Heteroatom-Substituted Aluminophosphates

Joanna K. Wyles

Ph.D. 1999
Abstract

The work described in this thesis focuses on the synthesis and structural properties of heteroatom-substituted aluminophosphates with the chabazite structure, an important class of materials in the field of catalysis. Efforts have been made to design new template molecules for the synthesis of these materials, to understand the overall framework structure and derive the coordination geometry around the heteroatom both in the as-synthesised state and after producing the active catalyst.

Two new organic molecules have been identified and used in the synthesis of heteroatom substituted aluminophosphates; these templates were chosen using two techniques: the de novo computer code ZEBEDDE predicted the template 4-piperidinopiperidine would produce a material with a chabazite structure; using rational design the template 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO) was identified for the synthesis of a small pore aluminophosphate. Chabazite type materials were produced in both cases. From a detailed characterisation using both laboratory and synchrotron radiation based techniques, we have been able to study the active sites in these materials and therefore predict their catalytic performance.

A detailed study has also been carried out on the differences in the structure, stability and redox properties of CoAPO-34 synthesised using four different templates. From this study we are able to propose the best preparative route to produce a good catalyst for, in particular, the shape selective oxidation of linear alkanes.
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Acknowledgements

I would especially like to thank my supervisor, Professor Richard Catlow, for all his help and guidance during my three years at the Royal Institution and Dr. Sankar for his help, both at the RI and at Daresbury.

This research could not have taken place without technical assistance, therefore I would like to thank Mike Sheehy and Dave Madill at the Royal Institution and the staff at the Daresbury laboratory, in particular Simon Teat, Fred Mosselmans, Andy Dent, Chiu Tang and Ian Harvey for all their help. I would also like to thank Dewi Lewis for making the template predictions using ZEBEDDE, Robert Raja for his help with the oxidation catalysis and Simon Coles at the EPSRC Crystallography service for collecting the single crystal data for DAF-5.

I would also like to thank Andy Davies and Gavin Muncaster for their help during the last three years and everybody else at the Royal Institution for making it such an enjoyable place to work. Finally, I would like to thank the EPSRC and my parents for financial support and Steve Baskeyfield, Jo Waldron and Gayna Clark for being such great friends and keeping me sane when things weren't going as well as they could be.
Chapter 1

Introduction
1.1 Objectives of these studies

The aim of this work is to gain a greater understanding into the synthesis and formation of active sites in microporous heteroatom-substituted aluminophosphates.

Microporous materials are those which have pore sizes in the range 0.3 to 2.0nm, and include the aluminosilicate zeolites and silicates as well as aluminophosphates. These materials have been extensively studied and synthesised over the last 50 years; the main theme of research during this time has been focussed on a quest for new structures and compositions, with the aim of meeting the requirements of industrial applications. The uniform, rigid pore structure of these materials means they are suitable materials in the fields of catalysis, ion-exchange and molecular sieving.

This thesis focuses on microporous aluminophosphates; Chapter 2 gives an overview of the structural properties, synthesis and catalytic properties of these materials. Aluminophosphates are synthesised by including an organic amine in the synthesis gel, which acts as a structure-directing agent or ‘template’; therefore, by changing the template molecule we can synthesise different structures. In this work we describe the use of two new templates for the synthesis of microporous aluminophosphates; in Chapter 4 we discuss the design of the template 4-piperidinopiperidine using the *de-novo* computer code ZEBEDDE. In Chapter 5 we use rational design to identify the template 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane as a template for the synthesis of a small-pore aluminophosphate. Some structures
can be synthesised from a wide range of templates, for example CoAPO-34; in Chapter 6 we compare the synthesis of this material using four different templates.

A wide range of heteroatoms have been substituted into aluminophosphate frameworks. However, in this work we shall study silicon and cobalt-substituted aluminophosphates only as these materials have shown great potential in the field of acid- and oxidation-catalysis.\(^2\,^5\). The introduction of heteroatoms into the neutral aluminophosphate framework creates active sites into the structure, which are distributed in a spatially uniform manner throughout the microporous framework. Infra-red spectroscopy and combined XAS/XRD are invaluable techniques in studying active sites in microporous materials. These techniques are described in Chapter 3 and are used in this work to assess the presence of Brønsted acid sites and redox properties in the aluminophosphates synthesised. From the results we can predict how the material will perform in catalytic reactions; the reactions on which we will focus are the conversion of methanol to hydrocarbons, and the selective oxidation of linear alkanes.

The crystal sizes of the aluminophosphates synthesised are often too small for conventional single crystal diffraction. We have therefore used the recently developed microcrystalline diffraction technique\(^6\) which allows us to study crystals as small as 10 x 10 x 10\(\mu\)m. This technique is described in Chapter 3, together with other diffraction methods, and is used in Chapters 4 and 6 to determine the number of template molecules and their position inside the materials synthesised.
By using two new templates in the synthesis of heteroatom-substituted aluminophosphates, as well as studying CoAPO-34 using templates from the literature, we gain further insight into the synthesis process of these materials, in particular, relating to how differences in the synthesis process can affect the formation of active sites in these materials.

1.2 References


Chapter 2

Microporous Aluminophosphates: Structural Properties, Synthesis and Catalytic Activity
2.1 Aluminophosphates

In 1982, S. T. Wilson et al\(^1\) of the Union Carbide Corporation discovered a novel class of crystalline microporous aluminophosphate phases. These materials represented the first family of framework oxide molecular sieves synthesised without silica.

These new materials consisted of corner-sharing \(\text{TO}_4\) tetrahedra (\(T = \text{Al}, \text{P}\)) producing a \([\equiv\text{Al}-\text{O}-\text{P}≡]\) unit with strict Al/P alternation. They were given the name \(\text{AlPO}_4\)-n where \(n\) denotes a particular structure type. Wilson et al\(^1\) discovered about 20 different framework structures; of these at least 14 were 3-dimensional microporous structures consisting of cages and channels running through the structure; the remainder were 2-dimensional layer-type materials. Among the \(\text{AlPO}_4\) structures prepared, some have structures analogous to those of known zeolites; for example \(\text{AlPO}_4\)-17 has the erionite structure and \(\text{AlPO}_4\)-34 has the chabazite structure. Some structures however, have no zeolite counterparts e.g. \(\text{AlPO}_4\)-5. Each different structure type is listed in the Atlas of Zeolite Structures\(^2\) together with the frequently quoted three letter International Zeolite Association (IZA) framework codes, designed to categorise all microporous materials. Secondary building units (SBU’s) are also given for each structure; these are the basic building blocks for a particular structure type.

Pure aluminophosphate materials do not contain active sites essential for catalysis due to their neutral framework; however, active sites can be generated if heteroatoms
are incorporated into the framework; this is discussed further in Section 2.3.

Aluminophosphates can be divided into groups depending on their pore size: very small, small, medium, large and very large-pore. The pore sizes for each group and examples are given in Table 2.1. The largest class is the small pore (diameter 0.35-0.45nm, made up of rings containing 8 atoms), which contains over half the known structures.

<table>
<thead>
<tr>
<th>Pore sizes</th>
<th>T-atoms in largest ring</th>
<th>Diameters</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very large</td>
<td>18/20</td>
<td>&gt;10Å</td>
<td>JDF-20, VPI-5</td>
</tr>
<tr>
<td>Large</td>
<td>12</td>
<td>7-10Å</td>
<td>5, 36, 37, 40, 46, 50, DAF-1</td>
</tr>
<tr>
<td>Medium</td>
<td>10</td>
<td>5-6Å</td>
<td>11, 31, 41</td>
</tr>
<tr>
<td>Small</td>
<td>8</td>
<td>3-4Å</td>
<td>14, 17, 18, 22, 26, 33, 34, 35, 39, 42, 43, 44, 47, 52</td>
</tr>
<tr>
<td>Very small</td>
<td>6</td>
<td>&lt;3Å</td>
<td>16, 20</td>
</tr>
</tbody>
</table>

Table 2.1: A selection of aluminophosphates, showing the wide range of pore sizes. The numbers denote the structure AlPO₄-n.

Since the work of Wilson et al, many new aluminophosphate structures have been identified, both microporous and layered. In 1988, M. E. Davis et al prepared an
aluminophosphate which was named VPI-5; this material contains rings made up of 18 tetrahedral atoms and possessing a free diameter of approximately 12-13Å. Previously, the largest pore for an aluminophosphate was made up of 12 tetrahedral atoms, with a diameter of ~10Å. In 1993, Wright et al synthesised DAF-1, a magnesium containing aluminophosphate with a unique framework structure. DAF-1 possesses 2 large (12-membered) channel systems; the first has a pore opening of 7.3 x 7.3Å and contains periodic supercages, 16.3Å in diameter. The second is approximately 6.1 x 6.1Å in diameter and is linked perpendicularly by medium pore (10-membered ring) channels. The synthesis of these novel structures arises through a careful balance between the choice of templating species and the composition of the synthesis gel. The synthesis process is discussed further in the following section.

Figure 2.1 shows the pore size of selected aluminophosphates: a very large pore (VPI-5), a large pore (AlPO-5), a medium pore (AlPO-41) and a small pore (AlPO-34) aluminophosphate. An example of a cage (AlPO-34) and a channel structure (AlPO-5) are shown in Figure 2.2.
Figure 2.1: A selection of pore sizes present in aluminophosphates. Large spheres represent the tetrahedral Al, P or heteroatom; the small spheres represent the bridging oxygens.
2.2 Synthesis

These materials are synthesised hydrothermally at temperatures between 100°C and 250°C, usually from aqueous reaction mixtures containing a source of aluminium, phosphorus, and a metal or silicon if required. An organic amine or quaternary ammonium salt is also added which becomes trapped within the cages/pores of the material. The organic molecules fulfil an essential templating or structure-directing role in the synthesis of these microporous materials; without them, dense AIPO₄ structures or known hydrates AlPO₄.nH₂O form. These ‘templates’ can be removed from the structures by calcination i.e. heating the material in air or oxygen at
temperatures between 400 and 600°C, with the microporous structure remaining intact.

Lok et al\textsuperscript{13} defined the concept of templating in microporous materials as ‘the phenomenon occurring during the gelation or nucleation process whereby the organic molecule organises oxide tetrahedra into a particular geometric topology around itself and thus provides the initial building block for a particular structure type’. However, instances where there is an exact fit between template and host are very rare. A large proportion of known templates can direct the formation of several different structure types, for example di-n-propylamine can be used to synthesise AlPO-11, -31, -39, -41, -43, -46, -50 and VPI-5\textsuperscript{4,14}. Also some frameworks can be synthesised using a wide range of templates, for example AlPO-5 can be produced using at least 25 different organic molecules. AlPO-5 and AlPO-11 are the structures that show the lowest template specificity; they both contain unidimensional channels, which impose the lowest stereochemical constraints on the size and shape of the template\textsuperscript{15}. As well as a structure-directing role, templates can also act as charge-compensating species, especially if silicon or metal ions are present in the gel.

It is generally small organic molecules that are used as templates in the synthesis of aluminophosphates; however, recently Wright et al\textsuperscript{5} reported the use of long polymeric templates. By varying the chain length of the polymer, different structures have been formed. Using this method the novel structures STA-1 and STA-2 have been synthesised.
In most syntheses, especially when using templates that are known to direct the formation of several structures, it is the gel chemistry that is most important in forming the desired product. Template, silicon and metal ion concentrations and source of aluminium all have an effect on the product formed, as does synthesis time and temperature, gel aging and agitation. The pH of the synthesis gel also plays an important part in directing the final product and the rate of crystallisation. The pH of a synthesis gel is generally in the range 3.0 to 10.0 and it can be manipulated by varying the amounts of template or phosphoric acid present. At an initial pH of less than 3, dense phases are more likely.

In addition to the traditional syntheses using aqueous gels, there are a growing number of reports describing aluminophosphate syntheses using non-aqueous solvents. One of the first non-aqueous preparations was by Huo and Xu; AlPO-5, AlPO-11 and AlPO-21 were synthesised in the presence of ethylene glycol, propane-1,3-diol and hexanol. Non-aqueous gels have led to the synthesis of new structures, both microporous and layered, and products with larger crystal sizes. The novel aluminophosphate, JDF-20 has been synthesised by the use of a non-aqueous solvent with the template triethylamine; this material contains elliptically shaped 20-membered rings. JDF-20 differs from other aluminophosphates in that the Al:P ratio is 5:6 rather than 1:1 as is usually found. At higher temperatures or longer crystallisation times, AlPO-5 forms from the same gel. Oliver et al studied the effect of adding increasing amounts of water to initially non-aqueous gels, containing the template triethylamine. At low water contents, the product had a chain motif similar to the JDF-20 structure; at higher water concentrations, AlPO-15
and AlPO-5 are favoured, which was explained by the differing degrees of hydrolysis occurring in the system as various amounts of water were added. The ability to control the degree of hydrolysis by controlling the amount of water present in non-aqueous systems may lead to a route for the synthesis of novel aluminophosphates.

The addition of fluorine ions to aqueous synthesis gels has also resulted in the synthesis of novel materials\(^8,28\). In the presence of F\(^-\) ions, unsubstituted AlPO-34\(^29\) and AlPO-35\(^30\) have been prepared; both of these cannot be synthesised in the absence of fluoride ions if heteroatoms are not present. UiO-7\(^8\) was synthesised from a fluorine containing aluminophosphate gel, which in the absence of F\(^-\) forms AlPO-20. Known aluminophosphates have also been synthesised in the presence of fluoride ions\(^31-32\); in some cases this has led to the formation of larger, higher quality crystals\(^31\) or materials with a higher thermal stability\(^32\).

Recent work in the aluminophosphate field has concentrated on trying to elucidate the synthesis procedure, with the ultimate aim of being able to design a particular material for a particular application, and thus tailor the properties of solids to meet the demands of today's technology.
2.3 Acidity

Due to the neutral framework of the aluminophosphate, these materials have no mechanism for ion exchange behaviour and the lack of framework active sites means that, unless modified, they are unsuitable in the field of catalysis.

Acid sites can be introduced into the framework by partial substitution of either Al or P with a lower valent ion, which was first achieved in 1984 by Lok et al at Union Carbide\textsuperscript{34}; Si was partially substituted into the framework in place of P producing a silicoaluminophosphate or SAPO. This was followed by the substitution of Al by a divalent metal ion, Me(II) e.g. Co, Mn, Zn producing a MeAPO\textsuperscript{14}.

This partial replacement of P(V) by Si(IV) and Al(III) by Me(II) or both (to form a MeAPSO) results in a material which has retained its overall framework structure yet is no longer neutral; the resulting framework has an overall negative charge, which, in the as-prepared material is usually compensated by the template molecule. Upon heating the material in oxygen at about 550°C (calcination), the template molecule is lost leaving an empty negatively charged framework structure. In some cases, this charge can be compensated by loosely bound detachable protons attached to the bridging O atom adjacent to the lower valent ion; these provide the Brønsted acid sites as shown in Figure 2.3. This acidity is essential for certain catalytic applications and, as with other microporous systems, the product distribution depends on the pore structure of the material. Microporous aluminophosphates make good, selective catalysts due to the ability to discriminate between molecules on the basis of their size and shape.
Figure 2.3: Formation of a Brønsted acid site in a metal substituted aluminophosphate. If silicon is the heteroatom present in the aluminophosphate, the reduction stage is not required to form the Brønsted acid site.

Not all structures form Brønsted acid sites after substitution. It has been proposed\textsuperscript{35-37} that Lewis acid centres act as the balancing charge in CoAPO-5 and -11; no vibrational mode relating to the bridged hydroxyls usually expected for Brønsted sites were observed in the IR spectrum for these materials\textsuperscript{35}. Studies by Barrett et al\textsuperscript{37,38} reported that these Lewis acid sites arise due to the presence of anionic vacancies arising from missing lattice oxygens (Figure 2.4); such sites are thought to arise due to a dehydroxylation process\textsuperscript{38}.

\[\text{As-prepared MeAPO (Template compensates charge)}\]
Figure 2.4: Formation of Lewis acid sites in metal-substituted aluminophosphates. In the model proposed by Barrett et al, each anionic vacancy is accompanied by a four-coordinated heteroatom.

In addition, redox properties can be generated within the microporous framework when a small percentage of Al(III) is partially substituted by a metal ion which has the ability to change its oxidation state within the framework. For example, cobalt and manganese both show redox properties if they are incorporated in the aluminophosphate framework. In the Me(II) form, Bronsted acid sites are usually generated to compensate for the negative charge, but Me(II) can be oxidised in the framework to give Me(III) which remains in the framework (Figure 2.5). The oxidised metal can easily be reduced back to the divalent state by heating in hydrogen. For cobalt, this change in oxidation state is accompanied by a colour change from blue Co(II) to green Co(III).
Marchese et al.\textsuperscript{39} proved that Co(II)/Co(III) redox centres were closely associated with Brønsted acid sites by the use of FTIR spectroscopy. Upon calcination the Brønsted acidity which was present in the Co(II) form disappears. Verberckmoes et al.\textsuperscript{40} showed by diffuse reflectance spectroscopy that only framework Co\textsuperscript{2+} is susceptible to this reversible redox behaviour, extra-framework Co\textsuperscript{2+} remains in the divalent state both in oxidising and reducing conditions. Redox centres in aluminophosphates have also been studied using other analytical techniques, for example, electron absorption spectroscopy\textsuperscript{41-43}, infra-red spectroscopy\textsuperscript{39,42} and x-ray absorption spectroscopy\textsuperscript{36,44}.

\begin{center}
\begin{tikzpicture}
  \node[draw,rectangle] (calcination) at (0,0) {Calcination \(\text{(oxygen, 550°C)}\)};
  \node[draw,rectangle] (reduction) at (0,-2) {Reduction \(\text{(hydrogen, 400°C)}\)};
  \node[draw,circle] (bronsted) at (-1,-1) {\text{Brønsted Acid Site}};
  \node[draw,circle] (neutral) at (1,-1) {Neutral Framework};
  \draw[->] (calcination) -- (neutral);
  \draw[<-] (reduction) -- (bronsted);
\end{tikzpicture}
\end{center}

\emph{Figure 2.5: Redox properties can be introduced into the frameworks of aluminophosphates. Calcination of the as-prepared material forms the neutral\textit{\text{Me(III) substituted material which, when reduced, forms a Brønsted acid site.}}}
2.4 Catalysis

Microporous aluminophosphates owe their success in the field of catalysis to several factors:

(i) Size and shape selectivity is introduced due to the regular spatial dimensions of the channels and pores within the crystalline aluminophosphate framework.

(ii) The ability to introduce strong acid sites by the choice of structure and modification of the chemical composition.

(iii) The catalytic activity of metals e.g. the redox properties of Co, Mn, V can be incorporated into the aluminophosphate framework.

2.4.1 Catalysis due to Brønsted Acid Sites

One of the major Brønsted acid catalysed reactions studied is the conversion of methanol to light hydrocarbons. This industrially important reaction has stimulated extensive study as it provides a feasible economic route for supplying the basic materials of the petrochemical industry from an abundant methanol supply. SAPO-34, which has a structure analogous to the mineral chabazite, has been found to exhibit excellent catalytic activity in this reaction\textsuperscript{45-48} with the selective conversion of methanol to ethene and propene. This activity is due to the combination of a moderate acid strength and steric restrictions imposed by the small pore size. A \textsuperscript{13}C MAS NMR study by Salehirad and Anderson\textsuperscript{49} highlighted the importance of the acidity in the methanol to hydrocarbon conversion over SAPO-34. They reported that methanol reacts with the acid sites of SAPO-34 to form methoxy groups on the surface; these are involved in the formation of all hydrocarbon products. Hocevar
and Levic\textsuperscript{46} studied several metal-substituted silicoaluminophosphates and found that the incorporation of metal into the structure increased the acidity, yet lowered the catalytic activity compared to SAPO-34. By incorporating nickel into SAPO-34, Inui et al.\textsuperscript{50,51} found that a selectivity towards ethene of nearly 90\% is achievable.

\subsection*{2.4.2 Catalysis occurring at metal centres}

There are many catalytic reactions that occur at the metal centre itself (as opposed to the acid site generated when a metal is included in a structure). The ability of some metals, especially cobalt and manganese to exhibit redox properties has led to the application of these materials in oxidative transformations. The oxidation of cyclohexane to cyclohexanol and cyclohexanone is an industrially important reaction as the products can be converted into adipic acid, used in the synthesis of Nylon 6,6. Cyclohexane oxidation has been shown to occur over several cobalt-substituted aluminophosphates\textsuperscript{52,53}.

CoAPO-18 and MnAPO-18 have been shown\textsuperscript{54} to be good catalysts for the regio-selective oxidation of linear alkanes in air. Both materials are able to selectively oxidise the terminal methyl groups of the n-alkanes which is very difficult to achieve with other inorganic materials. Other oxidation reactions over aluminophosphates, which have been reported in the literature, are the oxidative dehydrogenation of alkanes\textsuperscript{55,56} and the selective oxidation of secondary alcohols\textsuperscript{57}.
2.5 References


Chapter 3:

Experimental Techniques
3.1 Summary

In this chapter we introduce the techniques used to investigate the microporous materials that we have synthesised. Powder and single crystal X-ray diffraction (XRD), extended X-ray absorption spectroscopy (EXAFS), combined XAS/XRD and infra-red spectroscopy are discussed. In each case, an overview of the technique is given followed by a simple description of the theory, practice and analysis procedures. We also describe the advantages of using synchrotron radiation over conventional x-ray sources.
3.2 X-ray Diffraction

3.2.1 Introduction

X-ray diffraction is one of the most standard laboratory techniques used in the area of solid state chemistry; it plays a crucial role in phase identification and structure solution. In the case of microporous aluminophosphates it can provide us with information about the structure of these ordered framework materials (for examples, see references 1-5). Also, diffraction techniques have been used to study structural changes during the synthesis of microporous materials\textsuperscript{6,7} and to determine the location of the template molecules inside the aluminophosphate framework\textsuperscript{8-11}.

Laboratory based powder x-ray diffraction is widely used for identifying materials and assessing their purity and crystallinity. Laboratory x-ray sources are also increasingly being used in structure solution. Using synchrotron radiation, very high-resolution x-ray diffraction patterns are obtainable with well-defined peak shapes and very narrow Bragg peaks, which means large complex crystal structures can be solved from powder data. If good quality single crystals are available, single crystal diffraction provides the best technique for structure solution; the use of synchrotron radiation means micro-crystals can now be studied\textsuperscript{8,10,11}. Energy-dispersive x-ray diffraction is not suitable for structure solution, however, it has very short data collection times which means time-dependant processes may be studied, for example, the synthesis of microporous materials\textsuperscript{6,7}. Structure solution from both powder and single crystal diffraction will be discussed in greater detail in a later section of this chapter.
3.2.1.1 Synchrotron Radiation

Synchrotron radiation is the name given to x-rays or light produced by electrons circulating in a storage ring at nearly the speed of light. In a synchrotron radiation source (SRS), electrons are accelerated and injected into the storage ring where a constant magnetic field keeps them at a fixed energy within the accelerators orbit. The synchrotron radiation is then emitted tangentially from the ring to the experimental areas via high vacuum lines. This process is shown in Figure 3.1. The electron beam loses a large amount of energy emitting synchrotron radiation; this energy is replenished by radiofrequency power, provided by a klystron. This way, the same electron beam can emit synchrotron radiation continuously for many hours.

