the isomerisation of but-1-ene on AlPO$_4$-5 (PT/1) calcined at different temperatures.
Figure 7.29 Reproducibility of the rate of reaction for the isomerisation of but-1-ene on AlPO₄-5 (ET/1/180/42) calcined at 823K.
Figure 7.30 Reproducibility of the product ratios for the isomerisation of but-1-ene on AlPO₄-5 (ET/1/180/42) calcined at 823K
<table>
<thead>
<tr>
<th>run number</th>
<th>$10^2k_{30}/s^{-1}$</th>
<th>$\left( \frac{c}{t}_0 \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.72</td>
<td>0.71</td>
</tr>
<tr>
<td>2</td>
<td>0.68</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Table 7.21 Rate constants and initial product ratios for but-1-ene isomerisation over AlPO₄-5 (ET/1/180/42) to show reproducibility of calcination procedure and kinetic measurements.

<table>
<thead>
<tr>
<th>reactant pressure /Nm⁻²</th>
<th>$10^2k_{30}/s^{-1}$</th>
<th>$\left( \frac{c}{t}_0 \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>39540 (normal)</td>
<td>2.24</td>
<td>0.76</td>
</tr>
<tr>
<td>52680 (increased)</td>
<td>1.72</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 7.22 Rate constants and initial product ratios for but-1-ene isomerisation on AlPO₄-5 (PT/4) at different reactant pressures.

As discussed in Section 7.2.1, the initial reactant pressure determines the surface coverage and can affect the catalytic activity [18]. Table 7.22 shows the results for a change in the initial pressure of but-1-ene over samples of PT/4. It can be seen that an increase in pressure results in a small decrease in activity (Figure 7.31), as well as a lower cis content in the product ratio (Figure 7.32).

The activity is the change in percentage of product in
Figure 7.31 Effect of increased initial reactant concentration on the rate of reaction for but-1-ene isomerisation on AlPO₄-5 (PT/4)

- ◆ normal conc.
- □ increased conc.
Figure 7.32 Effect of increased initial reactant concentration on the product ratios for but-1-ene isomerisation on AlPO4-5 (PT/4)

- ◊ normal conc.
- □ increased conc.
the total amount of detected gas; a decrease in activity therefore means that there was less conversion relative to the total amount present. As in this case the decrease occurred when the total number of molecules present was increased, then it would indicate that there was a limitation on the amount of conversion that could take place, and that the limit had almost been attained. The most probable limit for this system was the number of catalytic sites available, and the results suggest that occupancy of these sites had reached virtual saturation.

With regard to the product ratio, in Section 5.1.2.2 it was shown that the cis isomer was adsorbed in preference to the trans form. Hence it would not be inconceivable that an increase in pressure would result in a lower cis content in the products. Indeed the cis/trans ratio was always observed to be less than unity. This cannot be due to size constriction within the channel as the pore diameter is 0.8nm whereas the n-butene isomers have kinetic diameters of less than 0.6nm. The most probable cause is the preferential adsorption of the cis isomer, with subsequent conversion to but-1-ene or trans but-2-ene.

From the above experiments, it can be seen that by careful control of the pretreatment conditions, and of the reaction parameters, variations in these can be eliminated as the causes of the differences in catalytic activity observed for different samples.
7.3.3 Isomerisation Reactions and Activation Energies

This section deals with the reactions starting with 100\% of each isomer carried out on samples of the AlPO₄-5 batch PT/4. In all the experiments, only the interconversion between all three isomers was observed; there were no other gaseous products.

The activation energy for the conversion of each isomer was obtained by carrying out the reactions at several temperatures (Figure 7.33, Tables 7.23 to 7.25). The values obtained for \( E_a \) were 24.4±7.1kJ mol\(^{-1}\) (but-1-ene), 22.0±4.5kJ mol\(^{-1}\) (cis but-2-ene), and 21.7±2.4kJ mol\(^{-1}\) (trans but-2-ene). The observed \( E_a \) for but-1-ene was similar to that calculated for the reaction over EU-1 (Section 7.2.2). This suggests a similar reaction mechanism over the two catalysts.

<table>
<thead>
<tr>
<th>reaction temperature /K</th>
<th>( 10^2 k_{30}/s^{-1} )</th>
<th>( \frac{c}{t_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>447</td>
<td>1.34</td>
<td>0.76</td>
</tr>
<tr>
<td>473</td>
<td>2.24</td>
<td>0.76</td>
</tr>
<tr>
<td>495</td>
<td>2.49</td>
<td>0.78</td>
</tr>
</tbody>
</table>

*Table 7.23* Rate constants and initial product ratios for but-1-ene isomerisation on AlPO₄-5 (PT/4) at different reaction temperatures
Figure 7.33 Arrhenius plots for the isomerisation of the but-n-ene isomers on AlPO₄-5 (PT/4)
Table 7.24 Rate constants and initial product ratios for cis but-2-ene isomerisation on AlPO₄-5 at different reaction temperatures

<table>
<thead>
<tr>
<th>reaction temperature /K</th>
<th>$10^2k_{30}/s^{-1}$</th>
<th>$\frac{1}{t_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>449</td>
<td>0.83</td>
<td>0.13</td>
</tr>
<tr>
<td>476</td>
<td>1.30</td>
<td>0.16</td>
</tr>
<tr>
<td>495</td>
<td>1.29</td>
<td>0.21</td>
</tr>
<tr>
<td>518</td>
<td>1.95</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 7.25 Rate constants and initial product ratios for trans but-2-ene isomerisation over AlPO₄-5 (PT/4) at different reaction temperatures

<table>
<thead>
<tr>
<th>reaction temperature /K</th>
<th>$10^2k_{30}/s^{-1}$</th>
<th>$\frac{1}{t_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>447</td>
<td>0.87</td>
<td>0.34</td>
</tr>
<tr>
<td>475</td>
<td>1.38</td>
<td>0.16</td>
</tr>
<tr>
<td>495</td>
<td>1.55</td>
<td>0.22</td>
</tr>
<tr>
<td>516</td>
<td>1.95</td>
<td>0.22</td>
</tr>
</tbody>
</table>

The concurrence within experimental error of the activation energies for the three isomers over AlPO₄-5 indicates that the energy barriers for the interconversion of the three molecules were similar. Misono et al. [21] proposed that the three energy barriers were different for different catalysts, but were similar over catalysts with...
weak acid sites. Thus it would appear that these are the major type of catalytic site in the AlPO$_4$-5 sample.

