Structural Studies of the Crystallisation of Microporous Materials

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Abstract

A range of powerful synchrotron radiation characterisation techniques have been used to study fundamental aspects of the formation of microporous solids, specifically aluminosilicates, heteroatom substituted aluminophosphates and titanosilicates. This work has been performed with the aim of investigating in situ the structural changes occurring during crystallisation and post synthetic treatment. In situ EDXRD was used to follow the crystallisation of these materials under a wide range of synthesis conditions using a hydrothermal cell and a solid-state detector array. A quantitative analysis of the crystallisation kinetics was performed for the large pore aluminosilicate, zeolite A, using a simple mathematical model to calculate the activation energy of formation. The results obtained were found to closely agree with both the experimental results and theoretical models of others. A qualitative study of the effect of altering the synthesis conditions was also investigated for this material. Similar kinetic studies were then performed for a range of microporous aluminophosphates and their cobalt substituted derivatives in order to follow the effects of varying synthesis conditions such as the synthesis temperature, organic template type, and cobalt concentration. Distinct trends were noted in the formation times, stability and nature of the resulting crystalline phases as conditions were varied. The relationship between the cobalt and organic template molecules during crystallisation was considered in some detail with reference to other experimental data and theoretical models. The aluminophosphate studies were subsequently extended to a range of other heteroatom substituted aluminophosphates, using in situ EDXRD, complimented by EXAFS, which allowed investigation of the local environments around the heteroatoms within the microporous structure. EDXRD and EXAFS studies have been performed on the microporous titanosilicate, ETS-10, while the thermal stability of this material has also been investigated in situ using synchrotron X-ray diffraction in conjunction with a high temperature environmental cell.
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Chapter 1

Introduction, Background and Theory

1.1) Project Overview

The aim of this project has been to use a range of powerful X-ray techniques, available using a synchrotron radiation source, in order to study in detail the structural changes that occur during the synthesis of a range of microporous aluminosilicate, aluminophosphate and titanosilicate materials. The primary technique used during this work was Energy Dispersive X-ray Diffraction (EDXRD) carried out on station 16.4 at the Daresbury synchrotron radiation source, which, when used in a conjunction with a specially designed hydrothermal cell (Evans et al. (1995))\(^1\) allowed us to observe in situ the crystallisation of these materials with a high degree of time resolution, typically 1 minute per scan. In addition, the use of a recently developed 3-element detector array, developed by Barnes et al.\(^3\) in conjunction with the Daresbury SRS, greatly increased the d-spacing range over which these in situ studies could be performed. In situ EDXRD was found to have considerable advantages over conventional synthetic studies where samples need to be removed and cooled for analysis, a procedure which can result in changes to the product and the destruction of highly unstable intermediate phases\(^5\) previously reported to form in situ\(^6\).

Using this experimental configuration, high quality data has been collected for use in a quantitative model for zeolite A crystallisation kinetics, while studies were also performed on the effect of changing synthesis parameters for this system. An investigation of competitive phase formation in cobalt substituted aluminophosphates
was then performed, during which the effects of changing the nature of the organic template and the level of cobalt substitution were considered.

This work was later extended to include a wide range of metal substituted aluminophosphates (MeAPOs), when the incorporation of small quantities of different metals was observed to have profound effects on both the crystallisation kinetics and the nature of the resulting crystalline phases. A finding of note during this series of experiments was the repeated observation of a possible transitory intermediate phase prior to the formation of a microporous zinc substituted aluminophosphate.

Finally, EDXRD was used to study the crystallisation of the recently discovered microporous titanosilicate, ETS-10 along with the effects of altering the gel composition of this material. Changing the nature of the cations associated with the hydroxide and fluoride source materials was found once again to have a major effect on the kinetics of crystallisation and the nature of the products. The *in situ* technique also allowed the decomposition of the titanium dioxide starting materials to be followed in relation to the formation of the titanosilicate product.