The data in this work were collected at Daresbury Synchrotron Radiation Source, which operates at 2GeV with a typical current in the range 150-250mA.

Figure 3.1: Synchrotron radiation is emitted tangentially from the storage ring.
3.2.2 Powder X-ray Diffraction

3.2.2.1 Laboratory-based XRD

Powder x-ray diffraction (XRD) is a widely used technique in the analysis of powdered crystalline materials as it allows quick and easy identification of the phases present. Each crystalline solid has a distinctive and unique powder pattern, which may be used as a 'fingerprint' for its identification. If a novel structure has been prepared, powder XRD coupled with an auto-indexing program e.g. TREOR provides a useful tool in obtaining cell parameters and unit cell dimensions.

3.2.2.2 X-ray diffraction with synchrotron radiation

The use of synchrotron radiation in the field of powder x-ray diffraction offers the following advantages:

1. The high intensity of the radiation means that data can be collected rapidly; thus time dependent processes and/or very small samples can be studied.

2. The tunability of the source means flexibility in the choice of the optimum wavelength for an experiment.

3. The collimation of the X-ray beam allows very narrow Bragg peaks with well-defined peak-shapes to be obtained, thus allowing the structure to be solved using the Rietveld profile analysis technique which is described in greater detail in Section 3.2.4.
3.2.3 Structure Solution of New Materials

In the powder method, a monochromatic beam of x-rays strikes the sample and a moveable detector measures the scattered intensity of the x-rays as a function of the angle. A powder sample should ideally contain an infinite number of randomly orientated crystallites. Each set of lattice planes within the sample will scatter the x-rays at the appropriate 2θ angle, according to the Bragg equation:

\[ n\lambda = 2d \sin\theta \]  

(1)

where \( \lambda \) is the wavelength of the x-rays used and \( n \) is the order of the reflection. An x-ray powder pattern is a plot of the intensity recorded against the angle, 2θ.

For the determination of the structure of new materials, a model needs to be developed of the structure that contains information on the atomic positions and their occupancy, temperature factors and unit cell dimensions. This model should produce a calculated diffraction pattern with identical peak positions and intensities to the experimental data.

The intensity of each reflection \( (I_{hkl}) \) is proportional to the square of the structure factor, \( F_{hkl} \), (Equation 2) which represents a mathematical description of each diffracted wave from the set of lattice planes hkl (Equation 3).

\[ I_{hkl} \propto F_{hkl}^2 \]  

(2)
\[ F_{hkl} = \sum_{i=1}^{n} f_i e^{2\pi i (hx_i + ky_i + lz_i)} \]  

(3)

\( f_i \) is the scattering factor which describes the scattering efficiency of the atom type \( i \) at the wavelength chosen. The exponent describes the phase where \( hkl \) are the Miller indices and \( x_i, y_i \) and \( z_i \) are the fractional coordinates of the \( i^{th} \) atom. Since x-rays are scattered primarily by the electrons, the atomic positions are defined by their electron clouds.

If we know the structure factors \( F_{hkl} \) for a complete set of x-ray reflections, we can calculate the electron density, \( \rho \), at any position \( xyz \) in the unit cell (and therefore the atomic positions) from Equation 4.

\[ \rho(x, y, z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} F_{hkl} e^{-2\pi i (hx + ky + lz)} \]  

(4)

As it is the intensities we are measuring, which are proportional to \( F_{hkl}^2 \), it means we are able to obtain the modulus of the structure factor, \( |F_{hkl}| \) i.e. the amplitude of the wave; however, no information on the sign (phase angle) is yielded directly from the measured data. Information on the phase is needed before the electron density can be calculated to give a starting model for the atomic positions. This dilemma is known as the **phase problem**.

Several techniques have been developed to overcome the phase problem and can be used to produce a starting model for a refinement. Direct methods and Patterson techniques are the two most commonly used. The Patterson technique is most useful.
where heavy atoms are present; a Patterson vector map is used to calculate the location and approximate phases of the heavy atoms, then this information is used to locate the other atoms. Direct methods is a statistical method for predicting phases and relies on the probabilistic relationship which the phases of the reflections have to the intensities. Direct methods was used for structure solution in this thesis.

The above structure solution methods will produce approximate coordinates for all the atoms in the cell.

3.2.4 Structure Refinement – Rietveld Profile Analysis

In powder diffraction, there is commonly a problem arising from the overlap of peaks in the diffraction pattern, especially at high scattering angles. Accurate intensities, and hence structure factors, for these reflections cannot be refined. A technique developed by Rietveld known as profile analysis is used to overcome this problem. The Rietveld method involves the refinement of a structural model to obtain the best fit between the observed and calculated diffraction profiles, rather than individual reflections, and relies on the ability to describe the peak shape of individual Bragg reflections using a parameterised analytical function. This method was originally developed for neutron diffraction data owing to the accurately Gaussian peak shapes obtained using monochromatised neutron beams from reactor sources. However, due to the narrow, well-defined Bragg peaks obtained from synchrotron radiation and the low background, the Rietveld method can also be applied to synchrotron powder data. The technique proceeds as follows.
At each point, I, in the diffraction pattern there is an intensity, $y_i$. A function (Equation 5) comprising of the observed and calculated intensity at each step in the diffraction pattern is minimised using a least squares procedure.

$$S = \sum w_i |y_i - y_{ic}|^2$$  \hspace{1cm} (5)

where:  
$w_i$ = weighting function where $w = 1/y_i$  
$y_i$ = observed intensity at the $i^{th}$ step  
$y_{ic}$ = calculated intensity at the $i^{th}$ step

and the sum is over all data points.

In the Rietveld method, no effort is made initially to allocate observed intensity to particular Bragg reflections, or to resolve overlapped reflections. Therefore a reasonably good starting model is required. To obtain a starting model, one can use the structure solution technique as detailed in the previous section, an isostructural material with a known structure or computer modelling techniques.$^{15}$

Typically, many Bragg reflections contribute to the observed intensity $y_i$, at any point I in the pattern. The calculated intensity $y_{ic}$ depends on the structure factor $|F_k|^2$ values calculated from the structural model. Other contributions are parameters defining the background, a function to describe the shape of the Bragg peaks and the zero-point error, which corrects for any shift in the peak position by detector errors. The full expression for the calculated intensity is given in Equation 6.
\[ y_{ic} = s \sum K \left| F_K \right|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{bl} \] (6)

s is the scale factor, to place the calculated data on the same scale as the experimental; \( K \) represents the Miller indices hkl for a Bragg reflection; \( L_K \) contains the Lorentz, polarisation and multiplicity factors; \( \phi \) corresponds to the chosen analytical function to represent the shape of the peaks; \( P_K \) is the preferred orientation function, used in samples where there is a strong tendency for the crystallites in a sample to be orientated more in one way than the others; \( A \) is an absorption factor, which differs with instrument geometry; \( y_{bl} \) is the background intensity at the 1\(^{th} \) step and \( 2\theta_i-2\theta_K \) is the zero-point corrected peak position.

The peak shapes observed are a function of both the sample and the instrument and they vary as a function of \( 2\theta \). The most widely used peak shape for x-ray data is the pseudo-Voigt approximation of the Voigt function, and is a linear combination of Lorentzian and Gaussian components.

To assess the quality of the model, there are several \( R \)-factors that are commonly used to calculate the goodness of fit, in particular:

R-profile

\[ R_p = \frac{\sum |y_i - y_{ic}|}{\sum y_i} \]

Weighted R-profile

\[ R_{wp} = \sqrt{\frac{\sum w_i (y_i - y_{ic})^2}{\sum w_i y_i^2}} \]
R-Bragg Factor

\[ R_B = \frac{\sum |I_{Ko} - I_{Kc}|}{\sum I_{Ko}} \]

R-Expected

\[ R_E = \frac{\sqrt{(N - P)}}{\sqrt{\sum w_i y_i^2}} \]

Goodness of fit

\[ \chi^2 = \frac{\sum w_j (y_j - y_{kc})^2}{(N - P)} = \left( \frac{R_{wp}}{R_E} \right)^2 \]

Where \( y_i \) and \( y_{kc} \) are the observed and calculated intensities at the \( i^{th} \) step; \( I_{Ko} \) and \( I_{Kc} \) are the observed and calculated intensities assigned to the \( K^{th} \) Bragg reflection at the end of the refinement cycles; \( w_i \) is a weighting factor; \( N \) is the number of observations (i.e. the number of \( y_i^8 \) used) and \( P \) is the number of parameters adjusted. Ideally \( R_{wp} \) should approach the statistically expected R-value, \( R_E \), which reflects the quality of the data. Therefore, the goodness-of-fit \( \chi^2 \), which is the ratio of the two, should approach 1 towards the end of the refinement.

Although these R-factors provide guidance as to the quality of the structural model, a difference profile plot, which displays the difference between the observed and calculated profiles, is the best way of following and guiding a Rietveld refinement. Also, chemical intuition in terms of the bond lengths and bond angles obtained must be applied. Constraints can be included in the refinement to ensure the geometry of the structural model remains sensible.

In a typical refinement, first the lattice parameters, the zero-point error and the background are refined, which is followed by the refinement of the peak shape.
variables. Once the profile has reached convergence, the atom coordinates can be entered and the structural model may be refined, i.e. the coordinates and the temperature factors (isotropic or anisotropic). Soft constraints are often included in the refinement of the structural model to help maintain realistic bond angles and lengths between the atoms; these can be removed once the model starts converging. At each stage of the refinement, the R-factors and the Goodness of fit, $\chi^2$, are calculated too, so the quality of the fit can be assessed. Once convergence is achieved, the parameters should be checked to ensure they are meaningful.

In this work, the program GSAS$^{16}$ was used in the refinement of the high-resolution x-ray powder diffraction data collected.

3.2.5 Experimental

3.2.5.1 Laboratory-based XRD

The x-ray diffraction patterns were collected at room temperature using a Siemens D500 diffractometer which uses Cu K\(\alpha\) radiation ($\lambda=1.5418\text{Å}$).

3.2.5.2 High-Resolution Powder Diffraction

The high-resolution x-ray diffraction data were collected at Station 2.3 of the Daresbury Synchrotron Radiation Source (SRS). The experimental set-up of the station is shown in Figure 3.2:
Figure 3.2: Set-up of the HRPD station 2.3, Daresbury SRS

A white beam of synchrotron radiation is monochromised by a Si(111) monochromator before striking the sample which can be mounted either in flat-plate or in capillary mode. The capillary mode is useful for small quantities of sample, if the material is air-sensitive or where the sample suffers preferred orientation. Preferred orientation arises when there is a stronger tendency for the crystallites in a specimen to be orientated more in one way than all the others. Both techniques involve the sample spinning about the axis to ensure the averaging of crystal orientation which is necessary for high quality reproducible data. Pre- and post-monochromator slits are introduced to reduce as far as possible the angular range of the scattered radiation entering the detector at a given position. Also, between the sample and the detector, a set of long, fine diffracted collimators are used to control
the scattered radiation entering the detector, and to fix precisely the value of 2θ. A silicon standard was used to calibrate the wavelength, with an accuracy of ±0.0001Å and a small 2θ offset (≤0.1°)\(^{17}\).

In a typical experiment, the data were collected from a 2θ value of 5 - 70°, with a step size of 0.01 and a counting time of between 1 and 5 seconds per step. The total data collection times ranged from 4 to 12 hours.

**Data Normalisation**

The x-ray flux is not constant as the current of the electron beam in the storage ring decays with time; therefore, the data need to be normalised to correct for the beam decay effect. In this work, the program PODSUM, available at the Daresbury Laboratories was used to normalise the raw data against the monitor count. This program is also useful for adding several data files together with normalisation. The normalised data was then analysed using the Rietveld analysis program, GSAS\(^{16}\).
3.3 Single Crystal Diffraction

3.3.1 Introduction

If suitable crystals are available, then single crystal diffraction provides the best method for structure determinations. In the case of aluminophosphates, powder diffraction can provide us with information about the framework, however, single crystal diffraction provides a means for studying the location and orientation of the template molecules inside the structure, which may also help us understand more about the concentration and positions of heteroatoms that can be incorporated in the aluminophosphate framework.

With the use of synchrotron radiation, accurate data can now be collected for micro-crystals\textsuperscript{8,10,11,18}, which has huge implications in the field of microporous materials as the crystal size of most of these materials are a few μm (typical sizes are in the range 10 to 50μm). In this thesis, micro-crystal diffraction has been used to locate the template molecules within several cobalt-substituted aluminophosphates.

3.3.2 Structure Solution

The refinement of single crystal diffraction data follows a very similar approach to that detailed for the powder diffraction method. A set of intensity data is collected, from which a list of |F_{hkl}| values are obtained. Structure solutions can be obtained from a combination of Direct Methods (or the Patterson method) and a least-squares refinement. Equation 7 shows the least-squares expression used to refine the data.
\[ S = \sum w_{hkl} \left( F_{obs, hkl}^2 - F_{calc, hkl}^2 \right)^2 \]  \hspace{1cm} (7)

Where \( F_{obs, hkl}^2 \) is the observed value for the structure factor, and \( F_{calc, hkl}^2 \) is the calculated value from the structural model; \( w_{hkl} \) is a weighting factor. To calculate the quality of the model, the following equations are generally used:

\[ R1 = \frac{\sum \left| F_{obs, hkl} \right| - \left| F_{calc, hkl} \right|}{\sum \left| F_{obs, hkl} \right|} \]

\[ wR2 = \left[ \frac{\sum w_{hkl} \left( F_{obs, hkl}^2 - F_{calc, hkl}^2 \right)^2}{\sum w_{hkl} \left( F_{obs, hkl}^2 \right)^2} \right]^{1/2} \]

\[ g.o.f = \left[ \frac{\sum w_{hkl} \left( F_{obs, hkl}^2 - F_{calc, hkl}^2 \right)^2}{N - P} \right]^{1/2} \]

G.o.f is the Goodness of fit, \( N \) is the number of observations and \( P \) is the number of parameters.

### 3.3.3 Experimental

The micro-crystal diffraction data were collected at the recently commissioned single-crystal diffraction facility at Station 9.8 of the Daresbury SRS\(^{18} \). The station has been designed to collect data precisely and rapidly using a Siemens SMART CCD area-detector, complete with a three-circle fixed-\( \chi \) goniometer, a silicon (111)
crystal monochromator and a palladium coated focusing mirror. High and low-
temperature facilities are available to cover the temperature range from 80K to
1000K. Data from crystals of sizes down to 10µm can be measured using this
technique.

In a typical experiment, the crystal to be studied is mounted on a glass fibre, inserted
into the goniometer and aligned to ensure the crystal remains in the synchrotron
beam throughout the experiment. An orientation matrix is collected; this ensures the
crystal is suitable for diffraction (e.g. whether the crystal is twinned, or scatters
enough) and to determine the orientation of the crystal with respect to the beam. The
cell parameters are also calculated from the matrix, which are needed to predict
where the spots should be in the data collection. Once the matrix has been obtained,
typically a hemisphere of data is collected for each sample at a temperature of 150K.
Data collection times are approximately 6 hours.

3.3.4 Data analysis

Once the data collection is complete, the intensity of the spots is integrated over three
frames to calculate the true intensity for each spot. A hkl file is generated and via a
combination of Direct methods and a least-squares refinement, using the
SHELXTL/SHELX-97 suite of programs\(^ \text{19} \), the structure can be obtained.
3.4 X-Ray Absorption Spectroscopy

3.4.1 Introduction

Because the distribution of heteroatoms in the aluminophosphates prepared in this thesis is not ordered, X-ray diffraction yields very little information on the local structure around the heteroatom. As the catalytically active sites (Brønsted acid or redox sites) of these materials are associated with the heteroatoms, we must be able to study the local structure to gain further information about the active sites.

X-ray absorption spectroscopy (XAS) which encompasses both XANES (X-ray absorption near edge spectroscopy) and EXAFS (extended X-ray absorption spectroscopy) is a technique for studying local structure. It yields structural information in the form of bond-distances, coordination numbers and the extent of static disorder of shells of atoms surrounding to the absorbing atom. XAS has been widely applied in this thesis to study the local structure around the cobalt atom in the cobalt-substituted aluminophosphates.

3.4.2 Theory

The absorption coefficient, \( \mu \), of a sample generally decreases with an increase in the photon energy until there is a sharp rise in \( \mu \) at the absorption edge of an element, corresponding to the ejection of a core electron. If other atoms surround the absorbing atom, oscillations in \( \mu \) can be seen at the high-energy side of the absorption edge. This is described further in Section 3.4.2.2. An x-ray absorption
spectrum is shown in Figure 3.3 showing the main components, the pre-edge, the XANES and the EXAFS region.

![X-ray absorption spectrum schematic](image)

Figure 3.3: Schematic of an x-ray absorption spectrum, with different regions shown.

### 3.4.2.1 XANES

The absorption edge shows fine structure associated with the various transitions to empty (or partially filled) electronic states. The XANES region can be used as a fingerprint and can be compared to those obtained from model compounds having known coordination geometries and oxidation states. Low energy photoelectrons also contribute to this region. However, due to extensive multiple scattering, it is difficult to analyse XANES data. The XANES region also contains the absorption edge; the most widely used definition of the edge position being the point of steepest slope which is clearly seen in the first derivative. The edge position is related to the
effective atomic number of the absorbing atom, and is thus correlated with its oxidation state.

3.4.2.2 EXAFS

EXAFS spectroscopy refers to the measurement of the x-ray absorption coefficient, \( \mu \), as a function of the photon energy \( E \) above the threshold of an absorption edge. For isolated atoms, the absorption coefficient decreases uniformly as a function of photon energy beyond the edge. However, for atoms in a molecule, the variation of the absorption coefficient at energies above the absorption edge displays a fine structure called EXAFS. Such fine structure may extend up to 1000eV above the edge, and may have an amplitude of between 1-20% of the edge jump.

The oscillations in the EXAFS part of the spectrum are due to the scattering of the photoelectron from the neighbouring atoms. The outgoing photoelectron can be thought of as a spherical wave and if the absorbing atom has neighbouring atoms, the outgoing waves will be backscattered producing an incoming wave (Figure 3.4). The constructive and destructive interference of these outgoing and incoming waves gives rise to the oscillatory intensity seen in the EXAFS spectrum.

A general expression derived from electron-scattering theory used in the interpretation of EXAFS data and which relates the structural parameters to the measured EXAFS oscillations is given below in Equation 8:

\[
\chi(k) = -A(k) \sum_j \frac{N_j}{kR_j^2} |f_j(k, \pi)| e^{-2\sigma_j^2 R_j^2} e^{-2R_j/\lambda_j} \sin(2kR_j + 2\delta_j + \psi_j)
\] (8)
Figure 3.4: Production of oscillations in the EXAFS spectrum. In an isolated molecule (left) $\mu$ decreases uniformly as a function of the photon energy after the edge. If neighbouring atoms are present (right) the outgoing photoelectron wave (solid lines) is backscattered by these atoms (dotted line), thus causing an interference pattern. This is seen in the EXAFS spectra as oscillations.

$\chi(k)$ is the magnitude of the EXAFS as a function of the photoelectron wavevector $k$; $N_j$ is the number of identical scattering atoms of type $j$ at a mean distance of $R_j$ from the excited atom; $|f_j(k,\pi)|$ is the backscattering amplitude of the photoelectron wave. The phase of the backscattered wave is largely due to the product of the photoelectron wavevector, $k$, and the total distance travelled, $2R_j$. The phase also contains contributions due to two phase shifts: $2\delta_j$ due to the absorbing atom and $\psi_j$.
due to the \(j^{th}\) neighbouring atom; the absorbing atom phase shift is experienced twice, once going out and once coming back. \(\lambda_j\) is the elastic mean free path of the photoelectron and \(A(k)\) is an amplitude reduction factor which measures the proportion of absorption events that result in the excitation of a single photoelectron. The Debye-Waller factor, \(\sigma_j^2\), is the mean-square variation in \(R_j\) and is composed of two contributions, a static and a dynamic factor.

The EXAFS is therefore dominated by the backscattering amplitude from the neighbouring atoms \(N_j|f_j(k,\pi)|\), modified by:

(i) A damping factor \(e^{-2R_j/\lambda_j}\) which accounts for electron losses due to, for example, inelastic scattering,

(ii) The amplitude reduction factor, \(A(k)\),

(iii) The Debye-Waller factor which accounts for damping to the amplitude due to thermal vibrations and static disorder,

(iv) The oscillations themselves which are a function of the distance \(kR_j^2\) and the phase shifts \(2\delta_i\) and \(\psi_j\),

(v) The distance dependence of \(1/kR_j^2\).

### 3.4.3 Experimental

Obtaining high quality EXAFS data requires a high signal/noise ratio for the x-ray absorption spectrum, hence, the majority of studies are now performed using synchrotron radiation sources as opposed to laboratory based conventional or rotating anode x-ray sources.
In this thesis, Co K-edge x-ray absorption data were collected in transmission mode at station 7.1 of the Daresbury Synchrotron Radiation Source, which operates at 2 GeV with a typical current between 120 and 250 mA. The set-up of this station is shown in Figure 3.5. Transmission is just one of several modes of EXAFS measurements. The fluorescence technique is used for samples with a very low concentration of absorbing atoms; it involves the measurement of the fluorescence radiation at a right angle to the incident beam. Other techniques such as partial electron yield or Auger electron detection are more specialised being commonly applied to the study of surfaces or low energy edges.

![Figure 3.5: Set-up of Station 7.1, Daresbury SRS](image)

A transmission experiment involves the measurement of the incident ($I_0$) and transmitted ($I_t$) beam intensities using ion chambers, which in this study were filled with an Ar/He mixture. Then, the absorption coefficient, $\mu$, or $\mu x$ (where $x$ is the sample thickness) is calculated by Equation 9:

$$\mu x = \ln \frac{I_0}{I_t}$$ (9)
In a typical experiment, a self-supporting wafer was prepared using ca. 30-60mg sample for samples with Co/P ratios of 0.04 – 0.2. The wafer was mounted in a metal holder and placed in the synchrotron beam.

Data were collected in three regions to optimise collection time:

(I) Pre-edge region (100 to 200eV below edge) – largest step size, but still retaining sufficient information to allow the slope of this part of the spectrum to be removed in the background removal part of the analysis.

(II) XANES – small step size (ca. 0.5eV) – detailed information is required to study changes in the oxidation state of the absorbing atom as well as changes in the fine structure associated with the coordination environment.

(III) EXAFS region – step size optimised by the data collection software to ensure an even set of points in k-space.

A typical data set takes 40 minutes to collect.

**3.4.4 Data Analysis**

Data analysis takes place in three stages: data normalisation, background subtraction and finally curve fitting analysis to derive the structural parameters. A suite of programs available at the Daresbury Laboratory were used, EXCALIB, EXBROOK, EXCURV92 and EXCURV98.
3.4.4.1 Data normalisation

In this stage, EXCALIB was used to convert the recorded data (i.e. the measured incident and transmitted intensities, $I_o$ and $I_t$ and the monochromator position in mdeg) to energy vs absorption coefficient.