The initial rate constants, $k_{30}$, (Tables 7.23 to 7.25) were in the order

$$\text{but-1-ene} > \text{cis but-2-ene} = \text{trans but-2-ene}$$

This is reflected in the respective frequency factors ($\ln A$, equation 7.17) of 10.0, 3.1, and 3.1, associated with the activation energies.

The initial $\text{cis/trans}$ ratio ($c/t_0$, Table 7.23) was observed to be temperature independent, as expected for the secondary carbonium ion mechanism [10]. However, the initial but-1-ene/but-2-ene ratios (Tables 7.24 to 7.25) showed a general increase with temperature. For all the reactions (Figures 7.34-7.36) the product ratios show only a slight variation with percentage conversion. As mentioned in Section 7.1.1, to break a primary C-H bond requires more energy than to break a secondary C-H bond, and so a low but-1-ene/but-2-ene would be expected from a secondary carbonium ion mechanism, as was seen here. The temperature dependency observed in this set of experiments further indicates that there is an energy difference between the formation of but-1-ene and but-2-ene from the secondary butyl carbonium ion.

This may also explain the $k_{30}$ values and the turnover numbers. But-1-ene is more likely to isomerise to but-2-ene, than to desorb unchanged, whereas the but-2-enes are more likely to remain as but-2-enes with an equal chance of desorbing unchanged.

The simultaneous formation of the other two isomers
Figure 7.34 Product ratios for the isomerisation of but-1-ene on AlPO₄-5 (PT/4) at different reaction temperatures.
Figure 7.35 Product ratios for the isomerisation of cis but-2-ene on AlPO₄-5 at different reaction temperatures.
Figure 7.36 Product ratios for the isomerisation of trans but-2-ene on AlPO₄-5 (PT/4) at different reaction temperatures.

The graph shows the percent trans but-2-ene converted on the x-axis and the but-1-ene/cis product ratio on the y-axis. The legend indicates the temperatures: 447K, 475K, 495K, and 516K.
from the reactant isomer, i.e. the initial product ratio was greater than zero, indicates the triangular reaction scheme shown in Figure 7.1 [1] applies. The individual relative rate constants $k_1$ to $k_6$ were calculated in accordance with the method of Haag and Pines [1], and are given in Figure 7.37. These show more clearly the preferential products from each of the individual isomers.

The initial product ratios from the above scheme can be correlated by equation 7.18. From the initial product ratios given in Tables 7.23 to 7.25, values of 1.32, and 1.22 were obtained for $k_1k_2k_4/k_3k_5k_6$ at 476K, and 495K respectively. (The product ratio for the cis but-2-ene conversion at 447K was higher than projected from the other data, and thus was deemed unsuitable for these calculations). The initial product ratios were obtained by extrapolation of the data points, a method which can be very prone to errors, depending upon the closeness and regularity of the experimental points. If an absolute error of ±0.03 is assumed in these product ratios, then the values for $k_1k_2k_4/k_3k_5k_6$ at 476K and 495K are 1.32±27% and 1.22±20% respectively. The error bars embrace the ideal value of 1 (equation 7.18).

The data for the reactions of the three isomers at 473K were plotted in triangular form (Figure 7.38). These reaction profiles are seen to be a trans convex shape, which is indicative of an acid catalyst [12].

The information reported in this section indicates that AlPO4-5 has a weak acid type catalytic sites, and that the n-butene isomerisation reaction over this catalyst gave
Figure 7.37 Individual relative rate constants for the interconversion of the but-n-ene isomers on AlPO₄-5 (PT/4) at 473K
Figure 7.38 Gas phase composition for but-n-ene isomerisation on AlPO$_4$-5 (PT/4) at 473K
full interconversion via the secondary butyl carbonium ion intermediate. However, no information on the location of the sites was obtained, nor on the difference in activity between catalyst batches.

7.3.4 Comparison of the Isomerisation Reaction over Various Synthesis Batches

In order to gain further insight into the relationship between synthesis procedure and the catalytic activity of the resultant AlPO$_4$-5 batch, the but-1-ene isomerisation reaction was carried out over selected samples. All the reactions were carried out at 473K with 0.1g weight of sample, which had been pretreated by heating in air at 723K overnight.

Initially, the two series of aged samples that were made available by Dr. C.D. Williams (Section 4.2.2.1) were used to ascertain if the activity was indeed a function of the gel aging time, as observed by Hunt [30].

It can be seen that, with the ET/a series (Table 7.27), there was an increase in $k_{30}$ with the gel aging period; however for the PT/a series (Table 7.26), the values were very similar for all the samples, with the exception of PT/10, which had the lowest initial rate constant for these ten samples. Examination of the samples by scanning electron microscopy revealed that this latter sample had the barrel shaped morphology, typically found for AlPO$_4$-5. This supports the view that the increased activity has a strong association with the sample morphology.
Table 7.26 Rate constants and initial product ratios for but-l-ene isomerisation on the AlPO₄-5 series PT/a

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$10^2k_{30}$/s⁻¹</th>
<th>($c/t_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT/0</td>
<td>2.33</td>
<td>0.78</td>
</tr>
<tr>
<td>PT/1</td>
<td>2.27</td>
<td>0.78</td>
</tr>
<tr>
<td>PT/2</td>
<td>2.62</td>
<td>0.67</td>
</tr>
<tr>
<td>PT/4</td>
<td>2.24</td>
<td>0.76</td>
</tr>
<tr>
<td>PT/10</td>
<td>0.89</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Table 7.27 Rate constants and initial product ratios for but-1-ene isomerisation on the AlPO₄-5 series ET/a

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$10^2k_{30}$/s⁻¹</th>
<th>($c/t_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ET/0</td>
<td>2.51</td>
<td>0.76</td>
</tr>
<tr>
<td>ET/1</td>
<td>1.86</td>
<td>0.70</td>
</tr>
<tr>
<td>ET/2</td>
<td>3.53</td>
<td>0.78</td>
</tr>
<tr>
<td>ET/4</td>
<td>3.91</td>
<td>0.73</td>
</tr>
<tr>
<td>ET/10</td>
<td>4.73</td>
<td>0.79</td>
</tr>
</tbody>
</table>

The product ratio was generally seen to be a function of the percentage of reactant converted for both series (Figures 7.39 and 7.40), although the PT/a series had a slightly wider spread. This indicates that the gel aging period did not affect the reaction mechanism or the
Figure 7.39 Product ratios for the isomerisation of but-1-ene on AlPO₄-5 samples crystallised from aged gels.

![Graph showing product ratios for the isomerisation of but-1-ene on AlPO₄-5 samples crystallised from aged gels.](image)
Figure 7.40 Product ratios for the isomerisation of but-1-ene on AlPO$_4$-5 samples crystallised from aged gels.
location of the reaction sites.