While the long range ordering of these crystalline systems was observed using EDXRD, backed up by laboratory powder X-ray diffraction, the short range ordering around selected elements could be studied using Extended X-ray Absorption Fine Structure (EXAFS). This versatile technique was used in the first instance to study the local structure around many of the metals incorporated in the aluminophosphate precursor gels. This allowed confirmation of the successful framework incorporation of these metals in several cases, while providing strong evidence that several other metals had only been incorporated within the structure as extra-framework moieties. EXAFS was also used to study the local structure around the framework titanium atoms in ETS-10 with reference to a published model by Sankar et al.⁷.
The value of a combined approach was also observed, for example, during the MeAPO syntheses, when a correlation could be observed between the crystallisation kinetics of MnAPO-5 formation with increasing levels of manganese substitution observed with EDXRD and the changing Mn-O bond length using EXAFS. These results indicated that, above a critical substitution level, manganese was no longer incorporated into the framework and this excess extraframework manganese additionally inhibited crystal growth of the microporous product.

A series of in situ studies of the thermal stability of ETS-10 were also performed on station 9.3 at the Daresbury SRS using a high temperature environmental cell. During these experiments, the ETS-10 structure and its sodium ion-exchanged derivative were observed to decompose to a structure closely resembling the natural mineral, Narsarsukite. This structure had only previously been reported during the decomposition of the much more thermally unstable titanosilicate, ETS-4.
1.2) An Overview of the Structure and Properties of Zeolites and Related Microporous Solids

Since the initial discovery and description of the zeolite, Stilbite, by Cronstedt in 1756, these microporous, crystalline aluminosilicates have become important industrial materials that find a wide variety of applications as catalysts, in addition to being used as ion exchangers, desiccants, and gas separation devices. New zeolite structures are continually being synthesised, while many more structures have been produced using similar framework structures known as zeotypes including aluminophosphates and titanosilicates. These related materials further widen the range of properties and applications available to those known for microporous materials.

Zeolites occur both as natural minerals and artificially synthesised forms. SiO$_4$ and AlO$_4$ tetrahedra (collectively known as TO$_4$) are linked via oxygen bridges to form regular, three-dimensional structures. The resulting frameworks are very open structures containing regular arrays of cavities and channels of a size allowing atoms and small molecules to travel through them. This open framework and the properties associated with it give the zeolites their alternative name of molecular sieves.$^{10-12}$

The aluminium in the structure causes the framework to be charged, which is balanced by the presence of cations such as sodium or potassium within specific sites throughout the structure. Such sites can also host water molecules, creating pore complexes with the cations, which can affect the overall zeolite structure properties. Another common component in the pores or channels of a synthetic zeolite is an organic template molecule such as a tetra-alkyl ammonium ion or a crown-ether, which acts to direct structure formation during synthesis. Such template molecules can be subsequently removed by calcining the zeolite under flowing oxygen at a
temperature high enough to decompose the organic without disrupting the zeolite framework. ¹⁰⁻¹³

The water contained within a zeolite can easily be driven off to create a dehydrated form and equally easily resorbed, with the consequence that zeolites make good desiccants. The cations are also free to trade sites, with different cations passing through the framework. These ion-exchange capabilities lead to further applications for zeolites such as the sodium form of Zeolite A, which can be used as a water softener in detergents, whereby calcium ions from hard water are taken into the structure, replacing the sodium ions within. The naturally occurring zeolites Mordenite and Clinoptilolite have found application in the nuclear industry where they can be used for the immobilisation of radioactive caesium and strontium isotopes from aqueous waste.¹⁰⁻¹² ¹⁴

The large internal surface areas found in zeolites, often twenty times larger than their external surfaces as in the case of Zeolites X and Y, give zeolites superior catalytic properties. Variable pore sizes between structures allow reactant, intermediate and product selectivity to occur by a process of ‘molecular sieving’. The cations also play an important part in the catalytic properties. Exchange of the cations with ammonium ions followed by calcination to convert these into a protonic form results in the production of high levels of acidity at specific points within the framework. These ‘active sites’ of high electrostatic field influence organic molecules, causing bond distortion and rupture, and thus catalysing the occurrence of molecular re-arrangements.¹⁰⁻¹²

The first commercially used zeolite catalyst was Zeolite X in 1962. This was later replaced by the more siliceous and thus more stable Zeolite Y. They were introduced after the hydrogen and rare earth forms of certain zeolites were found to
have catalytic cracking activities several orders of magnitude greater than conventional silica-alumina catalysts. In addition to having a high density of acid sites and exhibiting the high thermal stability required for catalysis (typically 823K in the case of the methanol to gasoline conversion), zeolites are also less susceptible to coking than conventional catalysts.\textsuperscript{10-12, 15-23}

Microporous structures containing framework substituted transition metals such as cobalt or titanium can be used in catalytic applications other than as traditional acid catalysts. Cobalt substituted aluminophosphates show promise as redox catalysts\textsuperscript{24-25}, while titanium substituted zeolite beta has proved to be an effective catalyst in a range of epoxidation reactions.\textsuperscript{26-34} With further advances in the synthesis of microporous materials such as the formation of materials capable of base catalysed reactions, including the titanosilicate ETS-10\textsuperscript{35-37} discussed in this thesis, whole new possibilities are opening up for microporous catalysts in the fine chemicals and pharmaceutical industries.