3.4.4.2 Background Subtraction

The background subtraction, using the program EXBROOK, occurs in several stages. Firstly the pre-edge is subtracted from the spectrum; the pre-edge is fitted with a polynomial that is extrapolated beyond the edge. The pre-edge fit is then subtracted from the measured absorption data.

Secondly, the function we are seeking to derive is $\chi(E)$. This can be obtained using Equation 10:

$$\chi(E) = \frac{\Delta \mu(E)}{\mu_o(E)}$$

where $\Delta \mu(E) = \mu(E) - \mu_o(E)$; $\mu(E)$ is the measured absorption and $\mu_o(E)$ is the absorption coefficient of the isolated atom. It is assumed the $\mu_o(E)$ can be taken to be a smooth background which passes through the oscillations of the spectrum. Therefore the background can be removed, and $\chi(E)$ obtained by fitting a simple polynomial or cubic spline through the experimental data and subtracting this from the experimentally measured $\mu(E)$ curve.
Finally, the photon energy \( E \) needs to be converted to the photoelectron wave vector \( k \) which is done using Equation 11:

\[
k = \sqrt{\frac{2m}{\hbar^2}} \left( E - E_o \right)
\]  

(11)

where \( \hbar^2 = h/2\pi \) (\( h \) = Plank's constant) and \( E_o \) is the threshold energy for a particular absorption edge.

In order to compensate for the attenuation of the EXAFS amplitude at high \( k \) values, \( \chi(k) \) is often multiplied by some power of \( k \) to give \( k^n \chi(k) \). A weight of 3 is normally chosen. This procedure is important as it prevents the larger amplitude oscillations from dominating the spectrum in the determination of interatomic distances, which only depends on the frequency of the oscillation, not the amplitude.

### 3.4.4.3 Derivation of structural parameters

EXCURV92\(^{24}\) and EXCURV98\(^{25}\) use the curve-fitting technique to best fit the \( k^n \chi(k) \) spectra to a model of the local structure. Least square methods, given in Equation 12, are used to refine the coordination number, \( N \), the interatomic distance, \( R \) and the Debye-Waller factor, \( A \) (where \( A = 2\sigma^2 \)) to obtain the best fit between the calculated and the observed spectrum.

\[
R = \sum_i \left[ (\chi^{obs}_i - \chi^{calc}_i) k^n i \right]^2
\]

(12)
\( \chi^{\text{obs}} \) is the observed spectrum; \( \chi^{\text{calc}} \) is the spectrum for the model, calculated using Equation 8 and \( k^n \) is the weighting factor.

3.4.4.4 Multiple Scattering

So far, only the single scattering of a photoelectron by its neighbours has been considered. However, if the absorbing atom, the nearest neighbour and the next nearest neighbour are arranged in a linear or nearly collinear array (between 130° and 180°), multiple scattering becomes important. In such cases, the outgoing photoelectron is strongly forward scattered by the intermediate atom resulting in a significant enhancement of the EXAFS amplitude (see Figure 3.6).

![Multiple scattering effect](image)

*Figure 3.6: Multiple scattering effect. The absorbing atom is shown in black, the nearest neighbours are shown in dark grey and the next-nearest neighbour is shown in light grey. The linear arrangement of the three atoms means that the outgoing photoelectron wave will be strongly forward scattered by the middle atom.*
In heteroatom-substituted aluminophosphates, the Me-O-P bond angles in the framework (where Me is the absorbing metal atom) are in the range 130 to 160°, therefore it is important to include multiple scattering in the refinement to obtain useful structural information. This is achieved in EXCURV92 or 98 by constructing a unit consisting of the three atoms that make up the bond. This bond angle is then refined along with the coordination number, the bond length and the Debye-Waller factor.
3.5 Combined XAS/XRD

3.5.1 Introduction

Over the last few years, the combination of x-ray diffraction and x-ray absorption spectroscopy has become a well-established technique. Several studies have been carried out where inorganic solids or catalysts have been investigated under operating conditions. The combination of these two complementary techniques permits the study of both the local and the long-range order of a material under identical conditions. In the case of aluminophosphates, we are therefore able to study the overall framework structure as well as the local structure around the heteroatom incorporated into the framework. The use of the quick EXAFS (QuEXAFS) technique and a position sensitive detector (PSD) for x-ray diffraction data collection means that good time resolution is obtainable. In this study the combined XAS/XRD technique is used to investigate the calcination process of the cobalt-substituted aluminophosphates prepared by heating the sample in air or oxygen to remove the template molecule. Stability of the material during this process is essential for catalytic purposes; the template molecule must be removed leaving a stable empty framework containing the active sites.

From the x-ray diffraction results, changes in the structure of the material are evident; x-ray absorption spectroscopy can tell whether the cobalt remains in the framework throughout the calcination and whether there are changes in the oxidation state or the local environment of the heteroatom. Thomas et al. showed that changes in oxidation state are essential in the field of shape-selective redox catalysis, e.g. the
oxidation of linear alkanes in air. As bond distances are sensitive to changes in the oxidation state of the central atom, they can be used as a guide to the extent of oxidation.

### 3.5.2 Experimental

The data were collected at Station 9.3 of the Daresbury Synchrotron Radiation Source. This station uses the set-up in Figure 3.7 to rapidly collect XRD and XAS data.

![Figure 3.7: Set-up of combined XAS/XRD, Station 9.3, Daresbury](image)

The use of a rapidly scanning Si (220) monochromator allows the EXAFS data to be collected quickly (in a few minutes, compared to ca. 40 minutes for conventional EXAFS) in either transmission or fluorescence mode, the so-called QuEXAFS technique. $I_0$ and $I_t$ are the reference and transmission ion chambers and are used to measure the QuEXAFS. The fluorescence detector, located at right angles to the
beam, measures the fluorescence data. Rapid X-ray diffraction data collection is achieved using an INEL position sensitive detector (PSD). The monochromator entrance and exit slits, define the energy resolution and limit the background scatter, respectively.

In these studies, the XRD data were collected for 180s and the transmission x-ray absorption spectra were collected for 380s, yielding a total cycle time of 10 minutes, which includes 40s of dead time. A silicon standard was used to calibrate the wavelength at which the XRD data were collected, and the PSD used for the measurement of the data.

In a typical experiment 25-40mg of the sample was pressed into a 13mm self-supporting wafer. This was placed in a controlled-environment in-situ cell (Figure 3.8) which can reach temperatures up to 1000°C; the cell allows both precise temperature control and allows the flow of desired gases whilst heating. In these experiments the materials were heated in a flow of air to 550°C. Typically, the heating rate was 5°C/min, but in some experiments, the heating rate was slowed down above 350°C to gain more insight into changes occurring when the template molecule is removed from the structure.

The QuEXAFS data were analysed using the EXAFS suite of programs available at Daresbury, EXCALIB, EXBROOK and EXCURV92\textsuperscript{24}, which are described in Section 3.4.4.
Figure 3.8: In-situ cell used in this work for the combined XAS/XRD experiments at Station 9.3, Daresbury SRS.
3.6 Infrared Spectroscopy

3.6.1 Introduction

Infrared spectroscopy is one of the most informative physiochemical methods that can be used for the routine investigation of acid sites in microporous catalysts. Alone, it is used to determine whether or not Brønsted acid sites are present in the material, or with the use of weak bases as probe molecules it can distinguish between different types of acid sites. Probe molecules that have been used for these studies are acetonitrile, carbon monoxide, ammonia, water, pyridine and nitrogen.

In this work, infrared spectroscopy is used to determine whether or not Brønsted acid sites are present in the cobalt and silicon substituted aluminophosphates prepared. From the results we can attempt to predict a trend in the activity of these materials in acid-catalysed reactions, for example, the conversion of methanol to light alkanes.

3.6.2 Theory

The infrared region of the electromagnetic spectrum extends from the red end of the visible spectrum to the microwave region i.e. 14,000 to 20 cm\(^{-1}\). The most informative region for infrared spectroscopy is the mid-IR region, 4000 to 200 cm\(^{-1}\).

Infrared spectroscopy involves the examination of the twisting, bending, rotating and vibrational motions of atoms in a molecule.
The peaks in an infrared spectrum can often be assigned to a specific functional group. Structural influences can shift these peaks from one compound to another. To study the acidity of aluminophosphates, the region we are interested in is 4000 – 3000cm\(^{-1}\), which is where the absorption bands of hydroxyl groups can be found. Care has to be taken when studying this region to ensure that there is no water present in the sample environment; the bands associated with the hydroxyl groups of water will mask out any useful information.

### 3.6.3 Experimental

Infrared measurements were recorded using a Perkin-Elmer 1725X FTIR spectrometer; Fourier-transform instruments offer the advantages of high sensitivity, resolution and speed of data acquisition (data for an entire spectrum can be obtained in 1s or less).

In a typical experiment, ca. 20-30mg of the sample is pressed into a 20mm diameter self-supporting wafer, which is inserted into the sample holder inside the in-situ cell shown in Figure 3.9. A background scan of the cell is recorded (40 scans are collected for each scan and added together to obtain high resolution) followed by a scan of the as-prepared sample to ensure the sample is not too thick. Using this cell we can carry out in-situ experiments, for example the calcination of aluminophosphates. Oxygen flows through the cell and the sample is raised into the heater and is heated at a rate of 5°C/min to 550°C, where it is kept for an hour. When the sample has cooled down, the cell is evacuated to remove any water that may have
been present. A background scan of the cell under vacuum is recorded before the data for the calcined sample is collected.

Figure 3.9: In-situ cell used for FTIR measurements
3.7 References


24. N. Binsted, J. W. Campbell, S. J. Gurman, P. C. Stephenson, CCLRC Daresbury Laboratory EXCURV92 Program


Chapter 4

Synthesis of the Chabazite-Type Aluminophosphate DAF-5 Using a Computer-Designed Template
4.1 Summary

The molecule 4-piperidinopiperidine was predicted by the computer methodology ZEBEDDE\(^1\) to produce a microporous framework with a structure analogous to that of the mineral chabazite. This template was used for the synthesis of a cobalt-substituted aluminophosphate, which was shown by powder and single crystal x-ray diffraction techniques to have a chabazite-type structure containing one 4-piperidinopiperidine molecule per cage and which fully occupied the cage. The material produced was designated DAF-5 (Davy Faraday No.5). Using the combined XAS/XRD technique, the stability of this material was studied during the calcination process i.e. removal of the occluded template molecule. However, the material was found to collapse at temperatures of 350-400°C, when the template was removed.

Following the example of Barrett et al\(^2\) we attempted to stabilise the structure by incorporating both cobalt and silicon in the structure to form a CoAPSO, and succeeded in producing a stable structure at a range of compositions. The redox properties and the Brønsted acidity of the CoAPSO’s were investigated using combined XAS/XRD and infra-red spectroscopy.
4.2 Introduction

A long-standing goal for chemists is the ability to design and synthesise materials with predetermined physical and catalytic properties. Recent progress means that we are close to being able to do this in the field of microporous materials\textsuperscript{1,3}. As mentioned in Chapter 2, in the preparation of these materials, the choice of the organic structure-directing agent or template is acknowledged to be of vital importance in directing the synthesis towards a particular structure. In choosing a new template molecule for the synthesis of a microporous material there are two methods which can be adopted; firstly, rational design can be used\textsuperscript{4,5} where the template is chosen by chemical intuition based on a knowledge of other systems. Secondly, the recently developed computer methodology ZEBEDDE\textsuperscript{1} allows us to design organic templates suitable for a targeted microporous framework. The ZEBEDDE code designs templates by computationally ‘growing’ them inside the target framework. In a recent study\textsuperscript{1,3} this technique predicted that 1,2-disubstituted cyclohexane templates would favour the formation of a levyne structure. In an independent study\textsuperscript{4} the amine 2-methylcyclohexylamine was chosen by rational design and used to synthesise a microporous cobalt-substituted aluminophosphate that crystallises with a structure analogous to that of levyne. The material was named DAF-4 and was found to convert methanol to light olefins with selective production of ethene and propene.
Aluminophosphates with structures analogous to the mineral chabazite (Figure 4.1), for example, the structure types -34 and -44, have attracted a great deal of attention recently. With pore dimensions 3.8 x 3.8Å (formed by the eight-membered rings of the cages), these materials display interesting catalytic activity in organic reactions involving small molecules, for example, the conversion of methanol to light olefins\textsuperscript{5-10}. The catalytic properties of these materials arise from the presence of Brønsted acid sites, which are formed when a small percentage of lower valent ions are incorporated into the aluminophosphate framework as discussed in Chapter 2. These Brønsted acid sites are believed to be distributed in a more or less spatially uniform fashion throughout the bulk of the solid\textsuperscript{10} and are accessible to reactants small enough to diffuse through their microporous structure.
In some silicon-substituted aluminophosphates, silicon can substitute for aluminium as well as phosphorus in the framework. This leads to the formation of silica-rich regions or ‘islands’ within the aluminophosphate where at least two adjacent T-sites (T = P or Al) are substituted by silicon. Computational studies by Sastre et al\textsuperscript{11,12} showed that aggregation of silicon only occurs above certain thresholds which are determined by the structure type.

Cobalt-substituted aluminophosphates have attracted considerable attention, due to the potential of these materials to be used in both acid- and redox-catalysed reactions\textsuperscript{8,9,13-15}. Of all the first row transition metals, the Co(II) ions most readily adopt a tetrahedral stereochemistry\textsuperscript{16} and the intense blue colour of most Co(II) compounds formed is helpful in assigning this geometry and thus determining whether or not Co(II) is incorporated in a tetrahedral position in the aluminophosphate framework. It has been shown\textsuperscript{17-22} that Co(II) is able to be oxidised to Co(III) whilst remaining in the aluminophosphate framework, resulting in a colour change from blue to green. However, some workers\textsuperscript{23-25} disagree with this model and put the colour change down to distortion of the tetrahedral Co(II) environment.

Usually, small amines are used in the synthesis of chabazite-type aluminophosphates, for example triethylamine\textsuperscript{26,27}, morpholine\textsuperscript{19,28,29}, TEAOH\textsuperscript{30-32}, piperidine\textsuperscript{18,33}, cyclohexylamine\textsuperscript{34,35} and isopropylamine\textsuperscript{36}. Using both experimental\textsuperscript{26,37,38} and computational\textsuperscript{39} methods it has been shown that in many cases, two of these molecules can fit inside the CHA cage. Such a templating requires a relatively high
concentration of heteroatoms in the framework to compensate the charge on the template. This leads to problems in the synthesis of these materials, for example, from experiments it has been reported that if the template or heteroatom concentration is insufficient, competitive formation of the AlPO-5 (AFI) phase occurs\(^{27,40-42}\). Due to the channel system of the AFI framework, template ordering is not as crucial in this material.

### 4.2.1 Synthesis Strategy

The aim of this work was to synthesise an aluminophosphate-based material with a chabazite-type structure using a new template. The template was designed using the de novo methodology ZEBEDDE\(^1\), where the template is grown in the target structure from a seed molecule. Growth occurs by a number of random actions using a fragment library as a source of new atoms until the void space in the framework has been filled.

Our aim was that the selected template would form a chabazite-type material quickly and in phase pure form, with little or no extraneous microporous phases. We therefore decided that the template should be present at a concentration of one molecule per unit cell and must fully occupy the CHA cage. It would also be an advantage if the charge on the template could be varied to accommodate a range of metal concentrations in the framework and thus allow a degree of control over the catalytic behaviour arising from the presence of these substituents.
ZEBEDDE predicted that templates based on the molecule bicyclohexane would fulfil the above criteria. The template studied in this work is 4-piperidinopiperidine (Figure 4.2) and a cobalt-substituted aluminophosphate was synthesised using this molecule as the template.

![Structure of 4-piperidinopiperidine](image)

*Figure 4.2: Structure of 4-piperidinopiperidine*

The structure of the material synthesised was obtained using x-ray diffraction and single crystal diffraction. X-ray absorption spectroscopy, combined XAS/XRD and infrared spectroscopy were used to further characterise the material and study its potential catalytic activity.
4.3 Experimental

4.3.1 Synthesis

A cobalt-substituted aluminophosphate (CoAPO) was prepared using 4-piperidinopiperidine as the template. Cobalt was chosen as the heteroatom as, in addition to the catalytic applications of CoAPO's, incorporation of cobalt in the framework is confirmed by an intense blue colour; this is useful for optimising the synthesis conditions. Once these are established, other heteroatoms can then be substituted in the framework.

An aqueous synthesis gel was prepared using hydrated aluminium hydroxide, cobalt acetate tetrahydrate, 85% phosphoric acid, the template and distilled H₂O. A small amount of water was added to the template and the cobalt acetate until they dissolved; the remainder of the water was added to the phosphoric acid. The aluminium hydroxide was then added to the acid, followed by the cobalt acetate solution, then the template. The gel was stirred vigorously after each addition. The gel was heated hydrothermally in a stainless steel autoclave with a PTFE liner. The synthesis conditions such as gel composition, pH, synthesis time and temperature were optimised to produce a pure phase. The material produced was filtered, washed with distilled water and dried.

A pure phase was obtained at two different pH's. The optimum conditions for both are shown in Table 4.1. The acidic starting gel was obtained using a gel of the composition shown in Table 4.1, then adding excess 85% phosphoric acid until the
pH reached 3-4. The same blue crystalline phase was formed at the two different pH's and was designated DAF-5 (Davy-Faraday No. 5). At any other pH, a pure phase was not obtained; traces of a dense tridymitic phase were obtained.

<table>
<thead>
<tr>
<th>Gel Composition (moles)</th>
<th>Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(ac)$_2$ Al$_2$O$_3$ H$_3$PO$_4$ H$_2$O R</td>
<td>2 – 5 hours (pH 3-4) 150-160°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 days (pH 8-9) 150-160°C</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Optimum synthesis conditions for the synthesis of DAF-5 (R = 4-piperidinopiperidine).

We have also synthesised a CoAPO with a cobalt concentration of 0.1; however, this synthesis did not show good reproducibility. Competitive formation of an AlPO-5 phase was not observed under any of the synthesis conditions. The syntheses at both pHs produced single crystals, the acidic starting gel producing micro-crystals (30 x 30 x 30μm) and the basic gel giving much larger crystals (50 x 70 x 70μm).

4.3.2 X-ray diffraction

The two starting gels produced materials with identical powder x-ray diffraction patterns; both show similarities to that of the mineral chabazite (Figure 4.3)
Figure 4.3: X-ray diffraction patterns of DAF-5 (top) and chabazite (bottom) which was generated from the Atlas of Zeolite Structure Types\textsuperscript{43}.
4.3.3 X-ray Absorption Spectroscopy

As discussed in Chapter 3, x-ray absorption spectroscopy allows us to study the local structure about a particular element. In this work we investigated the local structure around the cobalt atom. The data were collected at Station 7.1 of the Daresbury Synchrotron Radiation Source (SRS). For both samples, ca. 40mg of sample was pressed into a self-supporting wafer and the Co K-edge EXAFS spectra were collected in transmission mode. The data were normalised, background subtracted then analysed to obtain the structural parameters using the programs EXCALIB, EXBROOK and EXCURV92 available at Daresbury Laboratory. This procedure is described further in Chapter 3.

From the structural parameters obtained from analysis of the EXAFS data, we can determine whether or not cobalt is incorporated in the aluminophosphate framework. Analysis of the Co K-edge EXAFS for DAF-5 synthesised from both the acidic and basic starting gel (Figures 4.4 and 4.5) show that cobalt has a coordination number of 4; it is therefore very likely to be incorporated in a tetrahedral site in the aluminophosphate framework in place of aluminium. The Co-O and Co-P bond lengths and Co-O-P bond angles obtained are shown in Tables 4.2 and 4.3 together with the coordination number (N) and the Debye-Waller factor ($2\sigma^2$). The blue colour of the sample and the values of the average Co-O bond lengths indicate the presence of divalent cobalt in the framework. The bond lengths and angles are comparable to those of other cobalt-substituted aluminophosphates.
Figure 4.4: Co K-edge EXAFS (top) and associated Fourier transforms (bottom) from the acidic starting gel. The blue line represents the experimental data and the pink line shows the calculated fit.

<table>
<thead>
<tr>
<th>Atom Pair</th>
<th>N</th>
<th>R(Å)</th>
<th>$2\sigma^2$ (Å$^2$)</th>
<th>Co-O-P bond angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-O</td>
<td>4.1</td>
<td>1.94</td>
<td>0.009</td>
<td>-</td>
</tr>
<tr>
<td>Co-P</td>
<td>2.6</td>
<td>3.17</td>
<td>0.012</td>
<td>133</td>
</tr>
<tr>
<td>Co-P</td>
<td>1.5</td>
<td>3.33</td>
<td>0.012</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 4.2: Structural parameters obtained from analysis of the EXAFS data (acidic gel) using the multiple scattering technique described in Chapter 3.
Figure 4.5: Co K-edge EXAFS (top) and associated Fourier transforms (bottom) from the basic starting gel. The blue line represents the experimental data and the pink line shows the calculated fit.

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>N</th>
<th>R(Å)</th>
<th>$2\sigma^2$ (Å$^2$)</th>
<th>Co-O-P bond angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-O</td>
<td>4.1</td>
<td>1.934</td>
<td>0.009</td>
<td>-</td>
</tr>
<tr>
<td>Co-P</td>
<td>2.0</td>
<td>3.213</td>
<td>0.015</td>
<td>137</td>
</tr>
<tr>
<td>Co-P</td>
<td>2.1</td>
<td>3.367</td>
<td>0.015</td>
<td>156</td>
</tr>
</tbody>
</table>

Table 4.3: Structural parameters obtained from analysis of the EXAFS data (basic gel) using the multiple scattering technique described in Chapter 3.
4.3.4 High Resolution X-ray powder diffraction

High resolution X-ray powder diffraction was used to determine the structure of DAF-5. The pattern was obtained at Station 2.3, Daresbury Synchrotron Radiation Source in capillary mode using a wavelength of 1.39994 Å. The data were collected from 6 to 80° 2θ with a step increment of 0.01° and the time for each step was 2 seconds; 3 complete patterns were recorded and the data summed.

The pattern could be readily indexed using the auto-indexing program TREOR to a hexagonal cell with cell parameters $a=b=13.537\,\text{Å}$, $c=15.480\,\text{Å}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$, cell volume=$2457\,\text{Å}^3$. These parameters are similar to those of the mineral chabazite which has cell parameters $a=b=13.675\,\text{Å}$, $c=14.767\,\text{Å}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$, cell volume=$2391\,\text{Å}^3$.

The presence of the organic template molecule makes a full structural determination difficult. However, a good model for the framework was obtained from a Rietveld refinement of the data obtained using the program GSAS, employing the space group $R\bar{3}$. Firstly the cell parameters and the zero-point error were refined; a manually interpolated background was used. When convergence was achieved, the peak shape parameters were refined; a pseudo-Voigt function was used to describe the peak shape. The Direct Methods program SIRPOW was used to obtain approximate atom positions for the refinement; no attempt was made to distinguish between aluminium and cobalt at this stage. The atom positions and the thermal parameters were refined until the model reached convergence. Soft constraints were included for the framework bonds and angles. Finally cobalt was inserted into the
model in the same position as aluminium, with a fractional occupancy of 0.2; the model was refined again. The final agreement factors were $R_{wp} = 0.1170$, $R_p = 0.0710$ and $\chi^2 = 4.581$ and the final model has a cage structure similar to that of chabazite. The x-ray diffraction pattern together with the best fit obtained from the refinement of the framework is shown in Figure 4.6.