From these results, it is clear that the gel aging period had little effect upon the catalytic activity of the samples.

In Chapter 4, it was observed that the samples had different relative crystallinities, and amounts of amorphous material present. To investigate the effect this might have on the catalytic behaviour, the isomerisation reaction was carried out on samples from the ET/a/T/t series in which portions of the parent gel were reacted for increased crystallisation times (Section 4.1.2.2). The results are given in Table 7.28.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$10^2 k_{30}/s^{-1}$</th>
<th>$\frac{c}{t_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaiser alumina</td>
<td>0.61</td>
<td>0.30</td>
</tr>
<tr>
<td>ET/1/150-2/1</td>
<td>0$^a$</td>
<td>0.14</td>
</tr>
<tr>
<td>ET/1/150-2/1.75</td>
<td>5.45</td>
<td>0.68</td>
</tr>
<tr>
<td>ET/1/180/3</td>
<td>1.46</td>
<td>1.02</td>
</tr>
<tr>
<td>ET/1/150-1/5</td>
<td>3.91</td>
<td>0.89</td>
</tr>
<tr>
<td>ET/1/180/42</td>
<td>0.72</td>
<td>0.71</td>
</tr>
<tr>
<td>DP2</td>
<td>no reaction</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ no reaction observed at 30s

Table 7.28 Rate constants and initial product ratios for the isomerisation of but-1-ene on samples produced from various stages of AlPO$_4$-5 synthesis
In addition to these AlPO₄-5 samples, the but-1-ene 
isomerisation reaction was carried out over two other 
samples. One was Kaiser alumina, the aluminium source in 
the aluminophosphate gel. This was to determine if the 
activity was due to unreacted Kaiser alumina in the AlPO₄-5 
samples. The second sample was of the aluminophosphate 
dense phase material DP2 (Section 4.2.2.2), which contained 
81.7% AlPO₄-tridymite, the dense phase material observed in 
the PT/a samples. Again, this was to determine if there was 
any contribution to the catalytic activity of the sample. 
Although this was thought to be unlikely, it was important 
to establish that the dense phase was inactive as an 
allowance was made for its presence in the mass of sample 
used.

The samples were chosen for their wide ranging values 
of relative AlPO₄-5 crystallinity, and relative amorphous 
material content. The calculated amounts, along with those 
for the ET/a and PT/a samples, are given in Table 7.29. 
Graphs of $k_{30}$ plotted against the relative AlPO₄-5 
crystallinity (Figure 7.41) and relative amorphous material 
content (Figure 7.42) were produced to highlight any 
relationship between the two.

The two extremes of relative crystallinity i.e. very 
high and very low, showed low catalytic activity, whereas 
within the mid-range, a wide range of activity was obtained 
for similar relative crystallinities (Figure 7.41).
<table>
<thead>
<tr>
<th>catalyst</th>
<th>relative crystallinity /%</th>
<th>relative amorphous material content /%</th>
<th>AlPO₄-tridymite content /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT/0</td>
<td>46.6</td>
<td>44.0</td>
<td>12.1</td>
</tr>
<tr>
<td>PT/1</td>
<td>44.2</td>
<td>43.3</td>
<td>13.3</td>
</tr>
<tr>
<td>PT/2</td>
<td>48.6</td>
<td>39.7</td>
<td>12.0</td>
</tr>
<tr>
<td>PT/4</td>
<td>40.4</td>
<td>40.4</td>
<td>12.6</td>
</tr>
<tr>
<td>PT/10</td>
<td>41.4</td>
<td>39.7</td>
<td>22.9</td>
</tr>
<tr>
<td>ET/0</td>
<td>44.8</td>
<td>38.3</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/1</td>
<td>47.1</td>
<td>41.8</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/2</td>
<td>44.1</td>
<td>41.8</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/4</td>
<td>55.8</td>
<td>45.3</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/10</td>
<td>46.3</td>
<td>47.5</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/1/150-2/1</td>
<td>0.0</td>
<td>82.3</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/1/150-2/1.75</td>
<td>38.4</td>
<td>68.1</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/1/150-1/5</td>
<td>67.1</td>
<td>66.7</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/1/180/3</td>
<td>68.2</td>
<td>61.0</td>
<td>0.0</td>
</tr>
<tr>
<td>ET/1/180/42</td>
<td>86.3</td>
<td>61.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Kaiser alumina</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>DP2</td>
<td>0.0</td>
<td>0.0</td>
<td>81.7</td>
</tr>
</tbody>
</table>

Table 7.29 Relative AlPO₄-5 crystallinity, relative amorphous material content, and percentage AlPO₄-tridymite content of catalysts
Figure 7.41 Relationship between the relative crystallinity and the initial rate constant for the but-1-ene isomerisation reaction on various AlPO₄-5 samples.
Figure 7.42 Relationship between the relative amorphous material content and the initial rate constant for the but-1-ene isomerisation reaction on various AlPO₄-5 samples.

- PT/a
- ET/a
- ΔET/1/T/t
- ▼ Kaiser alumina

Relative amorphous content vs. $10^2 k_{30}$/s−1
Figure 7.42 revealed no apparent relationship between the activity and the relative amorphous content of the samples. However, it must be noted that sample ET/1/150-2/1 which was purely amorphous material (determined by X-ray powder diffraction) showed little catalytic activity.

The dense phase sample DP2 showed no catalytic activity (Table 7.28), and so this can be eliminated from the investigations.

The sample of Kaiser alumina did show some catalytic activity (Table 7.28), although the $k_{30}$ value for this amount of material indicates that if there was a small amount of unreacted Kaiser alumina present in the AlPO$_4$-5 sample, it would not make any significant contribution to the overall catalytic activity of the sample.

Although the above observations do not indicate a definite feature to account for the variation in AlPO$_4$-5 catalytic activity, the information is supportive of the theory that the active sites are terminal hydroxyl groups at framework defect sites. This stems from the comparison of $k_{30}$ values with the relative sample crystallinity. The greater the sample crystallinity, the less framework defect sites there should be, and hence a lower catalytic activity is expected, as was the observed trend. In the case of decreasing sample crystallinity, it is proposed that below a critical value no significant catalytic activity is possible. With the mid-range samples a range of catalytic activities was observed and it is suggested that some of these materials contain an optimum amount of framework defect sites. It is not envisaged that these sites are
uniformly spread throughout the crystallites. Concentrated areas may exist, and these could lead to localised collapse of the framework, and thus render that part of the crystal unavailable for catalysis. The greater the number of these localised areas, the lower the apparent activity of the sample. This may explain why these samples exhibit such a range of catalytic activities. A more quantitative measure of the acid sites in each sample would help to verify this theory, e.g. by temperature programmed desorption of a basic material such as ammonia.