1.3) The Structure and Classification of Microporous Framework Structures

As previously stated, zeolites are composed of SiO\textsubscript{4} and AlO\textsubscript{4} tetrahedra (PO\textsubscript{4} and AlO\textsubscript{4} for AlPOs), linked together through the oxygen atoms. These tetrahedra can link in many different ways to form infinite crystalline lattices composed of repeating unit cells.

A simple method of zeolite classification is to define a system of secondary building units (SBUs) which only denote the Si, Al, P and O positions in space relative to each other. Any framework cations and water molecules are thus excluded.
For general use, this is considered a much less cumbersome method than a full description of the often complex unit cell. For added simplification, the oxygen atoms are often omitted from the models produced using SBUs and are simply inferred by the presence of a straight line between two T (i.e. Si or Al etc.) atoms, resembling a single bond in organic chemistry. A list of currently used SBUs is shown in figure 1.1 below,\textsuperscript{38} while a polyhedral representation of the industrially important large pore aluminosilicate, zeolite A is shown in figure 1.2 as an example of a typical framework structure, which is discussed in detail in chapter 2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{A range of secondary building units (SBUs) identifiable in zeolite frameworks. Figure adapted from an original diagram by Meier et al. (1968)\textsuperscript{38}.}
\end{figure}
Figure 1.2 – The view in the ab plane of the simulated structure of zeolite A (LTA) with silica tetrahedra represented in yellow, alumina tetrahedra represented in pink and oxygen atoms represented as red spheres. The eight ring channels clearly seen in this structure open out into the large sodalite cages.
1.4) Synthesis of Microporous Materials

1.4.1) An Historical Perspective

In 1862, Deville reported the first zeolite synthesis, that of Levynite, produced by heating potassium silicate with sodium aluminate in a sealed glass tube. Such early claims could only be backed by mineralogical evidence, due to the unavailability of X-Ray Diffraction as a characterisation technique. It was not until around 1940 that R.M. Barrer and co-workers produced reliable syntheses, characterised by modern physical and chemical techniques. Early attempts at zeolite synthesis were based on trying to match the conditions under which zeolite minerals are produced naturally in igneous and metamorphic geological environments. Such conditions involve greatly elevated temperatures and pressures.

In 1949, the synthesis of Zeolite A by Milton, Breck et al. at Union Carbide Laboratories\textsuperscript{39-41} became the first widely recognised and completely characterised example of a new zeolite structure unknown in nature. This discovery was significant both because of the industrial importance of zeolite A and also because of the mild conditions of the synthesis used. This synthesis had been carried out below 100°C and at atmospheric pressure from a high water content reaction mixture. Similar conditions have since been discovered to be responsible for the formation of large sedimentary deposits of zeolite minerals found naturally throughout the world.\textsuperscript{12,14}

Zeolite frameworks have a wide variety of possible structures. There are sixty possible topologies and several variations within each topology. Over one hundred and fifty zeolite structures have so far been synthesised, but computer predictions indicate that there are around six million conceivable structures still to be synthesised.\textsuperscript{10-12}
During the early eighties, researchers at Union Carbide succeeded in crystallising a range of stable non-silica molecular sieves consisting of aluminophosphate frameworks. While many of these were analogous to known zeolite structures, for example AlPO-37 and AlPO-20 have the faujasite and sodalite structures respectively, others such as AlPO-5 were found to exhibit novel structures. It is from this family of zeotype materials that extra-large-pore structures such as VPI-5 (ca. 12Å diameter) have since been synthesised.