![X-ray diffraction pattern](image)

*Figure 4.6: High-Resolution X-ray powder diffraction pattern (red solid line) together with the best fit from a Rietveld refinement (blue dotted line). The difference profile is shown at the bottom. The wavelength used is 1.39994Å.*

The atom positions and the thermal parameters obtained from the Rietveld refinement are shown in Table 4.4; the bond angles and lengths for the framework are given in Table 4.5.
Table 4.4: Atom positions and isotropic thermal factors for the DAF-5 framework from a Rietveld refinement of the HRPD data.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq.) Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>0.23474</td>
<td>-0.00518</td>
<td>0.59773</td>
<td>0.01825</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0.23474</td>
<td>-0.00518</td>
<td>0.59773</td>
<td>0.01825</td>
</tr>
<tr>
<td>P(1)</td>
<td>0.23384</td>
<td>0.00325</td>
<td>0.39955</td>
<td>0.01825</td>
</tr>
<tr>
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Table 4.5: Selected bond lengths and angles for the DAF-5 framework; e.s.d's are shown in brackets.

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Table 4.5: Selected bond lengths and angles for the DAF-5 framework; e.s.d's are shown in brackets.
A fragment of the DAF-5 framework showing a cage and the 6-membered rings is shown in Figure 4.7.

Figure 4.7: Final model for the framework of DAF-5 from a Rietveld refinement of the HRPD data. Tetrahedral atoms (Al, Co and P) are shown in green, the bridging oxygen’s are shown in red.
4.3.5 Single Crystal Diffraction

4.3.5.1 Acidic starting gel (pH 3-4)

In order to determine the location of the template molecule inside the DAF-5 framework, single crystal diffraction techniques were employed, using the recently developed micro-single crystal diffraction technique at Station 9.8, Daresbury Synchrotron Radiation Source\textsuperscript{50} described in Chapter 3. A single crystal of DAF-5 with dimensions 30 x 30 x 30μm (obtained from the acidic starting gel of pH 3-4) was chosen, mounted on a glass fibre and inserted into the goniometer. Data were collected at 295K employing a wavelength of 0.6889Å, on a Siemens SMART CCD area detector diffractometer equipped with a silicon (111) crystal monochromator. Coverage of a hemisphere of reciprocal space was achieved by 0.2° frame increments in ω, with a θ collection range of 2.11 to 26.47° (Index ranges -5 ≤ h ≤ 16, -16 ≤ k ≤ 4, -15 ≤ l ≤ 19). A total of 2188 reflections were collected and merged to yield 969 unique reflections.

The data were analysed via a least-squares refinement coupled with direct methods (using the program SHELX97\textsuperscript{51}) to obtain starting coordinates for the template molecule. The data were processed using the space group R 3; no attempt was made to distinguish between carbon and nitrogen in the template. Plausible template orientations were obtained; there appears to be a distinct 3-fold disorder resulting in several orientations of the template molecule. However, it is clear from diffraction studies that there is only one molecule present per cage. One of the possible template orientations is shown together with the DAF-5 cage in Figure 4.8.
Figure 4.8: DAF-5 cage showing one of the possible orientations of the template molecule. The C atoms of the template are shown in grey, the N atoms are shown in blue and the H atoms are shown in white.

Both elemental analysis and single crystal diffraction give a framework composition of Co_{0.28}Al_{0.72}PO_4. The cell parameters obtained are a=b=13.537\,\text{Å}, c=15.480\,\text{Å}, 
\alpha=\beta=90^\circ, \gamma=120^\circ, \text{cell volume }= 2457\,\text{Å}^3.

The agreement factors for the final crystallographic model are shown in Table 4.6.
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<th>Final R indices [I&gt;2σ(I)]</th>
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Table 4.6: Agreement factors for the final DAF-5 model (synthesised from acidic starting gel).

The atom positions and the thermal parameters obtained from the refinement are shown in Table 4.7 and the bond distance and angles for the DAF-5 framework are shown in Table 4.8. All bonds and angles obtained for the template look reasonable. The anisotropic displacement parameters for DAF-5 are shown in Table 4.9.

The structure of DAF-5 is similar to those of other chabazite-type aluminophosphates, for example, heteroatom-substituted AlPO-34 and -44. The main difference between the two is one of chemical composition. AlPO-34 is generally synthesised with lower heteroatom concentrations than AlPO-44 (~10% for -34, ~20% for -44). It has also been reported that there are differences in the lattice symmetries of -34 and -44; heteroatom-substituted AlPO-34 is generally refined in the space group \( \overline{R} \overline{3} \)\textsuperscript{52,53} whereas -44 has been refined in \( P \overline{1} \)\textsuperscript{54}. However, a recent single crystal study by Muncaster et al\textsuperscript{37} successfully used the space group \( R \overline{3} \) to solve the structure of CoAPSO-44. In this work, the structure of DAF-5 was solved using \( R \overline{3} \), however the material can be synthesised using a wider range of heteroatom concentrations than is generally observed for AlPO-34.
<table>
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Table 4.7: Atomic coordinates and thermal parameters for DAF-5 (from the acidic starting gel). U(eq) is equivalent to the isotropic temperature factor; e.s.d’s are shown in brackets.
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Table 4.8: Selected bond lengths and angles for DAF-5. Co is assumed to be in the same position as Al; N(1) and N(2) in the same positions as C(1) and C(2) respectively.
Table 4.9: Anisotropic displacement parameters (Å²) for DAF-5

The anisotropic displacement factor takes the form: 

\[-2\pi^2 \left[ h^2 a^* U_{11} + k^2 b^* U_{22} \\
+ l^2 c^* U_{33} + 2hk a^* b^* U_{23} + 2hl a^* c^* U_{13} + 2hk a^* b^* U_{12} \right] \]
4.3.5.2 Basic Starting gel (pH 8-9)

The data for the larger crystal (dimensions 70 x 50 x 50μm), from the basic starting gel, pH 8-9, was collected at the EPSRC crystallography service. Data were collected at 293K at a wavelength of 0.71069Å. The collection range was 2.17 to 24.84° 2θ (Index range -15 ≤ h ≤ 15, -15 ≤ k ≤ 14, -17 ≤ l ≤ 14). A total of 3228 reflections were collected and merged to yield 870 unique reflections.

The data were refined in the space group $\overline{R}3$; the cell parameters obtained are $a=b=13.579Å$, $c=15.558Å$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$, cell volume $= 2484Å^3$. The unit cell is significantly bigger than that obtained for the micro-crystal along the c-direction.

The empirical formula deduced from this refinement was $Co_{0.27}Al_{0.73}PO_4.CH_2N_0.33$.

The structure from this refinement is almost identical to that obtained from the acidic starting gel; again, it is clear that there is only one 4-piperidinopiperidine molecule per cage as in Figure 4.8. The agreement factors for the refinement are shown in Table 4.10. The atomic coordinates together with the thermal parameters obtained are given in Table 4.11; selected bond angles and lengths are given in Table 4.12 and the anisotropic displacement parameters are shown in Table 4.13.

The R-factors indicate a better fit than for the micro-crystal studied. However, the C2-C3 bond distance in the template is very long at 1.92Å, whilst the C1-C1 bond distance, which is the distance between the two piperidine rings, is too short at 1.22Å. These anomalies may arise from the disorder of the template inside the DAF-5 cage.
Final R indices [$I>2\sigma(I)$]  
\[ R_1=0.0447 \quad \text{WR}_2=0.0694 \]

R indices (All data)  
\[ R_1=0.0856 \quad \text{WR}_2=0.1535 \]

Goodness of fit on $F^2$  
0.632

Table 4.10: Agreement factors for DAF-5, synthesised from the starting gel of pH 8-9

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Table 4.11: Atomic coordinates and thermal parameters obtained from a single crystal analysis of DAF-5. U(eq) is equivalent to the isotropic temperature factor; e.s.d’s are shown in brackets.
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<tr>
<td>C(1)-C(4)</td>
<td>1.49(2)</td>
<td>C(4)-C(1)-C(4)</td>
<td>98(2)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.55(4)</td>
<td>C(3)-C(2)-C(3)</td>
<td>98(2)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.92(4)</td>
<td>C(2)-C(3)-C(4)</td>
<td>98(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(1)-C(4)-C(3)</td>
<td>101(3)</td>
</tr>
</tbody>
</table>

Table 4.12: Selected bond lengths and angles for DAF-5; Co is assumed to be in the same position as Al; N(1) and N(2) in the same position as C(1) and C(2) respectively. e.s.d’s are shown in brackets.
<table>
<thead>
<tr>
<th></th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>0.025(1)</td>
<td>0.019(1)</td>
<td>0.018(1)</td>
<td>-0.003(1)</td>
<td>-0.007(1)</td>
<td>0.006(1)</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0.025(1)</td>
<td>0.019(1)</td>
<td>0.018(1)</td>
<td>-0.003(1)</td>
<td>-0.007(1)</td>
<td>0.006(1)</td>
</tr>
<tr>
<td>P(1)</td>
<td>0.041(2)</td>
<td>0.031(2)</td>
<td>0.027(2)</td>
<td>0.000(1)</td>
<td>0.006(1)</td>
<td>0.020(2)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.053(5)</td>
<td>0.073(5)</td>
<td>0.049(3)</td>
<td>-0.012(4)</td>
<td>0.030(3)</td>
<td>0.031(4)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.058(5)</td>
<td>0.068(5)</td>
<td>0.032(3)</td>
<td>0.004(3)</td>
<td>-0.011(3)</td>
<td>0.034(4)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.033(5)</td>
<td>0.050(5)</td>
<td>0.061(4)</td>
<td>-0.010(4)</td>
<td>0.000(4)</td>
<td>-0.001(4)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.121(7)</td>
<td>0.033(4)</td>
<td>0.060(4)</td>
<td>0.013(3)</td>
<td>0.006(4)</td>
<td>0.050(5)</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.398(39)</td>
<td>0.398(39)</td>
<td>0.032(21)</td>
<td>0</td>
<td>0</td>
<td>0.199(19)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.398(39)</td>
<td>0.398(39)</td>
<td>0.032(21)</td>
<td>0</td>
<td>0</td>
<td>0.199(19)</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.315(31)</td>
<td>0.315(31)</td>
<td>0.032(16)</td>
<td>0</td>
<td>0</td>
<td>0.158(15)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.315(31)</td>
<td>0.315(31)</td>
<td>0.032(16)</td>
<td>0</td>
<td>0</td>
<td>0.158(15)</td>
</tr>
<tr>
<td>C(3)</td>
<td>1.041(143)</td>
<td>0.199(31)</td>
<td>0.071(11)</td>
<td>-0.012(16)</td>
<td>-0.030(32)</td>
<td>0.151(42)</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.174(27)</td>
<td>0.466(66)</td>
<td>0.112(14)</td>
<td>0.038(20)</td>
<td>0.018(14)</td>
<td>-0.008(23)</td>
</tr>
</tbody>
</table>

Table 4.13: Anisotropic displacement parameters ($\text{Å}^2$) for DAF-5; e.s.d's are shown in brackets.

The anisotropic displacement factor takes the form: 
$$-2\pi^2 \left[ h^2 a^2 U_{11} + k^2 b^2 U_{22} + l^2 c^2 U_{33} + 2hk b^c U_{23} + 2hl a^c U_{13} + 2hk a^b U_{12} \right]$$
4.3.6 Combined XAS/XRD

For the material synthesised to be useful as a catalyst, the occluded template molecule must be removed by calcination, leaving the empty framework containing the active sites i.e. Brønsted acid sites or redox sites. The combined XAS/XRD technique, discussed in Chapter 3, was used to investigate the stability of the material during this calcination process.

**Experimental**

The data were collected at Station 9.3 of the Daresbury Synchrotron Radiation Source. In these experiments, the XRD data were collected for 180 s and the transmission X-ray absorption spectra were collected for 380 s yielding a total cycle time of 10 minutes including 40 s of dead time. 25-30mg of DAF-5 was pressed into a 13mm self-supporting wafer and mounted in the *in-situ* cell. In this experiment the material was heated from room temperature to 350°C, at a heating rate of 5°C/min, then at 2°C/min to 550°C in a flow of air. The temperature was kept a 550°C for 1 hour.

The stability of the microporous framework can be assessed from a plot of the XRD patterns as a function of temperature. Figure 4.9 shows the X-ray diffraction patterns in the range 2θ = 21 to 31° together with a plot of the XAS spectra.
Figure 4.9: XRD patterns (top) and Co k-edge QuEXAFS spectra (bottom) of DAF-5 plotted as a function of temperature. The heating rate was 5°C/min to 350°C, then 2°C/min to 550°C. The temperature was sustained at 550°C for 1 hour.
The XRD plot reveals that the material is not stable upon removal of the template molecule. The material begins to lose its structure at 350-400°C, which is known to be the temperature at which the template molecule is lost from the framework.

This result is similar to that obtained by Barrett et al.\textsuperscript{2} in a combined XAS/XRD study of CoAPO-44. This material has a structure analogous to that of chabazite and like DAF-5 it is difficult to synthesise at total heteroatom concentrations lower than 20 wt\%. Results for CoAPO-44 shows that at temperatures above 300°C, this material undergoes a structural collapse with the subsequent formation of a trydimitic dense phase. However, Barrett et al then went on to show that the incorporation of silicon into the CoAPO-44 framework results in a stabilisation of the framework. The overall heteroatom concentration remained the same but by incorporating some silicon in place of phosphorus, the cobalt content could be reduced to about 8 wt\%.

The resulting material, CoAPSO-44, contains Brønsted acid sites, as shown in an infra-red study,\textsuperscript{23} and shows good catalytic activity in the conversion of methanol to light olefins.\textsuperscript{8}

Following the example of Barrett et al, we attempted to stabilise DAF-5 by incorporating silicon as well as cobalt into the microporous framework, thus lowering the overall cobalt content.
4.4 DAF-5: CoAPSO

4.4.1 Synthesis

The CoAPSO form of DAF-5 was prepared using two different cobalt and silicon concentrations. The gels were prepared in a similar manner to the CoAPO (synthesised from the basic starting gel) using the compositions shown in Table 4.14. The pH of both of the starting gels was 9.

Table 4.14: Gel compositions (moles) used in the syntheses of DAF-5 CoAPSO's

<table>
<thead>
<tr>
<th>Co(ac)$_2$</th>
<th>Al(OH)$_3$</th>
<th>SiO$_2$</th>
<th>H$_3$PO$_4$</th>
<th>T</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.96</td>
<td>0.16</td>
<td>1.34</td>
<td>2.0</td>
<td>30</td>
</tr>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>0.1</td>
<td>1.4</td>
<td>2.0</td>
<td>30</td>
</tr>
</tbody>
</table>

The gels were heated hydrothermally in a stainless steel autoclave with a PTFE liner at 165°C for ca. 2 days. Blue crystalline materials were produced in both cases, however, no single crystals were obtained.

4.4.2 X-ray diffraction

X-ray diffraction patterns of the materials formed are shown in Figure 4.10. A pure phase was produced for both gel compositions; the powder x-ray diffraction patterns are identical to that of DAF-5 CoAPO.
4.4.3 Elemental Analysis

The results obtained from elemental analysis are shown in Table 4.15:

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0.05</td>
<td>0.353</td>
<td>0.234</td>
<td>0.363</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0.02</td>
<td>0.42</td>
<td>0.22</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 4.15: Framework compositions for DAF-5 CoAPSO’s from elemental analysis results.
From the results, the two materials formed have the formulae \( \text{Co}_{0.04}\text{Al}_{0.84}\text{Si}_{0.44}\text{P}_{0.68}\text{O}_4 \) and \( \text{Co}_{0.1}\text{Al}_{0.70}\text{Si}_{0.47}\text{P}_{0.73}\text{O}_4 \). Because cobalt substitutes exclusively for aluminium, if silicon was only substituting for phosphorus in the aluminophosphate framework, 
\[ (\text{Al}+\text{Co})=(\text{Si}+\text{P}) \]. This is not the case; 
\[ (\text{Al}+\text{Co}+\text{Si}+\text{P})=1 \], however 
\[ (\text{Si}+\text{P}) \] is always greater than 0.5. Therefore some silicon must be substituting for aluminium as well as phosphorus in the framework. In Sample 1 with the higher cobalt content, almost one third of the silicon is being substituted in place of aluminium, in Sample 2 approximately one fifth of the silicon replaces aluminium.

A similar result has been reported for SAPO-44\textsuperscript{35,56,57} where silicon is incorporated in the aluminophosphate framework by simultaneous substitution of aluminium and phosphorus. The acidity in the material is therefore located at the edge of the silicon rich regions.

4.4.4 Combined XAS/XRD

Using the same experimental set-up as detailed for DAF-5: CoAPO, we used combined XRD/XAS to study the stability of the two CoAPSO’s during the calcination process which removes the occluded template molecule. The heating rate was 5°C/min to 550°C; the temperature was sustained at 550°C for 30 minutes. The XRD and EXAFS plots as a function of temperature are shown in Figures 4.11 and 4.12. XRD results show there is no evidence of the framework collapsing on removal of the template, or loss of crystallinity throughout the calcination process. Therefore we have successfully stabilised the structure by incorporating silicon as well as cobalt into the aluminophosphate framework.
Figure 4.11: XRD (top) and Co k-edge EXAFS (bottom) plots as a function of
temperature for DAF-5 CoAPSO, Co=0.04. The heating rate was 5°C/min to 550°C;
the temperature was sustained at 550°C for 30 minutes.
Figure 4.12: XRD (top) and Co k-edge QuEXAFS (bottom) plots as a function of temperature for DAF-5 CoAPSO, Co=0.1. The heating rate was 5°C/min to 550°C; this temperature was sustained for 30 minutes.
The edge positions of the XAS spectra for both materials are shown in Figures 4.13 and 4.14. Two temperatures are shown: 100°C and 550°C.

**Figure 4.13:** XANES (Co k-edge) for DAF-5 CoAPSO, Co=0.04, before (100°C) and after (550°C) removal of the template.

**Figure 4.14:** XANES (Co k-edge) for DAF-5 CoAPSO, Co=0.1, before (100°C) and after (550°C) removal of the template.
From the XANES at 100°C and 550°C for both of the CoAPSO materials, it is clear that there is no shift in the edge position between temperatures. Therefore it does not seem likely that there is a significant oxidation state change from Co(II) to Co(III) in the materials.

The EXAFS data were analysed using the program EXCURV98. As we are only interested in changes in the immediate local environment about the cobalt atom, only the first shell has been analysed. The change in the cobalt coordination number, N, the average Co-O bond distance, R and the Debye Waller factor, A (where $A=2\sigma^2$) as a function of temperature for the two CoAPSO materials are shown in Figures 4.15 and 4.16. There is little difference in the structural parameters between the CoAPSO’s with the two cobalt concentrations. The coordination number remains constant at 4 (within the experimental error of 10%) throughout the calcination. Therefore it is likely that the cobalt remains in the aluminophosphate framework throughout the heating process. The Debye-Waller factor increases during the heating process, due to an increase in the thermal and static disorder.

The average Co-O bond distance remains at about 1.94 until the temperature reaches 450°C which is consistent with a Co(II)-O bond length. At 450°C there is a decrease to 1.89 for Co=0.04, and 1.908 for Co=0.1, which was accompanied by a colour change from blue to green for both, indicating that some of the Co(II) has undergone a change in oxidation state to Co(III). There is very little data in the literature for Co(III)-O bond lengths where the cobalt is in tetrahedral coordination. However, a recent single crystal diffraction study by Muncaster et al. on heteropolytungstate...
\[ K_5[CoW_{12}O_{40}]20H_2O, \] where cobalt is in the +3 oxidation state and surrounded tetrahedrally by 4 oxygens, gives an average Co(III)-O bond length of 1.79 Å. Therefore it seems only a small percentage of the Co(II) in the framework has been oxidised during the calcination. The amount of oxidised Co in the framework can be estimated using the Vegard Relationship described by Barrett et al.\(^2\) They assumed that all the Co(II) is oxidised to Co(III) in CoAPO-18. Therefore, the Co(III)-O bond length can be taken as the Co-O bond length in calcined CoAPO-18, i.e. 1.83 Å. The percentage of oxidised cobalt can then be calculated using the equation shown below:

\[
R_{1x} + R_2(1-x) = R
\]

Where \( R_1 \) = Co(III)-O distance from CoAPO-18 (1.83 Å)

\( R_2 \) = Co(II) – O distance (1.94 Å)

\( R \) = Average distance from EXAFS

\( X \) = Fraction of oxidised Co

This approach can be used for the DAF-5 CoAPSOs and the results obtained are shown in Table 4.16:

<table>
<thead>
<tr>
<th>Co content</th>
<th>Average Co-O Bond length in the calcined sample</th>
<th>Percentage of oxidised Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>1.89</td>
<td>45%</td>
</tr>
<tr>
<td>0.1</td>
<td>1.908</td>
<td>27%</td>
</tr>
</tbody>
</table>

Table 4.16: Percentage of oxidised cobalt in the calcined CoAPSO materials.
Figure 4.15: Change in the structural parameters: coordination number, $N$, average Co-O bond distance, $R$ and Debye-Waller factor, $A$, as a function of temperature for DAF-5 CoAPSO, $Co=0.04$. The temperature was sustained at 550°C for 30 minutes.
Figure 4.16: Change in the structural parameters $N$, $R$ and $A$ as a function of temperature for DAF-5 CoAPSO, Co=0.1. The temperature was kept at 550°C for 30 minutes.
A study by Thomas et al.\textsuperscript{15} correlated the catalytic activity of several CoAPO's in the selective oxidation of linear alkanes with the amount of oxidised cobalt in the calcined sample. CoAPO-18 which has 100% Co(III) in the calcined material was shown to be a superior catalyst to CoAPO's with a lower amount of oxidised cobalt. Therefore from the low Co(III) concentrations from the combined XAS/XRD study for DAF-5 CoAPSO's we can predict that these materials are unlikely to show good catalytic activity in redox-catalysed oxidation reactions.

\subsection*{4.4.5 Infrared Spectroscopy}

Both of the DAF-5 CoAPSO's were studied using infrared spectroscopy, discussed in Chapter 3, to investigate the extent of acidity in the materials.

\textbf{Experimental}

In both cases, approximately 10mg of the sample was mixed with ca. 3-4 mg MCM-41, pressed into a self-supporting wafer and mounted inside the \textit{in-situ} cell detailed in Chapter 3, which is attached to the FTIR spectrophotometer. MCM-41 was necessary, as pellets of the as-prepared CoAPSO's could not be prepared. MCM-41 allows thin wafers to be prepared and does not mask out any of the bands associated with the Brønsted acidity that may be present. The pellet was then heated in a flow of oxygen to 550°C at a heating rate of 5°C/min; this temperature was sustained for one hour before cooling down. When the temperature of the cell had cooled to 150°C, the cell was evacuated to remove all traces of water. A background scan of the evacuated cell was obtained before recording the spectrum for the calcined material.
Results

The IR spectra for the two DAF-5 CoAPSO's are given in Figures 4.17 and 4.18. Only the region from 3900 to 3400 cm$^{-1}$ is shown as this is where we would expect to see the presence of Brønsted acidity. 