The ability to increase the catalytic activity by the introduction of framework defect sites may not be limited to AlPO$_4$-5. It seems likely that other wide pore microporous aluminophosphates such as VPI-5 may show similar behaviour, and it could be that this is the only means by which pure aluminophosphates may be prepared as weak acid catalysts.
7.4 References


[26] Reference 22, p93


CHAPTER 8

Summary

8.1 Zeolite EU-1

The synthesis procedure given in the European patent EP42226 (Casci et al., 1981) gave good, well defined samples of EU-1. Overrun of the crystallisation period gave the dense phase material tridymite. Results from the initial characterisation experiments (Chapter 3) were in agreement with those of previous workers.

The adsorption of the n-butene isomers by H-EU-1 at room temperature gave isotherms with large hysteresis loops that appeared not to close. This was attributed to chemisorption and possible polymerisation of the n-butenes. The but-2-ene isomers were seen to be sorbed more strongly than but-1-ene. It was found that the sorbed but-1-ene could not be completely removed by exposure of the sample to a vacuum at room temperature, and nitrogen sorption on such a sample showed that its pore volume was reduced by 46%. Comparison of this figure with that for a similarly treated sample of AlPO₄-5 (66%) suggested that, as the pore system for the latter had straight channels which were larger in diameter than those in EU-1, then the chemisorption of the but-1-ene occurred preferentially in the side pockets of EU-1.

Desorption of pyridine from H-EU-1 gave two weight losses as expected. The high temperature weight loss was equivalent to 0.88 pyridine molecules per aluminium site. The inaccessibility of certain sites was thought to arise
when more than one site was present in a single side pocket.

The isomerisation of but-1-ene over EU-1 was found to proceed through a secondary butyl carbonium ion intermediate. However, the reaction did not appear to follow first order kinetics; this was attributed to deactivation of the acid sites caused by polymerisation of the n-butanes at the surface. The polymerisation was thought to begin at the outset of the isomerisation reaction.

The initial $cis/\text{trans}$ ratio $((c/t)_0)$ was, in many cases, found to be less than one. This was believed to be due to the diffusional constraints of the zeolite channel system (pore diameter 0.6nm) which restricted the outward diffusion of the $cis$ but-2-ene isomer (kinetic diameter 0.55nm). The effect of these diffusional constraints was further illustrated when the $c/t$ product ratio was seen to decrease when the reaction temperature was increased. This was attributed to the lower activation energy of diffusion for the smaller $\text{trans}$ isomer.

But-1-ene isomerisation over samples of EU-1 that had been calcined but not $H^+$ ion exchanged indicated that the aluminium sites that were balanced by sodium cations had little, if any, catalytic activity. However it appeared that the presence of these $Na^+$ cations increased the amount of strongly adsorbed hydrocarbon species. A further experiment involving uncalcined EU-1 revealed that the external surface of the crystallites had an insignificant amount of active sites.
The isomerisation of cis and trans but-2-ene over EU-1 was investigated. The triangular reaction profile (gaseous composition) starting with 100% of each isomer was typical of that shown by an acid catalyst. Initial product ratios \(((\text{but-1-ene/but-2-ene})_0)\) of less than one were observed, consistent with the carbonium ion mechanism. This low value indicates that preferential geometric isomerisation has taken place which indicates that there is no restriction of the rotation of the C\(_2\)-C\(_3\) bond (the arc of this rotation is greater than the EU-1 main channel diameter) and hence the reaction takes place in the side pockets off the main channel.

The zeolite was seen to deactivate more rapidly when using the but-2-ene isomers, which supports the theory that the but-2-enes initiate the polymerisation.

Heating the EU-1 catalyst in vacuo at 723K overnight after the isomerisation reaction (regeneration) caused an increase in the initial activity of the catalyst. Low temperature (i.e. reaction temperature) regeneration for a short time had no such affect. The increased activity is thought to be due to a modification of the carbonaceous residue that generated acid sites on the coke when it was heated to a high temperature in an inert atmosphere. The change in the acid sites was reflected by the higher product ratios that were observed. Regeneration in air caused only a slight change in the sample activity, provided that it was not interspersed with vacuum regeneration.

Thus the presence of coke may be used to an advantage.
in catalytic reactions in the control of reaction rates and product ratios.

8.2 Aluminophosphate AlPO₄₋₅

The hydrothermal crystallisation of an aluminophosphate gel of composition

$$\text{R TPABr Al}_2\text{O}_3 \text{ P}_2\text{O}_5 \text{ 4}0\text{H}_2\text{O}$$

where R is triethylamine or tripropylamine, in a static system produces the AlPO₄₋₅ phase in the form of spherical agglomerates of hexagonal crystals. This morphology is thought to arise from a pseudomorphic transformation of the spherical particles of Kaiser alumina, the aluminium source used in the gel. Both R and TPABr were thought to be employed by the crystallisation process, as they were both observed to be removed from the AlPO₄₋₅ channel system when the as-synthesised samples were subjected to thermal analysis.

Monitoring the crystallisation of the above gel (R=Et₃N) by measuring the pH of the solution produces an S-shaped curve, as seen in zeolite synthesis. The X-ray diffraction patterns of the solid phase of the gel shows that an amorphous phase is initially formed, followed by the aluminophosphate hydrate phase AlPO₄₋H₃, and then the AlPO₄₋₅ phase appears. In all the X-ray diffraction patterns for AlPO₄₋₅, both from this work and in the open literature, a deviation from the base line between 19 and 35° 20 was observed, which corresponds to the broad hump that characterised the X-ray diffraction pattern for the amorphous solid that preceded the hydrate phase in the gel
crystallisation. This indicates that a pure AlPO₄-5 phase cannot be synthesised by these routes.

Crystallisation of the above gel composition, where R=Pr₃N, under conditions identical with those for R=Et₃N produces an AlPO₄-5 phase contaminated with the dense phase AlPO₄-tridymite, which indicates that the gel containing Pr₃N is more reactive.

Crystallisation of the above aluminophosphate gel without any organic template results in the formation of a series of AlPO₄ hydrate and dense phases in the order AlPO₄-H₄, AlPO₄-tridymite, and berlinite, which reflects an increase in stability and crystal density.