Unlike traditional zeolites, AlPO\textsubscript{4-n} frameworks are intrinsically neutral, and therefore have no ion exchange capacity. On the other hand, due to the mildly acidic synthesis conditions of synthesis such materials are much better suited to framework substitution by metals than zeolites, since the highly alkali conditions of zeolite formation often cause any metals to precipitate out of the system into stable oxides and hydroxides. As well as these MeAPO structures, silica has been incorporated to form SAPOs and furthermore MeAPSOs, resulting in the synthesis of many useful, catalytically active materials. A range of MeAPOs have been investigated in this project and are described in detail in chapters 2 and 3. In addition to incorporating various metals into existing AlPO frameworks, completely new frameworks have been synthesised including the cobalt substituted aluminophosphate DAF-4 and the magnesium aluminophosphate STA-1.

Over the last decade, while there have been continued developments in the number of zeolite and AlPO structures, a whole range of new microporous framework structures have been developed, including those of the titanosilicates ETS-10 and ETS-4, first reported by Engelhard in 1990. Other novel microporous frameworks include the cobalt phosphate DAF-2, and the very large pore gallophosphate, Cloverite which has a pore diameter of ca. 13Å. Cloverite is thus comparable in size...
to the very large pore aluminophosphate JDF-20, which has a pore diameter of 14Å.
While the present levels of interest continue in these microporous structures it is likely
that this spread across the periodic table is set to continue.

1.4.2) Synthesis Components and Conditions

Zeolites are generally synthesised by crystallisation from a reaction hydro-gel. The gel comprises sources of silica and aluminium in an aqueous environment under high pH conditions, usually generated by a source of hydroxide ions, typically NaOH or KOH. A wide range of possible silica and aluminium sources are available, and the nature of the source can cause profound changes in reaction kinetics and even influence the type of zeolite structures produced. Silica sources include stabilised colloidal silica solutions e.g. Ludox HS-40 (Aldrich), and highly reactive fumed silicas such as Cab-O-Sil (Fluka). Reactive aluminium sources come in many forms, including aluminium hydroxides, alkali metal aluminates and even in combination with silica in precursors such as metakaolin, an X-ray amorphous, highly reactive product formed by dehydroxylation of the clay mineral kaolinite (Al₂O₃·2SiO₂·2H₂O).

In comparison, AlPOs are produced under conditions ranging from mildly acidic to mildly basic with the silica source being replaced by phosphoric acid. AlPO structures, like many traditional aluminosilicate zeolites, require the addition of a template molecule, typically an organic quaternary ammonium species, to act as a structure directing agent in the hydrothermal synthesis.\(^{12,15,44,46}\)
The novel titanosilicate structures such as ETS-10 and ETS-4 are, however synthesised under similar high pH conditions to zeolites, with the titanium being supplied initially in a soluble form such as TiCl₃⁴⁹. However, more recent syntheses have used insoluble TiO₂⁵⁴, often from a relatively cheap industrial source as described in *chapter 5*.

To produce the desired crystalline microporous phase is not a straightforward process. All of the synthesis components and conditions can contribute to its formation, with the relationships between these variables often being very complicated. Minor changes in any one variable may lead to the formation of an impure or even totally different, phase or mixture of phases. The effects of such variables on a typical aluminosilicate zeolite synthesis are considered below to illustrate some of the complications involved in producing microporous materials. A comparison with the formation mechanism of the aluminophosphate systems also dealt with in this project is then considered below.

**1.4.2.1) Gross Composition**

By altering the SiO₂ : Al₂O₃ ratio of the reaction mixture, the final framework composition of the product can be controlled. In a typical synthesis, all of the available aluminium is taken into the structure. A notable exception to this is zeolite A, where the Si/Al ratio is approximately 1:1. In most cases excess silica will be left in the supernatant liquid.

The concentration of hydroxide ions in the system is important in that the ions often accelerate the reaction of silicate and aluminate species and shorten the
induction period that precedes crystal formation from the reaction mixture. The hydroxide ions work in conjunction with the water, acting to transport the silicate and aluminate species to the crystalline zeolite phase from the amorphous phase. Therefore, nucleation time decreases as hydroxide concentration increases. The hydroxide content can also affect crystal growth and control phase purity. The reaction mixtures usually have an excess of hydroxide present.

In order to overcome the problems of substituting metals into zeolite frameworks, the use of fluoride ions in the place of hydroxide ions makes it possible to carry out such syntheses at lower pH values. In addition, introducing such ions to a standard gel mixture has been shown to have an effect on the morphology and uniformity of the product. The use of HF in the synthesis of ferrierite has been found to promote the formation of large, well formed crystals.55

Both organic and inorganic cations can occur within zeolite structures, where they act to balance the charge produced by the presence of aluminium in the framework. Cations are also believed to be a dominant factor in governing which structure is obtained. Structure is controlled by the cation acting as a template.