Figure 4.17: Infrared spectrum for DAF-5 CoAPSO, Co=0.04. The sample was mixed with a small amount of MCM-41 (see experimental section); the Si-OH peak at 3745 cm$^{-1}$ is largely due to the presence of MCM-41.
Figure 4.18: Infrared spectrum for DAF-5 CoAPSO, Co=0.1. Again, the sample has been mixed with a small amount of MCM-41, which contributes to the Si-OH peak at 3745 cm\(^{-1}\).

Several infrared studies have been carried out on heteroatom-substituted aluminophosphates. Infrared studies of SAPO-34\(^{59,60,63}\) show the presence of Brønsted acidity in this material. Bands at 3600 and 3626 cm\(^{-1}\) can be seen in the spectra; these correspond to bridging Si-OH-Al hydroxyls. These OH groups arise from the attachment of charge-balancing protons to the structure, and infer Brønsted acidity. Similar bands were also seen for SAPO-44\(^{56}\).

For the two DAF-5 materials studied, there are two main bands apparent in this region, which can be assigned to Si-OH at 3745 cm\(^{-1}\) (arising mainly from the MCM-41) and P-OH at 3675 cm\(^{-1}\) (from the aluminophosphate). Due to the presence of
MCM-41, we cannot say what contribution the CoAPSO has to the Si-OH band observed. As this band does not infer Brønsted acidity, this is not important. For the CoAPSO with 4% Co, there is a very small peak at ca. 3580 cm\(^{-1}\), and there also seems to be a shoulder to the P-OH peak at about 3620 cm\(^{-1}\). These can be attributed to the Brønsted acid bands described in other chabazite-type materials\(^{56,59,60,63}\), although due to the lower intensity of these bands, we can assume that there are not as many acid sites. For the CoAPSO with 10% Co, all of the bands observed in this region have a lower intensity than for the 4% Co. Again, very low intensity bands can be seen at 3589 and 3625 cm\(^{-1}\), which most likely correspond to the presence of acid sites.

As mentioned previously, it is very likely that the silicon has substituted for aluminium and phosphorus in the DAF-5 CoAPSO’s with the probable formation of silicon islands. As Brønsted acidity will only occur around the edge of the islands, the acidity will be greatly reduced. Therefore, the weak bridging Si-OH-Al bands observed from this infra-red study supports well the idea of island formation in this material.

Strong Si-OH-Al bands associated with Brønsted acid sites in the infra-red spectrum are usually present in the infra-red spectrum of silicon-substituted aluminophosphates which show good activity in acid catalysed reactions, for example the conversion of methanol to light olefins. Therefore, we predict that DAF-5 will not show activity comparable with SAPO-34\(^{6,9}\) or CoAPSO-44\(^{8}\) for this reaction.
4.5 Conclusions

The molecule 4-piperidinopiperidine was predicted by the computer methodology ZEBEDDE\textsuperscript{1} to be a suitable template for the synthesis of an aluminophosphate with a chabazite-type structure, the template should completely fill the CHA cage, thus forming the product efficiently and preventing the competitive formation of other phases. A cobalt-substituted aluminophosphate was synthesised using this template; the product was a blue crystalline phase with an X-ray pattern similar to that of the mineral chabazite\textsuperscript{43}. The material formed much more quickly than other chabazite-type materials, in a few hours compared to several days. There was no evidence of competitive formation of any other phases. This material was designated DAF-5.

From a Rietveld refinement of the high-resolution powder diffraction data collected for this material, it was shown that this material did indeed have a framework structure similar to chabazite. Micro-single crystal diffraction (on a crystal of size $30 \times 30 \times 30 \mu m$) located only one template molecule per cage, and, as predicted this fully occupied the cage.

Combined XAS/XRD was used to study the stability of the material during the calcination process; the framework started collapsing at ca. 400°C, which is the temperature we would expect the template molecule to be lost from the framework. Following the example of Barrett et al\textsuperscript{2}, we attempted to stabilise the structure by incorporating silicon into the structure so the cobalt concentration could be lowered, whilst keeping the overall heteroatom concentration the same.
Two CoAPSO’s were prepared, with the cobalt concentrations reduced from 20% to 4% and 10%. Combined XAS/XRD showed that both of these materials were stable and retained their structure throughout the calcination process; the instability of DAF-5 CoAPO was almost certainly caused by having too much cobalt in the aluminophosphate framework. Analysis of the EXAFS data showed that there is a slight decrease in the Co-O bond length during the calcination for both materials; therefore only a small percentage of the Co(II) is being oxidised to Co(III). Also, there was no shift in the edge positions after the calcination, which is what we would expect if a change in oxidation state is occurring. Elemental analysis showed a significant amount (20 to 35%) of silicon replaces aluminium as well as phosphorus in the aluminophosphate framework with the formation of silicon islands. This is confirmed from the infra-red spectra: the bands one would expect if Brønsted acidity is present are very low in intensity compared to other CHA-type aluminophosphates. If silicon clusters are present, acidity will only occur at the edges of the Si-rich regions, thus greatly reducing the overall acidity.

In summary, from the results obtained we can conclude that on comparison of the DAF-5 materials with other chabazite-type structures, DAF-5 is not likely to show catalytic activity in either acid-catalysed reactions e.g. conversion of methanol to light alkenes, or in oxidation reactions where good redox properties are required. However, our work has demonstrated the power of the de-novo design technique in assisting the synthesis of microporous materials and has once more emphasised the important role of silicon in stabilising aluminophosphate materials.
4.6 References

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Chapter 5 :

Rational design of a new template for the synthesis of a Chabazite-type aluminophosphate
5.1 Summary

In this chapter we describe the synthesis of heteroatom-substituted aluminophosphates which have been synthesised using the rationally designed template 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane. X-ray diffraction patterns of the materials formed were similar to that of the mineral chabazite; high-resolution x-ray powder diffraction showed the materials to have identical structures to heteroatom-substituted AlPO-34.

To assess the potential catalytic activity of these materials, infra-red spectroscopy and combined XAS/XRD were used. Infra-red spectroscopy of the silicon-substituted material showed the presence of bands due to bridging Si-OH-Al groups, i.e. Brønsted acid sites. Combined XAS/XRD showed that upon calcination there is a decrease in the average Co-O bond length from 1.93Å to 1.83Å for CoAPO-34, indicating that there is virtually complete oxidation of Co(II) to Co(III).

Because of the promising redox properties of CoAPO-34, the catalytic activity of this material was investigated in the aerobic oxidation of n-hexane. Preliminary results showed CoAPO-34 has a similar conversion to CoAPO-18\(^1\), which has a similar structure, and also shows complete oxidation of Co(II) to Co(III)\(^2\). The products obtained are similar; however, in the case of CoAPO-34, there is the additional formation of adipic acid.
5.2 Introduction

In this chapter we discuss the synthesis and structural properties of another heteroatom-substituted aluminophosphate. As discussed in Chapter 3, the syntheses of new aluminophosphates are based mainly on the use of different templates to direct the formation of different structures. In the previous chapter we described the synthesis of the chabazite-type aluminophosphate, DAF-5 using the computer designed template, 4-piperidinopiperidine. However, DAF-5 did not show Brønsted acidity or redox properties, which are necessary for catalytic purposes.

As well as computational design, new templates can be identified using rational design, where templates are chosen based on a chemical knowledge of other systems. A number of rationally designed templates have been reported in the literature; these include tropine hydrate, a template for the levyne-type structure DAF-4\(^3\), and linear diquinuclidinium ions of the form \([(\text{C}_7\text{H}_{13}\text{N})-(\text{CH}_2)_n-(\text{NC}_7\text{H}_{13})]^2+\) have been used to synthesise the novel structures STA-1 and STA-2\(^4\).

In this chapter we will use rational design to identify a template for the synthesis of another small-pore heteroatom-substituted aluminophosphate.
5.2.1 Choice of template

Ideally, we want to synthesise an aluminophosphate that will show catalytic activity in either acid-catalysed or oxidation reactions. The material must therefore be stable and must contain active sites, either Brønsted acid or redox sites.

We identified the molecule 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO) (Figure 5.1) as a suitable template for the synthesis of a small-pore aluminophosphate.

![Structure of 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane](image)

*Figure 5.1: Structure of 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane.*

This molecule is a small amine, as is usually used in the synthesis of small-pore aluminophosphates. The presence of the amine group, when protonated, means the template will charge-compensate the heteroatoms incorporated in the framework. The size and shape of TMABO is similar to tropine hydrate (Figure 5.2), used in the synthesis of the material, DAF-4\(^3\), which is a levyne-type CoAPO and has been
shown to convert methanol to light alkenes with the selective production of ethene and propene.

![Structure of the template Tropine hydrate](image)

*Figure 5.2: Structure of the template Tropine hydrate – used in the synthesis of DAF-4, which has a structure analogous to that of the small-pore zeolite levyne.*

In this work, cobalt and silicon substituted aluminophosphates will be synthesised using TMABO as the template. The structure of the material prepared will be elucidated using high-resolution x-ray diffraction. Infra-red spectroscopy and combined XRD/XAS will be used to determine whether or not active sites are present and if the framework is stable. Preliminary catalytic studies will also be carried out to determine the activity of the material synthesised in the aerobic oxidation of n-hexane.
5.3 Experimental

5.3.1 Synthesis

A cobalt-substituted aluminophosphate was prepared using 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO) as the template. As mentioned in the previous chapter, we can determine whether or not cobalt has been incorporated into the aluminophosphate framework by the colour of the material, which is very useful to establish the optimum conditions for a particular synthesis.

An aqueous synthesis gel was prepared using hydrated aluminium hydroxide, cobalt acetate tetrahydrate, 85% phosphoric acid, the template and distilled H$_2$O. The water was added to the phosphoric acid. The aluminium hydroxide was then added to the acid followed by the cobalt acetate, then the template. The gel was stirred vigorously after each addition. The pH of the final gel was 8. The gel was heated hydrothermally in a stainless steel autoclave with a PTFE liner. The synthesis conditions such as gel composition, pH, synthesis time and temperature were optimised to produce a pure phase. The optimum conditions for the synthesis are shown in Table 5.1. The material formed was filtered, washed with distilled water then dried. The product has an X-ray diffraction pattern very similar to that of the mineral chabazite.
Table 5.1: Optimum synthesis conditions for the CoAPO synthesised with \( R=\text{TMABO} \) as the template.

If a lower metal ion or template concentration was used in the starting gel, competitive formation of an AlPO\(_4\)-5 phase (AFI) was observed. As mentioned in Chapter 4, this competitive formation is often seen in the synthesis of chabazite-type aluminophosphates using small amines. Pure AFI could be obtained at lower template/heteroatom concentrations. The synthesis conditions necessary to produce a pure CoAPO-5 phase are shown in Table 5.2.

Table 5.2: Synthesis conditions for CoAPO-5 using \( R=\text{TMABO} \) as the template.

The powder x-ray diffraction patterns for the chabazite-type CoAPO and CoAPO-5 synthesised with TMABO are shown in Figure 5.3.
Figure 5.3: X-ray diffraction patterns of the chabazite-type CoAPO (top) and CoAPO-5 (bottom) synthesised using TMABO
Silicon was also successfully substituted into the aluminophosphate framework after the optimum synthesis conditions were established using cobalt. Table 5.3 shows the gel compositions for the SAPO and the CoAPSO. The pH of both was between 8 and 9. Again, care has to be taken to ensure the heteroatom and template concentration is sufficient to prevent competitive formation of the AFI phase.

<table>
<thead>
<tr>
<th>Material</th>
<th>Gel Composition (moles)</th>
<th>Synthesis Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co(ac)$_2$</td>
<td>Al(OH)$_3$</td>
</tr>
<tr>
<td>CoAPSO</td>
<td>0.04</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAPO</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3: Gel compositions and synthesis conditions for the CoAPSO and SAPO synthesised with R=TMABO as the template.

Magnesium, manganese and zinc have also been successfully incorporated into the aluminophosphate framework using TMABO as the template. However, no further attempt was made to characterise these materials, as it is not in our current field of study.
5.3.2 High Resolution Powder diffraction of the SAPO synthesised with TMABO

High resolution X-ray powder diffraction was used to determine the framework structure of the chabazite-type SAPO synthesised using TMABO, and to try and locate the template molecule. The data were collected at Station 2.3, Daresbury Synchrotron Radiation Source, which is described in Chapter 3.

First, data for the as-prepared material were collected in capillary mode (to avoid preferred orientation effects) at a wavelength of 1.2998Å. Data were collected from 6 to 70° 2θ with a step increment of 0.01° and a counting time of 3 seconds. The pattern could be readily indexed using the auto-indexing program TREOR\textsuperscript{5} to a hexagonal cell with cell parameters \(a=b=13.7429\text{Å}, c=14.9875\text{Å}, \alpha=\beta=90°, \gamma=120°\).

Due to the disorder of the template molecule, we were unable to obtain a suitable model for the structure of the as-prepared SAPO.

To obtain a structure for the framework, we collected data for the calcined, completely dehydrated SAPO. The material was calcined in a flow of oxygen at 550°C for 6 hours, then poured into a capillary which was attached to a vacuum line. The capillary was heated at 200°C whilst being evacuated to remove all traces of water. The capillary was then sealed to prevent any exposure to air or water. The data for the calcined material were collected in capillary mode at a wavelength of 1.3004Å, from 7 to 70° 2θ, with a step size of 0.01° and a collection time of 4 seconds per step. Two complete scans were recorded and the data summed.
The structure was obtained from a Rietveld refinement of the data using the program GSAS\textsuperscript{6}, in the space group \textit{R \overline{3}}. First, the cell parameters and the zero-point error were refined followed by the peak shape parameters. A pseudo-Voigt function was used to describe the peak shape\textsuperscript{7} with a manually interpolated background. The atom positions for SAPO-34 synthesised using the template \textit{i}-propylamine\textsuperscript{8} were used as starting positions for the model and were refined once the peak shape had converged. Soft constraints were applied to the framework bond angles and bond lengths. At this stage no attempt was made to include silicon in the refinement. The temperature factors were refined once the atom positions had converged; then silicon was included in place of phosphorus, with a fractional occupancy of 0.1. This final model was then refined to convergence producing final agreement factors of R\textsubscript{wp}=0.0751, R\textsubscript{p}=0.0595 and \( \chi^2 = 1.555 \). The observed, calculated and difference profiles for the refinement are given in Figure 5.4.

The final structure was found to be identical to that of SAPO-34, and is shown in Figure 5.5. The atom positions obtained together with the thermal parameters are given in Table 5.4. The bond angles and bond lengths for the final model are shown in Table 5.5.
Figure 5.4: HRPD data for the TMABO-synthesised SAPO ($\lambda=1.3004\AA$). The dotted line represents the experimental data and the solid line is the calculated fit. The difference is shown below.
Figure 5.5: Structure of the SAPO-34 framework from the HRPD data. Top picture shows the structure along the x-axis and the bottom is looking down the z-axis. In both cases, the Al atoms are shown in green, P in blue and the O’s in red. Si is in the same position as P with an occupancy of 0.1.
Table 5.4: Atom positions and isotropic thermal factors for calcined TMABO-synthesised SAPO-34. Si has an occupancy of 0.1 and P has an occupancy of 0.9. All other occupancies are 1.0.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq) Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)</td>
<td>-0.00023</td>
<td>0.22847</td>
<td>-0.39481</td>
<td>0.00312</td>
</tr>
<tr>
<td>Si(1)</td>
<td>-0.00023</td>
<td>0.22847</td>
<td>-0.39481</td>
<td>0.00312</td>
</tr>
<tr>
<td>Al(1)</td>
<td>0.22860</td>
<td>0.22824</td>
<td>-0.40063</td>
<td>0.00312</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.98709</td>
<td>0.73251</td>
<td>0.49049</td>
<td>0.00424</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.88768</td>
<td>0.76099</td>
<td>0.36658</td>
<td>0.00424</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.80455</td>
<td>0.91434</td>
<td>0.38192</td>
<td>0.00424</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.67938</td>
<td>0.98117</td>
<td>0.33289</td>
<td>0.00424</td>
</tr>
</tbody>
</table>

Table 5.5: Selected bond lengths and angles for the framework of TMABO-synthesised SAPO-34

<table>
<thead>
<tr>
<th>Atom-Pair</th>
<th>Bond Length (Å)</th>
<th>Bond Angle</th>
<th>Degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)-O(1)</td>
<td>1.699</td>
<td>O(1)-Al(1)-O(2)</td>
<td>117.7</td>
</tr>
<tr>
<td>Al(1)-O(2)</td>
<td>1.749</td>
<td>O(1)-Al(1)-O(3)</td>
<td>105.2</td>
</tr>
<tr>
<td>Al(1)-O(3)</td>
<td>1.800</td>
<td>O(1)-Al(1)-O(4)</td>
<td>108.4</td>
</tr>
<tr>
<td>Al(1)-O(4)</td>
<td>1.762</td>
<td>O(2)-Al(1)-O(3)</td>
<td>107.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(2)-Al(1)-O(4)</td>
<td>110.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(3)-Al(1)-O(4)</td>
<td>106.9</td>
</tr>
<tr>
<td>P(1)-O(1)</td>
<td>1.509</td>
<td>O(1)-P(1)-O(2)</td>
<td>107.0</td>
</tr>
<tr>
<td>P(1)-O(2)</td>
<td>1.542</td>
<td>O(1)-P(1)-O(3)</td>
<td>114.0</td>
</tr>
<tr>
<td>P(1)-O(3)</td>
<td>1.468</td>
<td>O(1)-P(1)-O(4)</td>
<td>112.5</td>
</tr>
<tr>
<td>P(1)-O(4)</td>
<td>1.482</td>
<td>O(2)-P(1)-O(3)</td>
<td>106.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(2)-P(1)-O(4)</td>
<td>105.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(3)-P(1)-O(4)</td>
<td>111.0</td>
</tr>
</tbody>
</table>
5.3.3 Elemental analysis

The results obtained from elemental analysis for the CoAPO, SAPO and CoAPSO synthesised with TMABO are given in Table 5.6. The materials have the formulae Co$_{0.1}$Al$_{0.88}$P$_{1.02}$O$_4$, Si$_{0.22}$Al$_{1.02}$P$_{0.76}$O$_4$ and Co$_{0.04}$Al$_{0.92}$Si$_{0.24}$P$_{0.80}$O$_4$ respectively.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoAPO</td>
<td>0.05</td>
<td>0.44</td>
<td>-</td>
<td>0.51</td>
</tr>
<tr>
<td>SAPO</td>
<td>-</td>
<td>0.51</td>
<td>0.11</td>
<td>0.38</td>
</tr>
<tr>
<td>CoAPSO</td>
<td>0.02</td>
<td>0.46</td>
<td>0.12</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 5.6: Elemental analysis results for the heteroatom-substituted aluminophosphates prepared with TMABO.

As we would expect, in the CoAPO, cobalt substitutes exclusively for aluminium in the framework as (Co+Al)~0.5. Likewise, in the SAPO it appears that silicon substitutes for phosphorus only. In the CoAPSO there may be a small amount of silicon being incorporated in the framework in place of aluminium as (Si+P)>(Co+Al); this may give rise to the formation of silicon islands in the structure. However, the extent of silicon clustering will be minimal compared to the DAF5: CoAPSO materials described in the previous chapter. A similar result was reported by Ashtekar et al$^9$ for CoAPSO-34.
5.3.4 Effect of cobalt concentration on cell parameters

The incorporation of cobalt in place of aluminium in the aluminophosphate framework means a strain is introduced into the structure. For each cobalt substituted, four Al-O bonds (1.71Å) are replaced by four much longer (1.94Å) Co(II)-O bonds. The incorporation of high levels of cobalt in the aluminophosphate framework has been shown to have a deleterious effect, and may lead to the collapse of the structure upon calcination, once the template is removed\textsuperscript{10}. This was found to be the case for DAF-5 (Chapter 4) where cobalt replaces 20% of the aluminium in the framework; the material was found to collapse upon calcination. However, in the DAF-5 CoAPSO's with 4 and 10% cobalt substitution (yet still having 20% overall heteroatom concentration), the structure is stable.

In this work, we will study the change in the cell parameters with an increase of cobalt in the aluminophosphate framework. Four different cobalt concentrations will be studied: 0% (SAPO-34), 4 and 6% (CoAPSO-34) and 10% (CoAPO-34). The as-prepared materials (still with the template molecule intact) will be studied in each case. High-resolution powder diffraction data were collected for each of the four samples. The data for the 0, 4 and 6% Co were collected in flat-plate mode at a wavelength of 1.3001Å. One scan was run for each material from $2\theta = 6$ to $45^\circ$, with a step size of 0.01° and a counting time of 1 second. The data for the material containing a concentration of 10% cobalt were the same as collected in Section 5.3.2.

The cell parameters were obtained from a Rietveld refinement of the data using the GSAS program\textsuperscript{6}. A space group of $R\overline{3}$ was employed in each case. First, the cell
parameters were refined with the zero-point error, then the peak-shape parameters were included in the refinement. A pseudo-Voigt function was used to describe the peak shape and a manually interpolated background was used. Once convergence was achieved, the cell parameters were noted. We did not include atom positions in the refinement, as we are interested primarily in the cell lengths. The cell parameters and volumes obtained from the Rietveld refinements are given in Table 5.7.

<table>
<thead>
<tr>
<th>Co concentration (%</th>
<th>(a) / Å</th>
<th>(c) / Å</th>
<th>(Volume) / Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.753</td>
<td>14.900</td>
<td>2818.26</td>
</tr>
<tr>
<td>4</td>
<td>13.769</td>
<td>14.914</td>
<td>2827.48</td>
</tr>
<tr>
<td>6</td>
<td>13.771</td>
<td>14.919</td>
<td>2829.25</td>
</tr>
<tr>
<td>10</td>
<td>13.765</td>
<td>14.929</td>
<td>2828.67</td>
</tr>
</tbody>
</table>

Table 5.7: Cell parameters and volumes for AlPO₄-34 with different cobalt concentrations.

Figures 5.6 and 5.7 show the change in the cell parameters \(a\) and \(c\) as the cobalt concentration is increased. As expected, there is an increase in the cell lengths, however, the effect is more pronounced for \(c\) than for \(a\). There is an increase in \(a\) as cobalt is initially introduced into the framework. However, on increasing the concentration from 4% to 10% there is little change in this cell length. A similar trend for the volume can be seen from Table 5.7. On the other hand, there seems to be an almost linear increase in \(c\) as the cobalt concentration is increased. There is a change of approximately 0.03 Å between 0 and 10% cobalt concentrations, which may have some effect on the stability of the framework.
Figure 5.6: Change in the cell parameter, $a$, as the cobalt concentration is increased

Figure 5.7: Change in the cell parameter, $c$, as the cobalt concentration is increased.
The template molecules, which are still intact, inside the aluminophosphate framework, may have some effect on the change in the cell parameters; therefore a more detailed study using calcined materials is necessary to get a true picture of what is happening.