The aluminium to phosphorus ratio for selected samples was found to be close to the expected value of 1. An increase in the aging time of the gel before crystallisation was seen to decrease slightly the Al/P ratio. This seemed to be the only effect of aging the gel.

Adsorption experiments on both types of AlPO₄-5 morphology showed that the spherical agglomerates had a larger weight uptake of adsorbate than the barrel shaped crystals, indicative of the larger external surface area and intercrystalline void space of the former.

Adsorption of n-butenes on AlPO₄-5 (spherical morphology) gave adsorption isotherms with hysteresis loops similar to, though not as large as, those observed for EU-1. This is indicative of the weaker adsorption properties of AlPO₄-5 compared to EU-1. Sections of the monodimensional channel system in AlPO₄-5 were found to be isolated by strongly bound butene.
Adsorption of selected organic molecules showed that the AlPO₄-5 samples had a greater affinity for polar molecules which reflects the polar nature of the aluminophosphate surface. The uptakes and rates of uptake reflected the size of the adsorbate molecules. The Langmuir model for the adsorption of these molecules on AlPO₄-5 with the spherical morphology was seen to break down at relative pressures >0.45, indicative of the greater external surface area of these agglomerates which facilitates multilayer adsorption.

Desorption of pyridine was seen only to occur over a low temperature range that encompassed the boiling point of the adsorbate, reflecting the lack of strong acid sites in AlPO₄-5.

The AlPO₄-5 structure was seen to be degraded by aqueous salt solutions and, to a lesser extent, by distilled water. The structure was also seen to degrade when the samples were kept under ambient conditions for long periods of time. The effect was reduced by retaining the organic templates within the structure. Other aluminophosphate molecular sieves were subjected to similar treatments; the order of degradation was observed to be AlPO₄-5 > AlPO₄-11 > AlPO₄-25, which reflects the pore size and stability of their structures. The apparent attack of the AlPO₄-5 structure by mineral acids was thought to be due to the anion rather than the hydrogen ion. The potency of various anions suggests that the degradation is catalytic in nature, and that the reaction may involve nucleophilic attack.
Samples of AlPO₄-5 of both morphologies showed catalytic activity for the isomerisation of but-1-ene. However the samples with the spherical morphology had a greater activity.

The active sites were thought to be terminal hydroxyl groups at framework defect sites or crystal faces, or located on phase impurities. Activity by adsorbed butene on weak acid sites was also considered to be possible.

Low cis/trans product ratios were interpreted as preferential adsorption of the cis isomer with possible subsequent conversion to one of the other n-butene isomers.

Calcination of AlPO₄-5 samples at high temperatures reduced the sample activity; this is thought to be due to annealing of the framework defect sites by dehydroxylation. There also appeared to be a limited number of active sites available for the isomerisation reaction as seen by the apparent reduction in initial activity for an increased reactant pressure.

The activation energies for the conversion of the pure isomers were similar, indicative of a weak acid catalyst. The initial product ratios were consistent for a carbonium ion mechanism i.e. \( (c/t)_0 \) was temperature independent, and \( (1/c)_0 \) and \( (1/t)_0 \) were less than unity. In addition to this, the triangular reaction profile (gaseous composition) was typical of that shown by an acid catalyst.

Aging the gel before crystallisation did not appear to affect the reaction mechanism or the sample activity. Also, but-1-ene isomerisation on samples of the impure phases present in the AlPO₄-5 samples i.e. the amorphous phase, the
dense phase AlPO₄-tridymite, and the Kaiser alumina, showed that any catalytic activity that they possessed would have a negligible contribution to the overall sample activity.

Framework defect sites are the most likely source of the catalytic activity of AlPO₄-5. Highly crystalline samples, hence few defect sites, showed low catalytic activity. Samples of low crystallinity, which also showed low activity, were possibly of too low a microporosity and surface area to impart catalytic activity. Samples in the mid-spectrum showed a range of activities that may be a result of concentrated areas of defect sites causing localised framework collapse, and so reducing the catalytic activity.
APPENDIX 1

Results of First Attempt to Synthesise the Zeolite EU-1

The first attempt to synthesise zeolite EU-1 gave an unexpected product. The synthesis procedure was exactly as described in Section 4.1.2. The X-ray powder diffraction pattern for the as-synthesised material is shown in Figure A1.1(a) and Table A1.1. Comparison of the data in this Table with Table 2.1 shows that this material was not EU-1.

The optimum calcination temperature was determined by thermal analysis (Figure A1.2) to be 773K. The X-ray diffraction pattern for the calcined material is shown in Figure A1.1(b) (Table A1.1). Calcination of the material at 973K caused the framework to collapse (Figure A1.1(c)).

Scanning electron microscopy showed the crystal morphology to be flat ovals with truncated ends (Plate A1.1). The crystal dimensions ranged between (1-7\,\mu m) \times (0.5-3\,\mu m).

A comparison of the peak positions and relative intensities of the X-ray diffraction pattern of this material against those of known zeolite structure types showed that the MFI structure had the closest fit (Table A1.2). However, it must be noted that the most intense peak for the unknown structure (d=0.380\,nm) did not match the MFI pattern.

$^{13}$C MASNMR of the uncalcined unknown material, very kindly carried out at ICI, showed that the hexamethonium species seemed to be intact, in that C-C and C-N bonds were
Figure A1.1 X-ray diffraction patterns for the unknown material.
<table>
<thead>
<tr>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity (I/I₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.094</td>
<td>m</td>
<td>1.098</td>
<td>s</td>
</tr>
<tr>
<td>0.985</td>
<td>vs</td>
<td>0.993</td>
<td>sh</td>
</tr>
<tr>
<td>0.629</td>
<td>vw</td>
<td>0.981</td>
<td>vs</td>
</tr>
<tr>
<td>0.591</td>
<td>vw</td>
<td>0.628</td>
<td>vw</td>
</tr>
<tr>
<td>0.551</td>
<td>vw</td>
<td>0.590</td>
<td>w</td>
</tr>
<tr>
<td>0.540</td>
<td>vw</td>
<td>0.550</td>
<td>w</td>
</tr>
<tr>
<td>0.495</td>
<td>w</td>
<td>0.493</td>
<td>vw</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.485</td>
<td>vw</td>
</tr>
<tr>
<td>0.465</td>
<td>vw</td>
<td>0.462</td>
<td>vw</td>
</tr>
<tr>
<td>0.433</td>
<td>vw</td>
<td>0.431</td>
<td>vw</td>
</tr>
<tr>
<td>0.427</td>
<td>vw</td>
<td>0.423</td>
<td>vw</td>
</tr>
<tr>
<td>0.421</td>
<td>vw</td>
<td>0.417</td>
<td>vw</td>
</tr>
<tr>
<td>0.403</td>
<td>vw</td>
<td>0.401</td>
<td>w</td>
</tr>
<tr>
<td>0.383</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.380</td>
<td>vs</td>
<td>0.380</td>
<td>vs</td>
</tr>
<tr>
<td>0.371</td>
<td>m</td>
<td>0.367</td>
<td>s</td>
</tr>
<tr>
<td>0.362</td>
<td>w</td>
<td>0.357</td>
<td>w</td>
</tr>
<tr>
<td>0.345</td>
<td>vw</td>
<td>0.343</td>
<td>w</td>
</tr>
<tr>
<td>0.331</td>
<td>vw</td>
<td>0.329</td>
<td>w</td>
</tr>
<tr>
<td>0.315</td>
<td>vw</td>
<td>0.314</td>
<td>vw</td>
</tr>
<tr>
<td>0.296</td>
<td>vw</td>
<td>0.296</td>
<td>w</td>
</tr>
<tr>
<td>0.278</td>
<td>vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.249</td>
<td>vw</td>
<td>0.248</td>
<td>vw</td>
</tr>
</tbody>
</table>