Indeed, according to Szostak56 ‘An ion or neutral species is considered to be a template or crystal-directing agent if, on its addition to the reaction mixture, crystallisation is induced of a specific zeolite structure that could not be formed in the absence of this agent.’

Natural zeolites were found to contain inorganic cations such as the alkali and alkali earth metals, which led to the discovery by Barrer and Denny in 1961 that the use of certain organic cations such as the tetrapropylammonium cation commonly used in the synthesis of ZSM-5, could result in the formation of previously unknown zeolite phases. Work continues apace in this area with alternative compounds such as
organometallic cations being investigated as template molecules. Computer modelling of such systems is now also being carried out in order to predict suitable templates for synthesising new structures.

The water content of the starting mixture is important as it is believed to act with the cations in the structure, becoming part of the template around which the zeolite forms, which can result in the creation of a much larger template complex. The water content also alters the transportation qualities of the gel.

1.4.2.2) Temperature

While it is now known that certain zeolites such as Na-P can form at room temperature, with a few exceptions, the majority of zeolites and related microporous materials tend to form at temperatures below 523K. The industrially mass produced zeolites A, X, and Y are normally prepared at around 373K, while zeolites of higher silica content are traditionally prepared at higher temperatures and at elevated pressures. Temperature influences several factors in zeolite synthesis. The higher the temperature, the shorter the induction period before crystallisation begins. For example at 623K mordenite crystallises in one hour, but takes two days at 473K and four weeks at 373K. The rate of crystallisation also increases with increasing temperature. Finally, temperature can influence which zeolite phase is obtained and, if several phases are possible, temperature can alter the sequence of formation. The effect of temperature on the synthesis of a range of microporous materials is described in more detail in chapters 2 and 3.
Synthesis time is important for two reasons: firstly, zeolite yield can be optimised by an induction period, during which the reaction mixture is held near ambient temperature before being raised to the crystallisation temperature. This is often known as 'ageing' the mixture. Secondly, in some cases, a single reaction mixture may be able to synthesise several different zeolite phases, depending on the time over which the reaction takes place. Zeolites are metastable species, often occurring in nature as diagenetic sequences with structurally open zeolites converting over geological time into denser, less open species. Zeolites A, X, and Y are metastable and will eventually turn into the gismondine-like zeolite Na-P, while zeolite beta has been observed to form gismondine and analcime. Similar transformations occur in aluminophosphate systems, with large pore AlPO-5 eventually forming a dense phase such as tridymite cristobalite or berlinite.

Such transitions obey Ostwald's law of successive transformations. This law implies that, upon mixing the reagents for a zeolite synthesis, the system is in a disordered state. This mixture has higher entropy than the ordered, crystallised zeolite structure. If the crystallised system exists in several different polymorphic forms, it will first develop the form with the highest entropy from the highly disordered synthesis mixture.

A major problem that can arise when producing zeolites is that the desired phase is metastable compared to an unwanted phase and transforms into this more stable phase if the reaction time is prolonged. An example of such an unwanted change is the conversion of faujasite to zeolite Na-P. This problem can be overcome by knowing how the energy and entropy change during the synthesis. These changes
ultimately determine the relative stabilities of each phase formed. Once such information is gained, the correct parameters can be chosen to produce the desired metastable zeolite phase. Such a phase can be isolated and stabilised simply by quenching the reaction and subsequently removing the product from the mother liquor.11-12

1.4.3) The Hydrothermal Crystallisation Mechanism for Zeolites

While the alumina source can be considered to consist basically of Al(OH)$_4$ species, the silicate solution is made up of a complex mixture of monomeric silica species along with more complex polymeric units and colloidal material. These species keep in balance within the solution by a series of polymerisation-depolymerisation equilibria as follows.

\[
\equiv T\text{-OH} + HO\text{-T} \rightleftharpoons T\text{-O}\text{-T} + H_2O \\
\equiv T\text{-O}^+ + HO\text{-T} \rightleftharpoons T\text{-O}\text{-T} + OH^-
\]

When the aluminate and silicate solutions are mixed, along with a suitable template where required, a gel precipitates whereby the complex system of silicate polymers is further cross-linked by the aluminate. This gel has some short range order but no long range order and obeys Loewenstein’s rule in that there are no Al\textsuperscript{-}-O-Al\textsuperscript{-} bridges present.