5.3.5 X-ray Absorption Spectroscopy

Co K-edge EXAFS were collected for CoAPO-34 to confirm that cobalt had been incorporated into the aluminophosphate framework. Data were collected at Station 7.1 at Daresbury Synchrotron Radiation Source described in Chapter 3. 30mg of sample was pressed into a self-supporting wafer and Co K-edge EXAFS were collected in transmission mode. As previously, the data was processed using the programs EXCALIB and EXBROOK, then EXCURV92 was used to obtain the structural parameters.

The data obtained is shown in Figure 5.8 together with the associated Fourier transforms. Table 5.8 gives the structural parameters from analysis of the data. A coordination number of 4 oxygen’s around the cobalt was obtained. Therefore cobalt must be incorporated in the framework, most likely in place of aluminium. The Co-O bond length of 1.93Å implies that cobalt is in a divalent oxidation state. The Co-O and Co-P bond lengths and Co-O-P bond angles are similar to those obtained for other Co-substituted aluminophosphates.

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Figure 5.8: Co k-edge EXAFS (top) and the associated Fourier Transforms (bottom) for as-prepared CoAPO-34. In both, the solid line represents the experimental data and the dotted line is the calculated fit.
<table>
<thead>
<tr>
<th>Atom Pair</th>
<th>N</th>
<th>R(Å)</th>
<th>$2\sigma^2$(Å²)</th>
<th>Co-O-P bond angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-O</td>
<td>4.0</td>
<td>1.93</td>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>Co-P</td>
<td>2.7</td>
<td>3.18</td>
<td>0.013</td>
<td>138</td>
</tr>
<tr>
<td>Co-P</td>
<td>1.3</td>
<td>3.35</td>
<td>0.013</td>
<td>155</td>
</tr>
</tbody>
</table>

Table 5.8: Structural parameters obtained from analysis of the Co K-edge EXAFS data for as-prepared CoAPO-34.

5.3.6 Infrared Spectroscopy

SAPO-34 prepared using TMABO was studied using infrared spectroscopy to determine whether or not Brønsted acidity is present. The presence of Brønsted acid sites also confirms the incorporation of silicon in the framework; lower valent heteroatoms are necessary for acid sites to form.

Experimental

Approximately 15mg of the sample was pressed into a self-supporting wafer and mounted inside the in-situ cell detailed in Chapter 3, which is attached to the FTIR spectrophotometer. The pellet was then heated in a flow of oxygen to 550°C at a heating rate of 5°C/min; this temperature was sustained for 1 hour before cooling down. When the temperature of the cell had cooled to 150°C, the cell was evacuated.
to remove all traces of water. A background scan of the evacuated cell was obtained before recording the spectrum for the calcined material.

The infrared spectrum for SAPO-34 is shown in Figure 5.9. Only the region from 3800 to 3450 cm\(^{-1}\) is shown.

![Infrared Spectrum for SAPO-34](image)

*Figure 5.9: Infrared spectrum for SAPO-34 showing the presence of Brønsted acidity.*

Three main bands can be seen in the spectrum. The band at 3685 cm\(^{-1}\) is due to P-OH groups; this is lower in intensity than the P-OH band observed for DAF-5 in Chapter 4, indicating that there are less terminal OH groups in SAPO-34. The bands at 3624 and 3598 cm\(^{-1}\) are due to the presence of Al-OH-Si groups, and clearly indicate the presence of Brønsted acidity in the material. The result is very similar to that described by other authors\(^{13-17}\) for SAPO-34 synthesised using other templates. The
two different Al-OH-Si bands arise because the oxygen’s lie on two
crystallographically distinct sites\textsuperscript{14,15,18}. The band at 3598cm\textsuperscript{-1} most likely arises from
a bridging Si-OH-Al present in the large cage of the chabazite structure whilst the
band at 3624cm\textsuperscript{-1} is associated with a bridging hydroxyl in the double six-ring of the
structure\textsuperscript{14}.

As mentioned in Section 5.3.3, elemental analysis results show that the Al content is
equal to the (Si+P) content in SAPO-34. Hence, we can assume that all the silicon is
substituted in place of phosphorus and no silicon clustering occurs. Therefore,
isolated acid sites occur in the structure with every phosphorus substituted, forming a
highly acidic structure. It is very likely that SAPO-34 prepared with TMABO will be
as good a catalyst in acid-catalysed reactions e.g. the conversion of methanol to light
olefins as SAPO-34 synthesised with other templates\textsuperscript{19,20}.

5.3.7 Combined XAS/XRD

The combined XAS/XRD technique was used to investigate the stability of CoAPO
and CoAPSO-34 during the calcination process.

The data were collected at Station 9.3 of the Daresbury Synchrotron Radiation
Source. In these experiments, 25-30mg of sample was pressed into a 13mm self-
supporting wafer and mounted in the \textit{in-situ} cell described in Chapter 3. Both
materials were heated from room temperature to 550°C in a flow of air; the CoAPSO
was heated at a heating rate of 5°C/min throughout, whereas the CoAPO was heated
at 5°C/min to 350°C then 2°C/min to 550°C. The final temperature was sustained for 30 minutes for the CoAPSO and 1 hour for the CoAPO. The XRD data were collected for 180 s and the transmission X-ray absorption spectra were collected for 380 s yielding a total cycle time of 10 minutes including 40 s of dead time.

Plots of the XRD and the XAS data as a function of temperature for the two materials studied are shown in Figures 5.10 and 5.11. Both materials are stable and retain their structure once the template molecule has been removed from the structure. The changes in intensity that can be seen in the XRD plots are likely to be due to the removal of the template molecule and water molecules present in the pores.

From the plots of the XAS spectra, one can see a shift in the edge position as the temperature exceeds ca. 400°C. This can be seen more clearly in Figure 5.12, where only two temperatures are plotted for each material: 200°C where the template is intact, and 550°C where just an empty framework exists. The edge shift is about 2.5eV for the CoAPO and 0.5eV for the CoAPSO. This shift means that a change in oxidation state of the cobalt has very likely occurred. Similar results have been seen for other heteroatom-substituted aluminophosphates\textsuperscript{10,21-23} where changes in the oxidation state of the absorbing atom have occurred.
Figure 5.10: XRD (top) and XAS (bottom) as a function of temperature for CoAPO-34. The sample was heated at 5°C/min to 350°C, then 2°C/min to 550°C. The temperature was sustained at 550°C for 1 hour.
Figure 5.11: XRD (top) and XAS (bottom) as a function of temperature for CoAPSO-34. The material was heated at 5 °C/min to 550°C; this temperature was sustained for 30 minutes.
Figure 5.12: Plot of XAS spectra before and after removal of template for CoAPO-34 (top) and CoAPSO-34 (bottom)
The EXAFS spectra at each temperature were analysed as usual using the programs EXCALIB, EXBROOK and EXCURV92, available at Daresbury laboratory. Only the first Co-O shell was analysed as we are primarily interested in the immediate environment around the cobalt atom; in particular, changes in the average Co-O bonds can give information on the extent of oxidation of the Co(II) to Co(III) in the structure.

The changes in the structural parameters for CoAPO-34 and CoAPSO-34 synthesised using TMABO are shown in Figures 5.13 and 5.14 as a function of temperature. In both materials the coordination number, N, remains fairly constant at 4 (within the experimental error of 10%) throughout the calcination. There is a slight decrease in N for the CoAPO from ca. 400°C, which may be due to a slight distortion of the structure. A similar result was observed by Barrett et al for CoAPSO-44 and CoAPO-18, though the effect was greater. In both of these cases the coordination number dropped from 4 to less than 3, which was explained by a distortion in the structure, to one with 3 short bonds and one longer bond. There is some difference in the Debye-Waller factors, A, as a function of temperature. For CoAPSO-34, the Debye-Waller factor increases almost linearly with temperature. However, this is not the case with the CoAPO. As discussed in Chapter 3, the Debye-Waller factor is composed of two contributions, from thermal effects and static disorder. The contribution due to thermal effects is likely to be the same for both materials, therefore, any changes are due to changes in the static disorder. The extent of the two contributions to the Debye-Waller factor for these materials is discussed further in Chapter 6.
Figure 5.13: Change in the coordination number (N), the average Co-O distance (R), and the Debye-Waller factor (A) for CoAPO-34 as a function of temperature. The temperature was kept at 550°C for 1 hour.
Figure 5.14: Change in the coordination number (N), the average Co-O distance (R), and the Debye-Waller factor (A) for CoAPSO-34 as a function of temperature. The temperature was kept at 550°C for 30 minutes.
In both materials, there is a decrease in the average Co-O bond length at temperatures above 400°C. The temperature at which the decrease starts is different in the two materials, which may, however, be due to the difference in the heating rates. The final Co-O bond lengths after heating for an hour at 550°C were 1.82Å for the CoAPO and 1.84Å for CoAPSO-34. This shortening of the Co-O bond can be explained by a change in oxidation state from Co(II) to Co(III). The colour of the sample changes from blue to green during the calcination, confirming that oxidation of Co(II) has occurred. As discussed in Chapter 4, Barrett et al.\(^2\) assumed that the average Co-O bond length of 1.83Å for CoAPO-18 corresponded to complete oxidation of Co(II) to Co(III). Therefore, in the CoAPO-34 and CoAPSO-34 synthesised with TMABO, we can assume there is almost complete oxidation of cobalt in the aluminophosphate framework.

In a recent catalytic study, Thomas et al.\(^1\) reported the use of heteroatom-substituted aluminophosphates as regioselective oxidation catalysts that operate with air as an oxidant. Several structures were tested, however CoAPO-18 and MnAPO-18 were found to be superior in the selective oxidation of linear alkanes. Other structures with larger pore sizes were not as selective. The CoAPO-18 (AEI) structure is similar to that of the chabazite-type aluminophosphates; both structures can be thought of as being built entirely out of double six-rings and the main structural difference lies in the orientation of these rings. Figure 5.15 shows the orientation of the double six-rings in CoAPO-18 and -34. Both structures have similar shaped cavities, and pore sizes of 3.8 x 3.8Å.
Because of the similar structural dimensions and the complete oxidation of Co(II) to Co(III) in the two structures, we predicted that, like CoAPO-18, CoAPO-34 will also show good selective catalytic activity in the oxidation of linear alkanes. There are differences in the concentration of cobalt in the frameworks of CoAPO-18 and -34; the material tested by Thomas et al\(^1\) contained a 4% substitution of cobalt for aluminium which is 2.5 times lower that that in the CoAPO (10%).
5.3.8 Oxidation Catalysis

CoAPO-34 was tested as a catalyst for the aerobic oxidation of n-hexane. After 24 hours, CoAPO-18 showed a 7.2 % conversion with a selectivity of 53.5 mole % for hexanoic acid in this reaction.

5.3.8.1 Experimental

The oxidation reactions were carried out in a high-pressure stainless steel catalytic reactor (Cambridge Reactor Design, Model 6000) lined with polytheretherketone. Approximately 0.6g of the calcined catalyst was added to ~50g of n-hexane and stirred at a constant speed of 400rpm. Dry air was pressurised into the reaction vessel (1.5 Mpa) and the reactor was sealed and heated to 373K. Small aliquots of the sample were removed at intervals, which was achieved using a liquid sampling valve and did not affect the pressure inside the reactor. The products of the oxidations were analysed using gas chromatography.

5.3.8.2 Results

Figure 5.16 shows the preliminary results for the oxidation of n-hexane for CoAPO-34. The CoAPO-18 data (taken from the work of Thomas et al.) is included for comparison. The percent conversion of CoAPO-34 (8.9%) is not vastly different from that of CoAPO-18 (7.4%) although the concentration of active cobalt centres (i.e. Co$^{3+}$) in CoAPO-34 is 2.5 times higher. Also, as well as the formation of hexanoic acid, CH$_3$(CH$_2$)$_4$COOH, we also see the formation of adipic acid, HOOC(CH$_2$)$_4$COOH. To our knowledge, this is the first report of the conversion of n-hexane to adipic acid.
Figure 5.16: Preliminary catalytic results for the oxidation of n-hexane using CoAPO-34 synthesised using the new template 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO). The results for CoAPO-18 are taken from the work of Thomas et al. and are included for comparison.
Adipic acid is an important precursor in the production of Nylon 6,6. Industrially, adipic acid is synthesised from cyclohexanol and cyclohexanone, the products from the oxidation of cyclohexane. Large-pore aluminophosphates (CoAPO-5$^{24}$ and CoAPO-36$^{25}$) have been shown to be effective catalysts for this oxidation of cyclohexane. As cyclohexane (~4.5Å) is too big to diffuse through the 8-membered rings of CHA or AEI-type aluminophosphates (pore size ~3.8 x 3.8Å), this reaction will not occur in these materials$^{1,2,25}$.

Although the reason for the direct conversion of n-hexane to adipic acid is not completely clear, the higher concentration of cobalt in the aluminophosphate framework compared to CoAPO-18 is obviously a major factor. We can calculate how many cobalt atoms will be in a unit cell of CoAPO-34 and CoAPO-18. As there are 18 aluminium atoms per unit cell, a 10% replacement of aluminium by cobalt means there will be 1.8 cobalt atoms per unit cell; in CoAPO-18, there will be 0.72 cobalt atoms per unit cell. In CoAPO-34, the higher cobalt concentration means there may be active sites sufficiently close in the aluminophosphate framework so that both terminal carbons of the n-hexane can be oxidised at the same time. In CoAPO-18, the Co atoms are far enough away so that only one end of the n-hexane molecule will be oxidised. The possibility of one carbon being oxidised, then the molecule diffusing through the pores to become oxidised at the other end was ruled out; if this happened, we would see a small amount of adipic acid in CoAPO-18. No trace of adipic acid was seen for this material.
5.4 Conclusions

In this chapter we describe the synthesis of heteroatom-substituted aluminophosphates which have been synthesised using the rationally chosen template 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO). This template was identified as it is similar in size and shape to other amines used in the synthesis of small-pore aluminophosphates. X-ray diffraction patterns of the materials formed were similar to that of the small-pore mineral chabazite; high-resolution x-ray powder diffraction showed the materials to have identical structures to heteroatom-substituted AlPO-34.

To study the effect of incorporating cobalt in the aluminophosphate framework, high-resolution x-ray diffraction patterns were collected for materials containing 0, 4, 6 and 10% cobalt and the cell parameters and volumes were calculated for each. There is a significant increase in the c direction of the unit cell with higher cobalt concentrations. If this trend were to continue at concentrations higher than 10% Co, it may cause instability in the aluminophosphate framework and cause the structure to collapse.

To assess the potential catalytic activity of these materials, infra-red spectroscopy and combined XAS/XRD were used. Infra-red spectroscopy of the silicon-substituted material showed the presence of bands due to the presence of bridging Si-OH-Al groups, i.e. Brønsted acid sites. These bands are very similar to those observed by other authors for SAPO-34 synthesised using different templates. Combined XAS/XRD showed that upon calcination for CoAPO-34 and CoAPSO-34 there is a
decrease in the bond length from 1.94Å to 1.82Å and 1.84Å respectively, indicating that there is virtually complete oxidation of Co(II) to Co(III) in both materials. A shift in the edge position and a colour change of the sample from blue to green support the idea of a change in oxidation state.

A recent catalytic result by Thomas et al. showed that CoAPO-18 exhibited selective oxidation of linear alkanes in air. As CoAPO-18 is similar in structure to CoAPO-34 and both show almost complete oxidation from Co(II) to Co(III) upon calcination, it follows that CoAPO-34 may show similar catalytic properties to CoAPO-18. As there are 2.5 times more active cobalt centres in the framework in CoAPO-34 than 18 we were expecting a higher overall conversion, however CoAPO-34 showed a much lower conversion than expected, only slightly higher than CoAPO-18. As well as forming hexanoic acid, CoAPO-34 also formed adipic acid as one of the products. Adipic acid is industrially produced from cyclohexanol and cyclohexanone using larger pore aluminophosphates and is an important precursor in the synthesis of Nylon 6,6. We believe this is the first report of adipic acid being formed from n-hexane.
5.5 References


11. N. Binsted, J. W. Campbell, S. J. Gurman, P. C. Stephenson, CCLRC Daresbury Laboratory, EXCURV92 Program


Chapter 6

Synthesis, Crystal Structure and Redox Properties of CoAPO-34 prepared using different templates
6.1 Summary

In this chapter the structure and properties of CoAPO-34 synthesised with different template molecules are studied. The templates used are 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO), which was described in the previous Chapter, morpholine, triethylamine (TEA) and tetraethylammonium hydroxide (TEAOH).

Single crystals of cubic morphology were obtained for three templates: triethylamine, morpholine and TMABO. Micro-single crystal diffraction was used to determine the number of template molecules present and their location in each structure. Results show that in morpholine-synthesised CoAPO-34 there are two templates per cage, whereas there is only one triethylamine or TMABO molecule per chabazite-type cage.

A combined XAS/XRD study showed that all structures were stable during the calcination process. As for TMABO which was discussed in the previous chapter, CoAPO-34 synthesised using TEAOH also showed complete oxidation of Co(II) to Co(III). Using morpholine and TEA, a much lower amount of oxidised cobalt was observed. By using CoAl$_2$O$_4$ as a model compound we are able to compare differences in the static disorder component of the Debye Waller factor for the materials studied. An increase in the static disorder between 300 and 500°C can be explained by the formation of Brønsted acid sites before oxidation to Co(III) occurs. 

1
We observe from the results obtained that CoAPO-34 synthesised with TEAOH has almost identical properties to that synthesised with TMABO. From the literature it is agreed that, as for TMABO, heteroatom-substituted AlPO-34 synthesised using TEAOH also contains one template molecule per cage. Both have similar amounts of cobalt in the framework, all of which can be oxidised to Co(III) upon calcination. It is therefore likely that CoAPO-34 synthesised with TEAOH will display catalytic properties similar to that of TMABO-synthesised CoAPO-34 in the oxidation of n-hexane. The lower amount of oxidisable cobalt in CoAPO-34 synthesised with morpholine and TEA suggests the catalytic activity will be far lower than that of the materials synthesised with the templates mentioned above.
6.2 Introduction

In the previous chapter we discussed the synthesis of heteroatom substituted AlPO-34 using the new rationally designed template 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO). The cobalt and silicon substituted materials showed potential in the field of catalysis; in particular, the formation of adipic acid from n-hexane using CoAPO-34 was reported for the first time. In this chapter, we extend our study by comparing the structures and redox properties of CoAPO-34 synthesised with four different templates.

Heteroatom-substituted aluminophosphates with the chabazite-type structure-34 were first synthesised in 1984 by the workers of Union Carbide. SAPO-34 was prepared using tetraethylammonium hydroxide (TEAOH) as the template. Divalent metal ions e.g. Co, Mn, Zn, Mg, Fe have also been incorporated in the AlPO-34 framework using the same template. Using TEAOH as the template, but without the presence of silicon or a metal, AlPO-5 or -18 forms.

Since this initial synthesis, many more templates have been identified for the synthesis of heteroatom-substituted AlPO-34, which include isopropylamine, morpholine, piperidine, and triethylamine. Also, the addition of HF in the synthesis gel has been widely reported. It is possible to synthesise pure AlPO-34 if HF is used (with morpholine as the template). Single crystal analysis showed the fluoride ions were present as bridges between Al atoms of the 4-membered rings, and
are removed upon calcination. HF has also been used for the synthesis of heteroatom-substituted AlPO-34 using the templates triethylamine and piperidine. Xu et al reported that the addition of HF leads to a reduction in nucleation time and an increase in the crystallinity of the products.

A high cobalt-containing CoAPO-34 was synthesised by Hill et al using TEAOH as the template; \([(CH_3CH_2)_4N]_2CoCl_4\) was included in the synthesis gel as a source of cobalt and an additional templating agent. A pure phase was achieved by replacing up to 0.4 mole fraction of Al by Co in the synthesis gel, which is more than double the concentration of Co that can be achieved using the templates reported above; however, some extra-framework cobalt may be present.

We have chosen to study the cobalt-substituted material in this work, as these materials have the potential to form both redox and Bronsted acid sites in the framework as discussed in Chapter 2; both are important in the field of catalysis. In the previous chapter we showed that in CoAPO-34 synthesised with TMABO, there is almost complete oxidation of Co(II) to Co(III) in the framework. As a result, the material showed very interesting catalytic properties in the regioselective oxidation of n-hexane. In contrast, Moen et al reported an x-ray absorption spectroscopic study of CoAPSO-34 synthesised with morpholine; they found that approximately two-thirds of the Co(II) was converted to octahedral Co\(^{III}\)(O)\(_6\) units upon calcination. The colour change from blue to green was thought to arise from mixing blue tetrahedral Co(II) and yellow octahedral Co(III).
Through single crystal or thermogravimetric studies, several authors have been able to calculate the number of templates inside the chabazite type cage of heteroatom-substituted AlPO-34. There are generally one or two templates per cage; the number varies depending on the template used and the type of heteroatom in the framework. Results for morpholine show that in most cases there are 2 templates per cage.\(^3,14\) However in a study by Marchese et al.\(^{18}\), 1.5 molecules of morpholine per cage and two molecules of water were located, which suggests that 50% of the cages might be occupied by 2 molecules of morpholine; the rest will have 1 molecule morpholine and 4 molecules water. Thermogravimetric analysis of SAPO-34 synthesised with triethylamine\(^13\) in the presence of HF showed there were two templates present per cage. Computational studies\(^{13,19}\) have confirmed that 2 triethylamine molecules can fit comfortably in the chabazite cage. In heteroatom-substituted AlPO-34 synthesised with tetraethylammonium hydroxide\(^{2,4}\) and 1-propylamine\(^8\) there was found to be only one template molecule per unit cell.

In this work we will compare CoAPO-34 synthesised using four different templates: morpholine, triethylamine (TEA), tetraethylammonium hydroxide (TEAOH) and the template we identified in the previous chapter, 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO). All four templates are shown in Figure 6.1.
The aim of this study is to gain a deeper insight into the formation of active sites in these materials. Combined XAS/XRD will be used to study the stability during the calcination process and the extent of oxidation of Co(II) to Co(III) in the framework. By using CoAl₂O₄ as a model compound, we can study the static disorder and thermal contribution to the Debye-Waller factor for the CoAPOs. Micro-single crystal diffraction will be used to identify the number of templates and their location inside the CoAPO-34 structure.
6.3 Experimental

6.3.1 Synthesis

The materials were synthesised from aqueous synthesis gels using hydrothermal methods. In each case the 85% phosphoric acid was diluted with the water, then the cobalt acetate was added and stirred vigorously. The aluminium hydroxide was added next and stirred until a homogeneous solution was obtained. The template was added last. The gel compositions used for the different templates are given in Table 6.1 together with the final pH for the gel.