**a** relative intensity (%)
- **vs**: 60-100
- **s**: 40-60
- **m**: 20-40
- **w**: 10-20
- **vw**: <10
- **sh**: shoulder

*Table A1.1* Interplanar spacings for unknown material
Figure A1.2 Thermal analysis of the unknown material
Plate A1.1 Scanning electron micrograph of unknown material
<table>
<thead>
<tr>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity(^a) (I/I_o)</th>
<th>interplanar spacing (d) /nm</th>
<th>relative peak intensity (I/I_o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.094</td>
<td>m</td>
<td>0.974</td>
<td>m</td>
</tr>
<tr>
<td>0.985</td>
<td>vs</td>
<td>0.974</td>
<td>m</td>
</tr>
<tr>
<td>0.629</td>
<td>vw</td>
<td>0.555</td>
<td>vw</td>
</tr>
<tr>
<td>0.591</td>
<td>vw</td>
<td>0.538</td>
<td>vw</td>
</tr>
<tr>
<td>0.551</td>
<td>vw</td>
<td>0.555</td>
<td>vw</td>
</tr>
<tr>
<td>0.540</td>
<td>vw</td>
<td>0.538</td>
<td>vw</td>
</tr>
<tr>
<td>0.495</td>
<td>w</td>
<td>0.428</td>
<td>vw</td>
</tr>
<tr>
<td>0.465</td>
<td>vw</td>
<td>0.427</td>
<td>vw</td>
</tr>
<tr>
<td>0.433</td>
<td>vw</td>
<td>0.426</td>
<td>vw</td>
</tr>
<tr>
<td>0.427</td>
<td>vw</td>
<td>0.427</td>
<td>vw</td>
</tr>
<tr>
<td>0.421</td>
<td>vw</td>
<td>0.426</td>
<td>vw</td>
</tr>
<tr>
<td>0.403</td>
<td>vw</td>
<td>0.401</td>
<td>vw</td>
</tr>
<tr>
<td>0.383</td>
<td>sh</td>
<td>0.383</td>
<td>vs</td>
</tr>
<tr>
<td>0.380</td>
<td>vs</td>
<td>0.383</td>
<td>vs</td>
</tr>
<tr>
<td>0.371</td>
<td>m</td>
<td>0.372</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.371</td>
<td>vw</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.370</td>
<td>vw</td>
</tr>
<tr>
<td>0.362</td>
<td>w</td>
<td>0.344</td>
<td>w</td>
</tr>
<tr>
<td>0.345</td>
<td>vw</td>
<td>0.331</td>
<td>vw</td>
</tr>
<tr>
<td>0.315</td>
<td>vw</td>
<td>0.316</td>
<td>vw</td>
</tr>
<tr>
<td>0.296</td>
<td>vw</td>
<td>0.297</td>
<td>vw</td>
</tr>
<tr>
<td>0.278</td>
<td>vw</td>
<td>0.249</td>
<td>vw</td>
</tr>
<tr>
<td>0.249</td>
<td>vw</td>
<td>0.248</td>
<td>vw</td>
</tr>
</tbody>
</table>

\(^a\) see Table A1.1

Table A1.2 Comparison of interplanar spacings for unknown material with those for the MFI structure

388
present.

The most likely explanation for the appearance of this material is that the hexamethonium bromide had decomposed, either at source or during the preparation. Loss of one of the quaternary ammonium groups would give a molecule that fits within the MFI channel system; the intact quaternary group sits in the channel junction with the carbon chain along one of the channels. The framework would be greatly distorted and strained, which would explain the poor fit for the X-ray diffraction pattern with the MFI structure, and the thermal instability of this material.
Degradation of AlPO₄-5 by aqueous salt solutions

Brian Hampson, H. Frank Leach, Barrie M. Lowe, and Craig D. Williams
Department of Chemistry, University of Edinburgh, Edinburgh, Scotland, UK

Calcin ed template-free AlPO₄-5 is attacked by liquid water and aqueous salt solutions at 25°C, whereas the "as-made" material is resistant to degradation. The extent to which the framework is attacked increases with the salt concentration and depends on the nature of the anion (OH⁻ > I⁻ > S₂O₇²⁻ > Br⁻ > Cl⁻). Phosphate is released to the solution phase and the pH decreases from ~ 5.5 to ~ 3.0. AlPO₄-11 and AlPO₄-25 are also attacked by salt solutions, but the effects are smaller than for AlPO₄-5.

Keywords: Aluminophosphates; degradation; aqueous salts; X-ray powder diffraction; AlPO₄-5; AlPO₄-11; AlPO₄-25; AlPO₄-tridymite

INTRODUCTION

Aluminophosphates molecular sieves have framework structures similar to those of zeolites, but with AlO₄ and PO₄ tetrahedra in strict alternation. Hence, their frameworks are uncharged, and in this respect they resemble crystalline silica molecular sieves. However, they lack the hydrothermal stability of silica frameworks, which have low solubilities in acid and neutral aqueous solutions. A recent study showed that when immersed in water under autogenous pressure at 200°C for 12 h AlPO₄-5 (Refs. 1, 4, 5) collapses to give a mixture of AlPO₄-tridymite (an isomorph of SiO₂-tridymite) and amorphous material. It was also observed that at 30°C AlPO₄-5 dissolves completely in aqueous HCl and aqueous NaOH at concentrations > 0.1 mol dm⁻³ and although the extent of dissolution was negligibly small in the pH range 5.0-5.5, the aluminophosphate crystallinity was reduced markedly except at pH values close to 7.0.