<table>
<thead>
<tr>
<th>Template</th>
<th>Co</th>
<th>Al</th>
<th>P</th>
<th>H₂O</th>
<th>Template</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMABO</td>
<td>0.1</td>
<td>0.9</td>
<td>1</td>
<td>30</td>
<td>1.5</td>
<td>9</td>
</tr>
<tr>
<td>Morpholine⁹</td>
<td>0.1</td>
<td>0.9</td>
<td>1</td>
<td>60</td>
<td>2.7</td>
<td>10</td>
</tr>
<tr>
<td>TEAOH</td>
<td>0.1</td>
<td>0.9</td>
<td>1</td>
<td>30</td>
<td>1.5</td>
<td>9</td>
</tr>
<tr>
<td>TEA¹²</td>
<td>0.1</td>
<td>0.9</td>
<td>1</td>
<td>60</td>
<td>2</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 6.1: Gel compositions (moles) and pHs used in the synthesis of CoAPO-34 with different templates. (The TMABO synthesis is from Chapter 5; the morpholine and TEA syntheses have been taken from the literature and for TEAOH, the TMABO gel composition was used.)
The gels were sealed in stainless steel autoclaves with PTFE liners then heated in an oven. The synthesis times and temperatures are given in Table 6.2. Blue crystalline solids were obtained in each case.

<table>
<thead>
<tr>
<th>Template</th>
<th>Synthesis Time</th>
<th>Synthesis Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMABO</td>
<td>6 days</td>
<td>180°C</td>
</tr>
<tr>
<td>Morpholine</td>
<td>3 days</td>
<td>180°C</td>
</tr>
<tr>
<td>TEAOH</td>
<td>2 days</td>
<td>180°C</td>
</tr>
<tr>
<td>TEA</td>
<td>4 days</td>
<td>170°C</td>
</tr>
</tbody>
</table>

Table 6.2: Synthesis times and temperatures for the four different CoAPO-34 templates.

X-ray diffraction confirmed that all materials formed had the CoAPO-34 structure. The XRD patterns obtained are shown in Figure 6.2. All patterns are similar to that of the mineral chabazite. There are differences in the positions of the peaks between the samples synthesised with the different templates, which is due to slight differences in the cell parameters. The differences in the intensities of the peaks are probably due to effects of the different templates inside the frameworks; preferred orientation may have an effect in the more crystalline materials. Despite the differences between the patterns, it is clear from the X-ray diffraction patterns that there is no competitive formation of CoAPO-5 (largest peak at 2θ = 7.423°).
6.3.2 Crystal morphology

The crystal morphologies of the materials synthesised were studied using an optical microscope equipped with a video camera, available at the Daresbury Laboratory. Images from the camera can be saved as computer files. CoAPO-34 synthesised with TEAOH and TMABO did not contain any crystals at all. However, small cubic crystals were present in CoAPSO-34 synthesised with TMABO. Blue, cubic crystals

Figure 6.2: XRD patterns for CoAPO-34 synthesised with morpholine, TEAOH, TEA and TMABO.
can also be seen for CoAPO-34 synthesised with morpholine and TEA. The morphology of these crystals agrees with the results of other workers for chabazite type materials\textsuperscript{8,9,21,22}. The size and shape of the crystals obtained in this study are shown in Figures 6.3 to 6.6.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6_3.jpg}
\caption{CoAPO-34 synthesised with TEAOH; no crystals can be seen in the sample. This is similar to CoAPO-34 synthesised with TMABO.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6_4.jpg}
\caption{CoAPSO-34 synthesised with TMABO.}
\end{figure}
The differences in the crystal size of CoAPO-34 synthesised with the different templates could possibly be explained by the compositions of the synthesis gels. In the morpholine and TEA gels, which produce the large crystals, there is twice as much water in the starting gel compared to the other templates.
6.3.3 Elemental Analysis

The framework compositions of the CoAPO-34 samples synthesised using the different templates were obtained from elemental analysis. The results obtained are given in Table 6.3. The results for CoAPO-34 synthesised using TMABO are given in the previous chapter.

<table>
<thead>
<tr>
<th>Template</th>
<th>Co</th>
<th>Al</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morpholine</td>
<td>0.103</td>
<td>0.400</td>
<td>0.497</td>
</tr>
<tr>
<td>TEA</td>
<td>0.05</td>
<td>0.45</td>
<td>0.50</td>
</tr>
<tr>
<td>TEAOH</td>
<td>0.05</td>
<td>0.452</td>
<td>0.498</td>
</tr>
</tbody>
</table>

Table 6.3: Framework composition (moles) of CoAPO-34 synthesised using the different templates. The results for TMABO-synthesised CoAPO-34 were presented in the previous chapter.

For each of the templates studied the (Co+Al) concentration is almost equal to the amount of phosphorus in the framework, which means cobalt is substituting exclusively for aluminium. From the previous chapter, TMABO produced a framework of structure Co$_{0.1}$Al$_{0.9}$PO$_4$ which is similar to that synthesised using TEAOH and TEA. CoAPO-34 from morpholine has twice as much cobalt in the framework as for the other templates.
6.3.4 Micro-crystalline Diffraction

Single crystal diffraction was used to locate the template molecules inside the CoAPO-34 framework. TEAOH and TMABO-synthesised CoAPO-34 were not studied, as single crystals were not obtained. Crystals for CoAPSO-34 synthesised with TMABO (detailed in the previous chapter) were found and were used in this study.

The data for the crystals were collected on Station 9.8 of Daresbury SRS using a Siemens SMART CCD area detector diffractometer equipped with a silicon (111) crystal monochromator as described in Chapter 3. A hemisphere of data was collected in each case at a temperature of 150K employing a wavelength of 0.71073Å. The data was analysed via a least-squares refinement combined with direct methods, using the SHELXTL/SHELX-97 suite of programs\textsuperscript{22}. The space group $\overline{R} 3$ was used for each of the structures.

6.3.4.1 Morpholine

A crystal of size 30 x 30 x 30μm was studied. The data were collected for a 2θ range of 2.19 to 30.49°; 1540 reflections were collected and merged to yield 1060 unique reflections. A unit cell of dimensions $a=b=13.844Å$, $c=14.726Å$, $α=β=90°$, $γ=120°$ and cell volume $2444.4Å^3$ was obtained from the data.

Due to the highly disordered state of the templates, it not possible to distinguish the different atoms in the 6-membered ring; for ease of analysis we have assigned all
template atoms as carbon. The disorder of the template can be seen from a plot of the thermal ellipsoids, generated using the program ORTEP\textsuperscript{23} (Figure 6.7), which shows the amount of movement of each atom away from the atom positions.

Figure 6.7: ORTEP thermal ellipsoid plot of the CoAPO-34 cage containing morpholine template molecules.

The large ellipsoid sizes of the atoms of the template molecules indicate that there is a lot of disorder associated with the positions of these atoms. In contrast there is very little disorder of the framework atoms. However, it is clear from Figure 6.7 that, despite the disorder, there are two morpholine templates present per cage.
The final R-factors from the refinement are given in Table 6.4. They show that there is an acceptably good fit between the model shown and the actual structure, despite the large amount of disorder of the template.

<table>
<thead>
<tr>
<th>Final R indices [I&gt;2σ(I)]</th>
<th>Ri=0.0937</th>
<th>WR2=0.3194</th>
</tr>
</thead>
<tbody>
<tr>
<td>R indices (All data)</td>
<td>Ri=0.1202</td>
<td>WR2=0.3324</td>
</tr>
<tr>
<td>Goodness of fit on F²</td>
<td>1.29</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4: R-factors and goodness of fit for single crystal refinement of CoAPO-34 synthesised with the template morpholine.

This result agrees with that obtained by other authors\(^3,14\) where two template molecules were found in AlPO-34 and heteroatom-substituted AlPO-34 synthesised using morpholine as the template. Vomschien et al\(^3\) studied SAPO-34; they found that irrespective of the amount of Si in the framework, there were always two template molecules per cage. Morpholine is similar in size and shape to cyclohexylamine, a template for the synthesis of heteroatom-substituted AlPO-44. A micro-single crystal study of CoAPSO-44 by Muncaster et al\(^21\) showed there were two cyclohexylamine templates per cage, orientated in a similar manner to morpholine in CoAPO-34.

The atom positions obtained from the refinement are given in Table 6.5, together with the thermal parameters. Table 6.6 lists selected bond lengths and angles for the
CoAPO-34 framework containing the morpholine template and Table 6.7 shows the anisotropic displacement factors.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U (\text{Å}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>0.33795(10)</td>
<td>-0.10386(10)</td>
<td>0.56119(9)</td>
<td>0.0189(5)</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0.33795(10)</td>
<td>-0.10386(10)</td>
<td>0.56119(9)</td>
<td>0.0189(5)</td>
</tr>
<tr>
<td>P(1)</td>
<td>0.11122(12)</td>
<td>-0.32773(12)</td>
<td>0.55401(10)</td>
<td>0.0344(5)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.2105(5)</td>
<td>-0.2173(5)</td>
<td>0.5275(4)</td>
<td>0.0740(18)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.3601(5)</td>
<td>0.0166(5)</td>
<td>0.5055(4)</td>
<td>0.0737(18)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.3390(5)</td>
<td>-0.0757(6)</td>
<td>0.6832(4)</td>
<td>0.0725(18)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.4444(4)</td>
<td>-0.1408(5)</td>
<td>0.5334(5)</td>
<td>0.0719(17)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.336(6)</td>
<td>-0.148(6)</td>
<td>0.379(5)</td>
<td>0.44(3)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.325(4)</td>
<td>-0.254(4)</td>
<td>0.352(4)</td>
<td>0.32(2)</td>
</tr>
<tr>
<td>C(3)</td>
<td>0.441(3)</td>
<td>-0.225(3)</td>
<td>0.2786(17)</td>
<td>0.246(12)</td>
</tr>
</tbody>
</table>

Table 6.5: Atom positions and thermal parameters for CoAPO-34 containing morpholine template. Due to the highly disordered nature of the template, N and O have been omitted from the template.

Co(1) has a fractional occupancy of 0.2, Al(1) is 0.8; the remaining atoms have an occupancy of 1. (The occupancies were not refined in this study)
<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond Angle</th>
<th>Degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)-O(1)</td>
<td>1.762(6)</td>
<td>O(1)-Al(1)-O(2)</td>
<td>108.2(3)</td>
</tr>
<tr>
<td>Al(1)-O(2)</td>
<td>1.766(6)</td>
<td>O(1)-Al(1)-O(3)</td>
<td>113.1(3)</td>
</tr>
<tr>
<td>Al(1)-O(3)</td>
<td>1.790(6)</td>
<td>O(1)-Al(1)-O(4)</td>
<td>107.2(3)</td>
</tr>
<tr>
<td>Al(1)-O(4)</td>
<td>1.842(6)</td>
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<td>105.0(3)</td>
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<td>O(2)-Al(1)-O(4)</td>
<td>110.8(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(3)-Al(1)-O(4)</td>
<td>112.5(3)</td>
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<tr>
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<td>106.4(4)</td>
</tr>
<tr>
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<td>1.486(6)</td>
<td>O(1)-P(1)-O(3)</td>
<td>111.2(4)</td>
</tr>
<tr>
<td>P(1)-O(3)</td>
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<td>O(1)-P(1)-O(4)</td>
<td>106.8(4)</td>
</tr>
<tr>
<td>P(1)-O(4)</td>
<td>1.509(6)</td>
<td>O(2)-P(1)-O(3)</td>
<td>109.7(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(2)-P(1)-O(4)</td>
<td>109.8(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(3)-P(1)-O(4)</td>
<td>112.8(4)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.46(7)</td>
<td>C(1)-C(2)-C(3)</td>
<td>119(5)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.66(5)</td>
<td>C(3)-C(2)-C(3)</td>
<td>97(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(3)-C(2)-C(2)</td>
<td>97(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(3)-C(3)-C(2)</td>
<td>102(2)</td>
</tr>
</tbody>
</table>

Table 6.6: Selected bond distances and angles for the CoAPO-34 framework containing morpholine as the template.

The bond angles and distances for the CoAPO-34 framework are as we would expect. The average of the two template C-C bond lengths obtained is very close to the expected value of 1.54Å. The deviation from this value probably arises due to the large amount of disorder in the system. We must remember however, that nitrogen and oxygen atoms are also present in morpholine; these were omitted from the refinement due to the highly disordered nature of the template.
Table 6.7: Anisotropic displacement factors (Å²) for CoAPO-34 (morpholine template) where the values for Co(1) are the same as Al(1). The anisotropic displacement factor takes the form:

\[-2\pi^2 \left[ h^2a^*U_{11} + k^2b^*U_{22} + l^2c^*U_{33} + 2hk a^*b^*U_{23} + 2hl a^*c^*U_{13} + 2hk a^*b^*U_{12} \right] \]

6.3.4.2 **TEA**

A crystal of size 15 x 15 x 15 μm was studied. We had difficulty in locating a suitable crystal for analysis as most were twinned. Data were collected in the 2θ range 2.2 to 30.2°; 1521 reflections were collected and merged to yield 1095 unique reflections. The cell parameters obtained were a=b=13.8161Å, c=14.7490Å, α=β=90°, γ=120°. The cell volume is 2438.21Å³.

Again the template molecule is disordered, as shown by the plot of the thermal ellipsoids in Figure 6.8. In contrast, there is very little disorder of the framework atoms. It is clear that there is only one template per cage and this molecule sits in the centre of the cage. The final R-factors for the refinement are given in Table 6.8. They
show a good fit between the model and the structure. We are therefore confident that the template has been correctly located.

Figure 6.8: Thermal ellipsoid plot of CoAPO-34 framework (black lines) containing the triethylamine template. The N atom of TEA is shown in red, the C atoms are shown in blue.
Table 6.8: R-factors and goodness of fit for single crystal refinement of CoAPO-34 synthesised with the template triethylamine.

This result disagrees with that of other authors, both experimental and computational. Lewis et al\textsuperscript{19} reported that it is energetically preferential for two template molecules to be accommodated per cage, which was calculated to provide a significant increase in stability over a single template. Xu et al\textsuperscript{13} synthesised CoAPSO-34 and SAPO-34 using triethylamine in the presence of HF; thermogravimetric analysis showed the presence of two triethylamine molecules per cage. Using computational techniques they also showed that two TEA molecules fit comfortably inside the chabazite cage. There is however, no single-crystal data reported for heteroatom-substituted AlPO-34 synthesised from triethylamine in the absence of HF. Without such data, and due to the disagreement between our result and other workers, we would have liked to repeat this analysis using another crystal. However, we could not find another non-twinned crystal that would be suitable for data collection. Further work on this problem is needed.

The atom positions obtained from the refinement are given in Table 6.9, together with the thermal parameters and Table 6.10 shows the anisotropic displacement factors. Selected bond lengths and angles are shown in Table 6.11.
Table 6.9: Atom positions for CoAPO-34 containing the template triethylamine. Co(1) has an occupancy of 0.1; Al(1) is 0.9. The remaining atoms all have an occupancy of 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>0.10849(11)</td>
<td>0.67105(10)</td>
<td>0.77051(8)</td>
<td>0.0118(4)</td>
</tr>
<tr>
<td>Co(1)</td>
<td>0.10849(11)</td>
<td>0.67105(10)</td>
<td>0.77051(8)</td>
<td>0.0118(4)</td>
</tr>
<tr>
<td>P(1)</td>
<td>0.10353(11)</td>
<td>0.44255(11)</td>
<td>0.77657(9)</td>
<td>0.0216(4)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.0928(5)</td>
<td>0.5426(4)</td>
<td>0.8024(3)</td>
<td>0.0436(12)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.0734(5)</td>
<td>0.4127(4)</td>
<td>0.6782(3)</td>
<td>0.0453(12)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.0223(4)</td>
<td>0.3449(4)</td>
<td>0.8343(3)</td>
<td>0.0433(12)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.2224(4)</td>
<td>0.4694(4)</td>
<td>0.7950(4)</td>
<td>0.0422(11)</td>
</tr>
<tr>
<td>N(1)</td>
<td>-0.3333</td>
<td>0.3333</td>
<td>0.8333</td>
<td>0.37(3)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.160(2)</td>
<td>0.593(2)</td>
<td>1.0343(19)</td>
<td>0.293(12)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.276(4)</td>
<td>0.645(7)</td>
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<td>0.46(2)</td>
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</tbody>
</table>

Table 6.10: Anisotropic displacement factors (Å²) for CoAPO-34 (triethylamine template); the values for Co(1) are the same as Al(1). The anisotropic displacement factor is defined in Table 7.

<table>
<thead>
<tr>
<th>Atom</th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₂₃</th>
<th>U₁₃</th>
<th>U₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>0.0160(7)</td>
<td>0.0084(6)</td>
<td>0.0135(7)</td>
<td>0.0002(4)</td>
<td>0.0052(5)</td>
<td>0.0080(5)</td>
</tr>
<tr>
<td>P(1)</td>
<td>0.0233(7)</td>
<td>0.0183(7)</td>
<td>0.0253(7)</td>
<td>0.0053(5)</td>
<td>0.0057(5)</td>
<td>0.0121(5)</td>
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<tr>
<td>O(1)</td>
<td>0.062(3)</td>
<td>0.039(2)</td>
<td>0.045(3)</td>
<td>0.004(2)</td>
<td>0.010(2)</td>
<td>0.037(2)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.058(3)</td>
<td>0.054(3)</td>
<td>0.029(2)</td>
<td>-0.001(2)</td>
<td>-0.001(2)</td>
<td>0.032(3)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.040(2)</td>
<td>0.036(2)</td>
<td>0.051(3)</td>
<td>0.021(2)</td>
<td>0.017(2)</td>
<td>0.017(2)</td>
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<tr>
<td>O(4)</td>
<td>0.027(2)</td>
<td>0.040(2)</td>
<td>0.061(3)</td>
<td>-0.003(2)</td>
<td>-0.002(2)</td>
<td>0.017(2)</td>
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</table>
Table 6.11: Selected bond distances and angles for the CoAPO-34 framework containing the template triethylamine. Co(1) is assumed to be in the same position as Al(1).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond Angle</th>
<th>Degrees</th>
</tr>
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<tbody>
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<td>Al(1)-O(1)</td>
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<td>O(1)-Al(1)-O(2)</td>
<td>111.3(2)</td>
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<tr>
<td>Al(1)-O(2)</td>
<td>1.751(5)</td>
<td>O(1)-Al(1)-O(3)</td>
<td>107.0(2)</td>
</tr>
<tr>
<td>Al(1)-O(3)</td>
<td>1.747(4)</td>
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<td>108.9(2)</td>
</tr>
<tr>
<td>Al(1)-O(4)</td>
<td>1.772(5)</td>
<td>O(2)-Al(1)-O(3)</td>
<td>107.9(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(2)-Al(1)-O(4)</td>
<td>110.3(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(3)-Al(1)-O(4)</td>
<td>111.5(2)</td>
</tr>
<tr>
<td>P(1)-O(1)</td>
<td>1.511(4)</td>
<td>O(1)-P(1)-O(2)</td>
<td>110.6(3)</td>
</tr>
<tr>
<td>P(1)-O(2)</td>
<td>1.509(4)</td>
<td>O(1)-P(1)-O(3)</td>
<td>107.8(3)</td>
</tr>
<tr>
<td>P(1)-O(3)</td>
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<td>O(1)-P(1)-O(4)</td>
<td>108.7(3)</td>
</tr>
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<td>P(1)-O(4)</td>
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<td>O(2)-P(1)-O(3)</td>
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<td>110.8(3)</td>
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<tr>
<td></td>
<td></td>
<td>O(3)-P(1)-O(4)</td>
<td>110.3(3)</td>
</tr>
<tr>
<td>N(1)-C(2)</td>
<td>1.60(4)</td>
<td>C(1)-C(2)-N(1)</td>
<td>135(3)</td>
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<tr>
<td>C(1)-C(2)</td>
<td>1.48(4)</td>
<td>C(2)-N(1)-C(2)</td>
<td>136(3)</td>
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6.3.4.3 TMABO

As the crystals of CoAPO-34 synthesised with TMABO were too small for single crystal diffraction, we studied the CoAPSO system instead. A crystal of approximate size 10 x 10 x 10 μm was investigated. Data were collected in the 2θ range 2.18 to 30.22°; 1475 reflections were collected and merged to yield 1076 unique reflections. The cell parameters obtained were a=b=13.8250Å, c=14.9755Å, α=β=90°, γ=120°. The cell volume is 2478.8Å³.
Again the template molecule is very disordered; a plot of the thermal ellipsoids is shown in Figure 6.9. As for triethylamine, there is only one template present in the centre of each cage. The template is bigger and a lot bulkier than the other two, so it is not surprising that only one template can be accommodated in each cage. Because the template is so disordered, we were unable to distinguish between the different atoms in TMABO; all atoms were assumed to be carbon. The final R-factors and the goodness of fit are given in Table 6.12.

Figure 6.9: Thermal ellipsoid plot of the CoAPSO-34 framework (black lines) containing the template TMABO. Only the C atoms of the template are shown (blue ellipsoids).
Table 6.12: R- factors and goodness of fit for a single crystal refinement of CoAPO-34 synthesised with the template TMABO.

The atom positions obtained from the refinement are given in Table 6.13, together with the thermal parameters. Table 6.14 shows the anisotropic displacement factors and Table 6.15 lists selected bond lengths and angles for the CoAPO-34 framework containing TMABO.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U (Å²)</th>
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</thead>
<tbody>
<tr>
<td>Al(1)</td>
<td>0.33770(7)</td>
<td>0.44167(8)</td>
<td>0.56395(7)</td>
<td>0.0078(3)</td>
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<tr>
<td>Co(1)</td>
<td>0.33770(7)</td>
<td>0.44167(8)</td>
<td>0.56395(7)</td>
<td>0.0078(3)</td>
</tr>
<tr>
<td>Si(1)</td>
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<td>0.43633(7)</td>
<td>0.55879(6)</td>
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</tr>
<tr>
<td>P(1)</td>
<td>0.10757(7)</td>
<td>0.43633(7)</td>
<td>0.55879(6)</td>
<td>0.0126(3)</td>
</tr>
<tr>
<td>O(1)</td>
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<td>0.4037(3)</td>
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<td>0.0272(7)</td>
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<td>O(2)</td>
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<td>0.5572(2)</td>
<td>0.5420(2)</td>
<td>0.0275(7)</td>
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<tr>
<td>O(3)</td>
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<td>0.3561(2)</td>
<td>0.4999(2)</td>
<td>0.0248(7)</td>
</tr>
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<td>O(4)</td>
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<td>0.4255(3)</td>
<td>0.5337(2)</td>
<td>0.0259(7)</td>
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<tr>
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<td>0.6667</td>
<td>0.244(4)</td>
<td>0.26(2)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.060(6)</td>
<td>0.100(5)</td>
<td>0.596(4)</td>
<td>0.46(3)</td>
</tr>
<tr>
<td>C(3)</td>
<td>-0.025(5)</td>
<td>0.106(4)</td>
<td>0.514(3)</td>
<td>0.318(17)</td>
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</table>

Table 6.13: Atom positions for CoAPO-34 containing the TMABO template.

Co(1) and Al(1) have occupancies of 0.1 and 0.9 respectively.
Table 6.14: Anisotropic displacement factors (Å²) for CoAPO-34 (TMABO template). The anisotropic displacement factor is defined in Table 7.