We now report the effect of aqueous salt solutions on the crystallinity of aluminophosphate molecular sieves. These investigations were pursued because of their possible implications for aluminophosphate synthesis and also as a basis for future sorption studies, particularly the imbition of salts from aqueous solution. Although aluminophosphate molecular sieves can be synthesized from reaction mixtures that contain simple anions, their presence offers few advantages and tends to produce dense phases. We are not aware of any previous work on the treatment of microporous aluminophosphates with aqueous salt solutions, but note that they were found to be "inappropriate" for the removal of triethylamine from as-synthesised AlPO₄-5.

EXPERIMENTAL

Synthesis of aluminophosphates

AlPO₄-5 was crystallized at 150°C from the composition 2Pr₃N P₂O₅ Al₂O₃ 40H₂O in a stirred 1 liter stainless steel autoclave. The product obtained after 24 h was washed, dried, and calcined for 16 h at 550°C. A second preparation was carried out by an identical procedure with the composition 1.2 Pr₃N 0.8Pr₄NBr P₂O₅ Al₂O₃ 40H₂O. The sample prepared with a single template will be referred to as AlPO₄-5(S) and that with the mixed template as AlPO₄-5(M). In both cases, X-ray powder diffraction showed the products to be good samples of AlPO₄-5 with only slight contamination by other crystalline materials and little evidence of amorphous impurities. Scanning electron micrographs showed that the products were mixtures of hexagonal barrel-shaped aggregates (11 x 8.6 μm) (cf. Refs. 3, 11) and 4.7 x 1.4 μm rod-shaped single crystals. There was also a small amount of amorphous material.

AlPO₄-11 was crystallized from the composition [(CH₃)₃N]₂NH P₂O₅ Al₂O₃ 40H₂O in a static PTFE-lined 125 cm³ bomb for 72 h at 200°C. The X-ray powder diffraction pattern was in good agreement with that for AlPO₄-11. A scanning electron micrograph showed that the material was made of bundles of rod-like crystals, ~ 3-μm long.

AlPO₄-21 was crystallized from the composition CH₃CH₂CH₂NH₂ P₂O₅ Al₂O₃ 40H₂O in a stirred PTFE-lined bomb for 8 d at 200°C and converted to AlPO₄-25 by calcination at 500°C for 16 h. The material was shown to be free from crystalline impurities by X-ray powder diffraction and found by...
scanning electron microscopy to consist of broken lath-like crystals, 5–30-μm long, in disordered aggregates.

All of the aluminophosphates were prepared from pseudoboehmite and Analalr phosphoric acid. Tripropylamine (≥ 98%), n-propylamine (≥ 99%), and tetrapropylammonium bromide (≥ 99%) were from Fluka. Di-isopropylamine (99%) was from Aldrich.

**Treatment with salt solutions**

The salts were Analala-grade materials from BDH Ltd. Solutions were prepared with distilled water and mixed with the aluminophosphates in polypropylene bottles. In some cases, the bottles were tumbled in a thermostat bath at 25°C, and in others, the mixtures were stirred at room temperature. Thereafter, the solid phase was separated by filtration, washed on the filter with distilled water, dried at 110°C, equilibrated with atmospheric water vapor, and then examined by X-ray powder diffraction (Philips diffractometer, CuKα radiation) and scanning electron microscopy (Cambridge Instruments Ltd. Model 90B Microscope). It was found to be quite difficult to remove all the salts from the materials treated with concentrated solutions, and it is believed that the salt ions inibibed by the molecular sieves, leached out slowly after the solid phase, had been washed with distilled water.

**RESULTS AND DISCUSSION**

**Action of aqueous salt solutions**

For these experiments, 0.5 g of calcined AlPO₄-5 was mixed with 25 cm³ of aqueous chloride solution (0.1, 1.0, 5.0 mol dm⁻³) and tumbled at 25°C for 18 h. Typical X-ray diffraction patterns of the material before and after treatment are shown in Figures 1 and 2. It can be seen that the predominant effect is a marked decrease in the peak heights; this corresponds to a breakdown of the crystal structure and the formation of amorphous material. For calcined AlPO₄-5 with 0.1 mol dm⁻³ NaCl, there was a 43% reduction in the height of the peak at 2θ = 12.9°, whereas with distilled water [1000 cm³ + 1g calcined AlPO₄-5(S)], there was only an 18% reduction. The extent of the structural degradation increased with the salt concentration, but was relatively insensitive to the nature of the alkali metal cation (Na or K). In all cases, the pH of the solution phase dropped from ~ 5.5 to ~ 3.0, the largest change being observed for the highest chloride ion concentration. The pH changes suggest that phosphoric acid is released to the solution phase, and this was confirmed by positive tests for phosphate. It can be seen by comparison of Figures 1 and 2 that the attack with 1.0 mol dm⁻³ KCl was more marked for AlPO₄-5(M) than for AlPO₄-5(S), although in other experiments, the reverse was observed. Scanning electron micrographs showed that the treated materials were extensively damaged and that much amorphous debris was formed. However, in the case of AlPO₄-5(M), the original hexagonal aggregates could still be clearly discerned.

**Figure 1** Treatment of calcined AlPO₄-5(S) with aqueous salts: (a) original calcined AlPO₄-5(S); (b) after treatment with 0.1 mol dm⁻³ NaCl; (c) after treatment with 1.0 mol dm⁻³ KCl; (d) after treatment with 5.0 mol dm⁻³ NaCl followed by calcination at 450°C
Degradation of AlPO₄ by aqueous salt solutions: B. Hampson et al.

After treatment with 5.0 mol dm⁻³ NaCl, whereas the treated AlPO₄-5(S) was in the form of amorphous-looking aggregates with sizes up to 25 μm. On subsequent calcination at 450°C, the structure of the AlPO₄-5(M) was partially retained and some AlPO₄-tridymite was formed (Figure 2), whereas with AlPO₄-5(S), complete conversion to AlPO₄-tridymite occurred (Figure 1). When the treatment with chloride solutions was repeated with uncalcined AlPO₄-5(S) and AlPO₄-5(M), there was virtually no effect on their X-ray diffraction patterns. It is not possible to tell whether the organic template stabilizes the lattice against degradation or merely slows down the process by preventing access of the chloride ions to the channel system.

To test the effect of other anions, 0.5 g samples of calcined AlPO₄-5(S) were mixed with 50 cm³ of 5 mol dm⁻³ solutions of NaI, NaBr, and Na₂S₂O₃ and a 1 mol dm⁻³ solution of Na₂SO₄ and tumbled at 25°C for 18 h. All the salts had some effect on the AlPO₄-5, but the range of behavior was quite wide. The percentage crystallinities based on the height of the major peak at 2θ = 12.9° were I⁻ (8%), S₂O₃²⁻ (9%), Br⁻ (19%), and SO₄²⁻ (48%). A similar experiment with a saturated solution of sodium carbonate completely destroyed the AlPO₄-5(S); in this case, it is probable that the active anion was not carbonate but hydroxide.

This experiment and a similar one in which the contact time was increased to 3 d showed that the order of lattice attack is OH⁻ > I⁻ > S₂O₃²⁻ > Br⁻ > Cl⁻. Similar 18-h treatments of AlPO₄-11 and AlPO₄-25 showed the same order of attack, but the effect was less than for AlPO₄-5 and least for the narrow pore AlPO₄-25. The percentage crystallinities for AlPO₄-11 based on the diffraction line at 2θ = 16.1° were I⁻ (11%), S₂O₃²⁻ (30%), Br⁻ (47%), and SO₄²⁻ (70%), and for AlPO₄-25 based on the line at 2θ = 15.1° were I⁻ (40%), S₂O₃²⁻ (74%), Br⁻ (91%), and SO₄²⁻ (91%).

**Action of aqueous acids**

Treatment of calcined AlPO₄-5(S) with 1 mol dm⁻³ HNO₃ acid by tumbling for 1 d at 25°C had a much smaller effect than that produced by 1 mol dm⁻³ KCl [% crystallinities KCl (56%), HNO₃ (72%)], and it appears that the marked effect observed with hydrochloric acid was due primarily to the chloride ion. Uncalcined AlPO₄-5(S) was not attacked by 1 mol dm⁻³ nitric acid. Treatment of calcined AlPO₄-5(S) with 1 mol dm⁻³ phosphoric acid at 25°C had very little effect on the X-ray diffraction pattern; the height of the major peak at 2θ = 22.4° remained unchanged, whereas that at 2θ = 19.7° showed a slight decrease in intensity.

**Damp materials**

It was observed that samples of calcined AlPO₄-5 that had been stored at room temperature for 7 months showed changes in their X-ray diffraction patterns. A new line appeared at 2θ = 21.6°, and there was a 44% reduction in crystallinity (based on the diffraction line at 2θ = 12.9°). It seemed possible that these changes could have been promoted by the presence of small quantities of water. To simulate and speed up this process, calcined AlPO₄-5(S) (0.5 g) was mixed with water (2 g) and held in a sealed container at 95°C for 18 h, 2 d, and 7 d. No new peaks were observed in the X-ray powder diffraction pattern, but there was a decrease in the crystallinity of the sample; the % crystallinities based on the peak at 2θ = 12.9° were 83, 76 and 59%, respectively (Figure 3). In a corresponding experiment with uncalcined AlPO₄-5(S), no effect on the X-ray powder diffraction pattern was observed. When calcined AlPO₄-5(S) was held at 95°C without the addition of water, the X-ray powder diffraction pattern remained unchanged after 2 d, but new peaks due to AlPO₄-tridymite appeared after 7 d and there was a 21% decrease in the crystallinity of the AlPO₄-5. When the original experiment with calcined AlPO₄-5(S) was repeated with 5 mol dm⁻³ aqueous NaCl, a total collapse of the AlPO₄-5 structure was observed at 95°C.

When calcined AlPO₄-11 (0.5 g) was treated with water (2 g) at 95°C, there was a significant decrease in

---

**Figure 2** Treatment of calcined AlPO₄-5(M) with aqueous salts: (a) original calcined AlPO₄-5(M); (b) after treatment with 1.0 mol dm⁻³ KCl; (c) after treatment with 5.0 mol dm⁻³ NaCl followed by calcination at 450°C.
Degradation of AlPO₄ by aqueous salt solutions: B. Hampson et al.

Figure 3 Treatment of AlPO₄-5(S) with water at 95°C: (a) untreated calcined AlPO₄-5(S); (b) after treatment for 2 d.

Crystallinity (Figure 4). In contrast, calcined AlPO₄-25 in an identical experiment remained unchanged after 2 d at 95°C (Figure 5), although a slight increase in amorphous content was observed after 7 d. It seems likely that most microporous aluminophosphates will be susceptible to attack by water and that the rate of reaction will be markedly dependent on the framework structure.

CONCLUSIONS

Although there is much scope for further investigations, the general pattern of behavior is clear. Aluminophosphate molecular sieves are attacked by water especially when in their calcined form and prolonged contact even at room temperature is likely to have a deleterious effect. The attack is very much more rapid in the presence of soluble salts, and although the exact mechanism is still to be determined, it seems likely that their action is essentially catalytic in nature. In general halides are more effective than are oxyanions, and although this may be related to the ease with which they can enter the channels, the potency of the

Figure 4 Treatment of AlPO₄-11 with water at 95°C: (a) untreated calcined AlPO₄-11; (b) after treatment for 2 d.

Figure 5 Treatment of AlPO₄-25 with water at 95°C: (a) untreated calcined AlPO₄-25; (b) after treatment for 2 d.
thiosulphate anion suggests that the mechanism may involve nucleophilic attack. Although it is believed that anions are primarily responsible for the rapid aqueous degradation of the aluminophosphates, it is clear that cations must also have some effect. In some cases, it appears that the potency of the anion can be mitigated by organic cations. Hence, AlPO₄-5 can be synthesized in the presence of bromide ions and the imbition of tetrapropylammonium bromide from aqueous solution by AlPO₄-5 can be studied with only slight lattice damage. The microporous aluminophosphates are much more reactive than are the crystalline microporous silicas, and it is apparent that a whole range of structural changes and dissolution processes are possible when they are contacted with water or with aqueous salt solutions. This reactivity must be taken into account when they are used and when they are stored for a prolonged time. It seems likely that the kinetics of their degradation will be markedly dependent on the quality of the as-made crystals and on the procedure used to remove the organic template. We suggest that aluminophosphate molecular sieves should be kept dry and stored in their as-made form.

ACKNOWLEDGEMENTS
We thank the S.E.R.C. for financial support.

REFERENCES
2 Lowe, B.M. and Young, D., Unpublished results
8 Tapp, N.J., Milestone, N.B. and Bibby, D.M. Zeolites 1988, 8, 183
10 Wilson, S.T., Lok, B.M. and Flanigen, E.M. US Pat. 4310440 (January 1982)