<table>
<thead>
<tr>
<th>Atom</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
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<td>Al(1)</td>
<td>0.0056(5)</td>
<td>0.0097(5)</td>
<td>0.0092(6)</td>
<td>-0.0025(3)</td>
<td>0.0000(3)</td>
<td>0.0046(4)</td>
</tr>
<tr>
<td>P(1)</td>
<td>0.0110(4)</td>
<td>0.0137(4)</td>
<td>0.0146(6)</td>
<td>-0.0024(3)</td>
<td>-0.0027(3)</td>
<td>0.0072(3)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.0304(16)</td>
<td>0.0333(16)</td>
<td>0.0189(17)</td>
<td>-0.0011(12)</td>
<td>-0.0003(12)</td>
<td>0.0168(14)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.0271(15)</td>
<td>0.0166(13)</td>
<td>0.040(2)</td>
<td>0.0035(12)</td>
<td>0.0048(12)</td>
<td>0.0117(12)</td>
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<tr>
<td>O(3)</td>
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<td>0.0249(17)</td>
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<td>-0.0112(11)</td>
<td>0.0088(12)</td>
</tr>
<tr>
<td>O(4)</td>
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<td>0.0348(17)</td>
<td>0.0294(18)</td>
<td>-0.0059(13)</td>
<td>-0.0023(11)</td>
<td>0.0182(12)</td>
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</table>

Table 6.15: Selected bond distances and angles for the CoAPO-34 framework containing TMABO.
6.3.5 Combined XAS/XRD

In this work, the stability of the framework and the change in the Co-O bond distance was investigated on removal of the four templates from the CoAPO-34 structure. The average Co-O distance gives us a measure of the extent of oxidation of Co(II) to Co(III) in the framework and thus we can predict the activity of the material in oxidation catalysis. CoAl₂O₄ was used as a model compound to investigate the contributions to the Debye-Waller factor for CoAPO-34. CoAl₂O₄ is a normal spinel containing Co(II) mainly in a tetrahedral site, similar to the environment of Co(II) in cobalt-substituted aluminophosphates. As mentioned in Chapter 3, the Debye-Waller factor is made up of two components, \( \sigma_s \) and \( \sigma_v \), which represent the contribution due to static disorder and thermal vibrations respectively. As the contribution due to thermal effects should be the same for CoAl₂O₄ and CoAPO-34, we can study differences in the static disorder between the systems.

6.3.5.1 Experimental

The data were collected at Station 9.3, Daresbury SRS. For each sample, approximately 20-25mg material was pressed into a 13mm self-supporting wafer, which was mounted in the in-situ cell described in Chapter 3. CoAl₂O₄ was heated in a flow of air from room temperature to 300°C at a heating rate of 5°C/min; then 2°C/min to 600°C; CoAPO-34 was heated at 5°C/min to 550°C. The maximum temperature in each case was sustained for 30 minutes before allowing the sample to cool to room temperature. The x-ray diffraction data were collected for 180s and the Co K-edge transmission x-ray absorption spectra were collected for 380s, yielding a
total cycle time of 10 minutes including 40s of dead time. The XAS data were processed and analysed using the programs EXCALIB, EXBROOK and EXCURV92 available at Daresbury laboratory. Only the first shell was analysed for each sample, as the primary aim of this study is to understand the immediate environment around the cobalt ions.

6.3.5.2 **CoAl₂O₄**

CoAl₂O₄ was chosen as a model compound because a large proportion of Co(II) in the material (86%) is in a similar tetrahedral environment to cobalt in aluminophosphates. It is a cobalt-containing normal spinel with Co(II) and Al(III) mainly occupying the tetrahedral and octahedral sites respectively. In this study it will enable us to investigate the contribution of the thermal and static disorder components to the Debye-Waller factor for CoAPO-34 synthesised using different template molecules. The x-ray diffraction patterns and x-ray absorption plots for CoAl₂O₄ as a function of temperature are shown in Figure 6.10. It is evident that the material is completely stable throughout the heating process and there is no shift in the edge position of the XAS spectra which would indicate a change in oxidation state. This is confirmed from a plot of the structural parameters during the heating process (Figure 6.11). The coordination number and the average Co-O bond length remain at 4 and 1.94 respectively throughout, indicating the environment about the cobalt atom does not change at all during the heating process. The Debye-Waller factor, A, increases linearly throughout; this must be arising due to thermal treatment and not to changes in static disorder as no structural or chemical changes occur.
Figure 6.10: XRD patterns (top) and QuEXAFS spectra (bottom) of CoAl₂O₄ plotted as a function of temperature. The heating rate was 5°C/min to 300°C, then 2°C to 600°C. The temperature was kept at 600°C for 30 minutes.
Figure 6.11: The coordination number, $N$, the average Co-O distance, $R$, and the Debye-Waller factor, $A$, for CoAl$_2$O$_4$, derived from analysis of the first shell of the Co K-edge EXAFS data plotted as a function of temperature. The temperature was kept at 600°C for 30 minutes.
6.3.5.3 CoAPO-34

TEAOH

The XRD and QuEXAFS plots for CoAPO-34 synthesised with TEAOH are shown in Figure 6.12. The material appears to be stable throughout the calcination; the changes in intensity are probably due to loss of the template or water. There does seem to be a shift in the XAS edge position indicating there may well be a change in oxidation state. The structural parameters obtained from analysis of the EXAFS data are shown in Figure 6.13 as a function of temperature. The change in the average Co-O bond length from 1.94 to 1.82Å confirms that there is a change in the oxidation state, which is accompanied by a colour change of the sample from blue to green. The results are similar to TMABO-synthesised CoAPO-34 (Chapter 4) and indicate that almost complete oxidation from Co(II) to Co(III) has occurred. There is a significant reduction of the coordination number from 4 to 3.3 as the calcination progresses; this may be due to a distortion in the tetrahedral environment of the cobalt\textsuperscript{25,26}. The Debye-Waller factor behaves in a similar manner to that for the TMABO-synthesised sample, as will be discussed in more detail later in this Chapter.
Figure 6.12: XRD plots (top) and QuEXAFS spectra (bottom) of CoAPO-34 (synthesised with TEAOH) as a function of temperature. The heating rate was 5°C/min to 550°C; this temperature was sustained for 30 minutes.
Figure 6.13: Change in the coordination number (N), the average Co-O bond length (R), and the Debye Waller factor (A) for CoAPO-34 synthesised with TEAOH as a function of temperature
Figure 6.14 shows a plot of the XANES before and after the TEAOH template is removed from CoAPO-34. There is a definite shift in the edge position, of about 2.5 eV which confirms that a change in oxidation state has occurred.

Figure 6.14: XAS plot of CoAPO-34 with TEAOH before (100°C) and after (550°C) removal of the template molecule.

TEA

The XRD and XAS plots for CoAPO-34 synthesised with TEA are shown in Figure 6.15 as a function of temperature. The changes in the structural parameters N, R and A during the calcination are shown in Figure 6.16.
Figure 6.15: XRD plot (top) and XAS spectra (bottom) as a function of temperature for CoAPO-34 synthesised with TEA. The heating rate was 5°C/min to 550°C; this temperature was sustained for 30 minutes.
Figure 6.16: Change in the coordination number (N), the average Co-O bond length (R), and the Debye Waller factor (A) for CoAPO-34 synthesised using TEA
It is evident from the plot of the average Co-O bond distance, $R$, as a function of temperature in Figure 6.16 that there is some oxidation of cobalt in the framework as the average Co-O bond distance is reduced from 1.93 to 1.86. This distance is higher that that found for the TMABO and TEAOH-synthesised samples suggesting that less Co(II) is oxidised to Co(III). We can calculate the approximate amount of Co(III) in the framework by using the Vegard relationship described in Chapter 4. If we assume that the bond distance of 1.83Å in CoAPO-34 synthesised with TMABO and TEAOH corresponds to 100% oxidation, then the amount of Co(III) in the TEA sample is approximately 73%.

The coordination number remains close to 4 throughout the calcination. However, towards the end it decreases in a similar manner to the other templates. The Debye-Waller factor increases throughout; there is no decrease at the end of the calcination as seen for TMABO and TEAOH-synthesised CoAPO-34.

Figure 6.17 shows the shift in the edge position confirming that there is some oxidation of the absorbing atom occurring. Two temperatures are shown: 125°C where the template is intact and 550°C, where the calcination is complete. The edge shift for TEA is approximately 1eV, which is considerably less than for TMABO or TEAOH.
Figure 6.17: Plot of the XAS spectra for CoAPO-34 synthesised with TEA before (125°C) and after (550°C) the calcination

Morpholine

The XRD plots and XAS spectra for CoAPO-34 synthesised with morpholine as the template are shown in Figure 6.18. The structural parameters R, N and A as a function of temperature are shown in Figure 6.19. Although the structure has not collapsed, it seems to have lost a lot of its crystallinity during the calcination process, compared to the materials synthesised with other templates. From the elemental analysis it was shown that there was twice as much cobalt in CoAPO-34 synthesised with morpholine compared to the others, which is very likely to destabilise the structure.
Figure 6.18: XRD plots (top) and XAS spectra (bottom) for the calcination of CoAPO-34 synthesised with morpholine as the template. The heating rate was 5°C/min to 550°C; this temperature was sustained for 30 minutes.
Figure 6.19: Change in the coordination number (N), the average Co-O bond length (R), and the Debye Waller factor (A) for CoAPO-34 synthesised with Morpholine.
There is very little change in the coordination number, N, or the average Co-O distance, R, throughout the calcination, which suggests that there is no change in the cobalt oxidation state when the template is removed. This is confirmed by Figure 6.20, which shows a plot of the XANES at 100°C (with the template) and 550°C (without template). There is no shift in the edge position as was seen for the other templates.

*Figure 6.20: Plot of XANES for CoAPO-34 with morpholine, before (100°C) and after (550°C) removal of the template.*
6.3.6 Debye-Waller Factors

6.3.6.1 CoAl₂O₄

As mentioned previously, as there are no structural or chemical changes occurring during the heating of CoAl₂O₄ in air, we can assume the Debye Waller factor for this material is composed only of thermal contributions. We can therefore define the following quantity:

\[ 2\Delta \sigma^2 = A_t - A_{rt} \]

\( 2\Delta \sigma^2 \) is the difference between the Debye-Waller factor at any temperature \( A_t \) and room temperature, \( A_{rt} \), and for CoAl₂O₄, it will be equal to the changes in the thermal contribution to the Debye-Waller factor. \( 2\Delta \sigma^2 \) for CoAl₂O₄ as a function of temperature is plotted in Figure 6.21; a best-fit line has been calculated and drawn through the points.

The contribution to the Debye Waller factor due to thermal effects is likely to be the same for CoAPO-34. Therefore, if we overlay the best fit line for CoAl₂O₄ on plots of \( 2\Delta \sigma^2 \) as a function of temperature for the CoAPO materials, changes in the static disorder during the calcination process can be studied by the deviations from this line.
Figure 6.21: A plot of the thermal disorder contribution to the Debye Waller factor for CoAl$_2$O$_4$ as a function of temperature; the line represents a best fit through the data points.

6.3.6.2 CoAPO-34

Figures 6.22 to 6.25 show the plots of 2\(\Delta\sigma^2\) as a function of temperature for CoAPO-34 synthesised from the four different templates. In each case the best-fit line calculated for CoAl$_2$O$_4$ is shown, which represents the thermal contribution to the Debye-Waller factor. In all of the figures, the data points fit well with the CoAl$_2$O$_4$ line until 300 to 350°C, indicating that the only contribution to the Debye Waller factor up until this point is the thermal vibration component. This finding is confirmed in the plots of the average Co-O bond distance and Co coordination number shown in Section 6.3.5 and 5.3.7. There is very little change below 300°C for any of the materials studied, which means there is unlikely to be any structural or chemical changes occurring that would contribute to changes in the static disorder. Above 300°C there are differences in the behaviour of the systems studied.
Figure 6.22: Change in the Debye Waller factor for CoAPO-34 synthesised with TEAOH; the solid line represents the thermal contribution to the Debye Waller factor as calculated from CoAl$_2$O$_4$.

Figure 6.23: Change in Debye Waller factor for CoAPO-34 synthesised with morpholine.
Figure 6.24: Change in the Debye Waller factor for CoAPO-34 synthesised with TMABO. The solid line represents the thermal component of the Debye Waller factor as calculated from CoAl₂O₄.

Figure 6.25: Change in the Debye Waller factor for CoAPO-34 synthesised with TEA.
**CoAPO-34 synthesised with TMABO and TEAOH**

Firstly, CoAPO-34 synthesised with TMABO and TEAOH will be considered. Both behave in a similar manner throughout the calcination process. There is a linear increase in $2\Delta\sigma^2$ as the temperature rises to 300°C, which is most likely due to thermal effects only. After 300°C a steeper increase occurs until 500°C, where the $2\Delta\sigma^2$ value drops to well below the line representing the thermal contribution.

Above 300°C, the template molecule collapses and there appears to be a proton transfer from the template to the aluminophosphate to balance the charge due to the incorporation of heteroatoms, thus giving rise to Brønsted acid sites. These sites are highly distorted\textsuperscript{25}; the Co-O bond to the hydroxyl group is much longer than the other Co-O bonds. This distortion leads to an increase in the static disorder and explains why we see an increase in the Debye-Waller factor above 300°C. In an x-ray absorption and infra-red spectroscopy study by Sankar and Thomas\textsuperscript{1} it was reported that in the calcination of CoAPO-18, Brønsted acid sites are formed before the oxidation of Co(II) to Co(III). The bridging hydroxyl groups characteristic of Brønsted acid sites can be seen in the infra-red spectra between 350 and 500°C. At 550°C these hydroxyl bands have disappeared and x-ray absorption spectroscopy showed that all of the Co(II) had been oxidised to Co(III).

In this study, the decrease in the Debye-Waller factor above 500°C is due to a decrease in the static disorder of the system when Co(II) is oxidised to Co(III). As mentioned previously, above 500°C, we see a decrease in the average Co-O bond length to 1.83Å for both materials, which indicates that complete oxidation to Co(III)
has occurred. This is accompanied by a shift in the EXAFS edge position by several eV. The decrease in the static disorder seen in these systems is therefore due to the loss of the Brønsted acid sites when Co(II) is oxidised; with the subsequent formation of much shorter, stronger Co(III)-O bonds.

**CoAPO-34 synthesised using TEA and morpholine**

CoAPO-34 synthesised using TEA and morpholine behave in a similar manner, which is quite different from that for the samples synthesised using the templates discussed in the previous section. From room temperature to 300°C, the increase in $2\Delta\sigma^2$ is very close to the line representing the thermal contribution. Above 300°C we start to see a sharp increase in the value of $2\Delta\sigma^2$ to almost 0.02 in both cases, indicating that we are now seeing an increase in the overall static disorder.

In CoAPO-34 synthesised with both of these templates there is not complete oxidation of Co(II) to Co(III) in either of them, unlike CoAPO-34 synthesised using TMABO and TEAOH. There is however, a big difference in the amount of oxidisable cobalt between CoAPO-34 synthesised with morpholine and TEA; for morpholine hardly any Co(II) is oxidised to Co(III) upon calcination, whereas for TEA almost 75% Co(III) is present in the calcined material. Despite this difference, both materials show very similar plots of $2\Delta\sigma^2$ as a function of temperature. It is possible that the increase in $2\Delta\sigma^2$ between 300 and 500°C is due to the formation of Brønsted acid sites. However, without accompanying infra-red studies we can not be certain.
Above 500°C, a further increase in static disorder can be attributed to several possibilities. Firstly, there may be a local structural collapse occurring; for example, Co may be coming out of the aluminophosphate framework, which is likely in the case of morpholine due to the high concentration of cobalt in the framework. However, there is no indication that this is happening from the XAS results.

Secondly, the increase in static disorder may be due to the presence of both short Co(III)-O and long Co(II)-O bonds, as was reported in a study by Barrett et al\textsuperscript{25}. Further studies will be required to pinpoint exactly what is happening here.
6.4 Conclusions

In this chapter we have shown that there are significant differences arising for the CoAPO-34 structure synthesised using different template molecules. Four different templates have been studied: triethylamine (TEA), morpholine, tetraethylammonium hydroxide (TEAOH) and 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO). In each case the pH's for the starting gels were all in the range 9-10. The products had completely different crystal sizes, the larger crystals were found in morpholine and TEA-synthesised CoAPO-34 whereas TEAOH and TMABO produced a powdery sample without visible crystals. The amount of water in the TEA and morpholine synthesis gel was double that for TEAOH and TMABO which may explain differences in crystal size. Elemental analysis results show that there is twice as much cobalt in the framework for the morpholine-synthesised CoAPO-34 as there is for those synthesised with the other three templates.

Micro-single crystal diffraction techniques were used to determine the number and position of the templates inside each structure. TEAOH-synthesised CoAPO-34 could not be studied as the crystals were too small (well below 1μm). For the TMABO template, we used the CoAPSO which was described in Chapter 5; crystals of approximate size 10 x 10 x 10μm were obtained for this material. Results for morpholine show there are two template molecules per cage, which agrees with other single crystal and thermogravimetric studies. For TMABO and TEA-synthesised CoAPO-34 only one template was present in each cage; the template sits in the middle of the cage in each case. The result for the TEA-synthesised material does
not, however, agree with other thermogravimetric and computational studies\textsuperscript{13,19}: both report that there should be two molecules per cage. We were unable to repeat the result as the majority of the crystals were twinned. Literature results for CoAPO-34 synthesised with TEAOH show that there is also only one template present per chabazite cage\textsuperscript{2,4}.

In a combined XAS/XRD study, differences between the samples synthesised with the various templates were seen. All the structures were stable during the calcination process, which is surprising for morpholine-synthesised CoAPO-34 as it has a much higher cobalt concentration than the others. In chapter 4 we showed that DAF-5 which has a similar cobalt concentration to morpholine-synthesised CoAPO-34 was unstable, as is CoAPO-44\textsuperscript{25}. There was, however, no indication of redox properties for morpholine; very little change in the average Co-O bond distance was observed during the calcination process. The other materials, all which contain one template per cage, show much better cobalt oxidation. For the TEA-synthesised material there is approximately 75\% Co(III) in the calcined material; TEAOH behaved identically to TMABO-synthesised CoAPO-34, discussed in Chapter 5, with all the Co(II) being oxidised to Co(III).

By also studying CoAl\textsubscript{2}O\textsubscript{4} under the same conditions, we were able to investigate the changes in the static disorder component of the Debye Waller factor for the CoAPO's. Again, TEAOH and TMABO-synthesised CoAPO-34 behaved in a similar manner, which was different from the other templates. In these systems, there is an increase in the static disorder between 300 and 500\^\circ C which can be attributed
to the formation of Brønsted acid sites. Above 500°C there is a significant decrease in the static contribution, corresponding to the complete conversion of Co(II)-O bonds (~1.94Å) to short Co(III)-O bonds (1.82Å). This process is shown in Figure 6.26.

Figure 6.26: Schematic showing the sequence of events during the calcination process of TEAOH or TMABO-synthesised CoAPO-34. Brønsted acid sites form between 300 and 500°C; this is followed by complete oxidation of Co(II) to Co(III).

In morpholine and TEA-synthesised CoAPO-34, the static disorder of the systems increases throughout the calcination process. There is no decrease above 500°C as for the other templates, which may be due to a combination of Co(II) and Co(III) in
the structure, or may indicate that cobalt is coming out of the framework. Further studies are required to determine exactly what is happening in these materials.

In conclusion, there appears to be some correlation between the number of templates in the cage and the amount of oxidisable cobalt. As mentioned in the previous chapter, TMABO-synthesised CoAPO-34 showed excellent activity for the selective oxidation of n-hexane, with the production of adipic acid. We predict that TEAOH-synthesised CoAPO-34 will produce similar results to that synthesised with TMABO, due to the similarities between the two materials. The morpholine and TEA-synthesised materials will probably not show the same activity, as there is incomplete oxidation.
6.5 References


22. G. M. Sheldrick, University of Gottingen (1997)


24. N. Binsted, J. W. Campbell, S. J. Gurman, P. C. Stephenson, CCLRC Daresbury Laboratory, *EXCURV92 Program*


Chapter 7:

Summary
7.1 Summary

The aim of this work was to gain an insight into the synthesis process of heteroatom-substituted aluminophosphates, in particular, designing new organic template molecules to produce specific structures and studying how differences in the synthesis process can affect the formation of active sites. We studied the effect of various templates in the synthesis of aluminophosphates with the chabazite structure. From the results it is clear that different templates result in different properties for the chabazite framework. There is a strong association between the number of template molecules inside the chabazite cage and the concentration of heteroatoms that can be successfully incorporated into the aluminophosphate framework, which then defines the stability of the structure in the calcination process and the formation of active sites.

Firstly, the DAF-5 study in Chapter 4 highlights the valuable use of the computer methodology ZEBEDDE in designing templates for a specific framework; in doing so we have produced a template that is observed to form a chabazite-type material without the competitive formation of an AIPO-5 phase which is often seen in these syntheses. Also, we were able to synthesise a pure phase of the material at different pH's, which is not possible with many other templates. Another important aspect of this study is the use of micro-crystalline diffraction, which allowed the location of the template molecules inside the structure to be elucidated which is consistent with the computational modelling studies.
If CoAPO-34 is synthesised using the templates 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (TMABO) as described in Chapter 5 or either triethylamine (TEA) or tetraethylammonium hydroxide (TEAOH) as in Chapter 6, only one template molecule can be seen per chabazite cage. All three materials have a 10% substitution of aluminium for cobalt, and are stable once the template is removed from the framework during the calcination process. X-ray absorption spectroscopy shows that there is oxidation of Co(II) to Co(III) occurring during the calcination. In particular, TMABO and TEAOH-synthesised CoAPO-34 both show almost 100% conversion to Co(III).

If either morpholine (Chapter 6) or 4-piperidinopiperidine (Chapter 4) are used as the structure-directing agents in the synthesis of cobalt-substituted aluminophosphates, the materials formed have much higher concentrations of cobalt substituted in the framework and thus have a reduced stability when the template molecule is removed. Single-crystal X-ray diffraction shows that there are two morpholine molecules per cage; there is only one 4-piperidinopiperidine molecule per cage, which can however, be thought as being two piperidine rings.

Preliminary catalytic results for TMABO-synthesised CoAPO-34 were very promising, in particular in the oxidation of linear alkanes. Based on the similarities between the structures synthesised with TMABO and TEAOH, we should see comparable catalytic activity for TEAOH-synthesised CoAPO-34. Further catalytic work is necessary to establish the relationship between the stability of the structure, the number of redox centres and the catalytic activity. All the structures can also be synthesised with silicon.
substituted in the framework. In Chapter 5 we showed that SAPO-34 synthesised using TMABO contains Brønsted acid sites, which are essential for acid-catalysed reactions.

Only five structure-directing agents and a few chemical compositions have been reported in this study. Although the present study begins to unravel some of the complexities arising in these syntheses, to gain a more complete picture of the effect of templates on the aluminophosphate framework, more detailed studies are required. In particular, it would be of particular interest to investigate the extent to which polar heteroatoms direct the transition metal substitutents to specific sites in the framework.