Once the gel has been formed and allowed to equilibrate by ageing, it is heated to the required reaction temperature so that a solution-mediated reaction
crystallisation process can occur\textsuperscript{11,62}. In this process the OH\textsuperscript{+} ions (and any F\textsuperscript{−} ions, if present) act to depolymerise the silica units into smaller monomeric and oligomeric units. These units then undergo a cation assisted ordering process whereby structure formation is influenced both by the presence of organic (template) and inorganic cations and by the interactions between these cations and water. While the precise mechanism of synthesis remains uncertain, it has been proposed, among other theories, that formation and breakdown of these structures is a continuous process until a few structures become large enough to achieve stability.\textsuperscript{11-12,62-67} Antonic et al.\textsuperscript{63} have proposed that the bulk of the nuclei are formed within the gel matrix during gel precipitation and/or ageing and are trapped until release during crystallisation, resulting in a rapid increase in the number of nuclei present to act as seeds for crystal growth. This idea is known as autocatalytic nucleation and is discussed in more detail in chapter 2. With large numbers of nuclei free in the liquid phase, growth can then proceed rapidly and can be seen as the steep gradient on a characteristically sigmoidal crystallinity versus time plot as described below.

1.4.4) Aluminophosphate Synthesis

As opposed to zeolites, aluminophosphate systems tend to form in a mildly basic to mildly acidic pH environment. They also appear to exhibit a simpler chemistry than zeolites, with the phosphoric acid and aluminium hydroxide reacting stoichiometrically in an aqueous medium to produce the aluminophosphate as follows:-

\[ \text{H}_3\text{PO}_4(\text{aq}) + \text{Al(OH)}_3(\text{s}) \rightarrow \text{AlPO}_4(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \]  

(1.1)
If the resulting gel is hydrothermally treated in the absence of a template, a dense phase aluminophosphate tends to form\textsuperscript{68}, which would appear to indicate a more straightforward chemistry for the formation of microporous aluminophosphates, whereby the template has a simple structure-directing role. However, it is likely that the template will interact with water molecules in the system and may also be affected by pH differences due to an excess of either acid or alkali in the pre-cursor gel. In some syntheses, such an excess is purposely introduced in order to produce the desired material.\textsuperscript{69} It must also be considered that the template itself can have an important role in determining gel pH as will be illustrated in chapter 3. The synthesis temperature may also have a role in determining the resulting phase. The aluminophosphate system becomes more complicated once we begin to substitute framework aluminium or phosphorous atoms with any one of a range of heteroatoms, leading to the formation of a charged framework. In many such cases, multiple crystalline phases can be observed to form with the same template, depending on the concentration of the substituted metal. Competitive formation of multiple phases in MeAPO systems are discussed in chapters 3 and 4.

1.4.5) The Kinetics of Zeolite Synthesis

A plot of the ratio of crystalline to non-crystalline material versus time for zeolite crystallisation produces a characteristic sigmoidal curve. This curve can be considered in its three component parts. The early part of the curve is flat and no crystal growth is observed using powder X-ray diffraction. After a certain period of time, depending on factors such as synthesis temperature, gel composition etc., crystal
growth starts and crystallinity rapidly increases to a maximum where the reagent source becomes depleted, resulting in a further levelling out of the plot.

This simple model does not explain the reasons for the sudden start of crystal growth, so other factors need to be considered. Using scanning electron microscope measurements of particle size distributions and linear growth rates Budd et al. observed a second profile which straddles the latter part of the period during which no crystallinity is observed and the first part of the crystal growth region. This second profile is the nucleation curve and represents the formation of microscopic nuclei around which crystal growth can commence. This curve reaches a maximum as significant crystal growth occurs and then drops, indicating an end to further nucleation. All further crystal growth then takes place around existing nuclei. A summary of this scheme is shown in figure 1.3 below.

Figure 1.3 – A schematic illustration of the nucleation and growth curves for a hydrothermal zeolite synthesis. The nucleation curve is measured in No. of nuclei versus time and the growth curve is measured in crystallinity versus time. Adapted from an original diagram by Budd et al. 

Budd et al.
The development of an accurate mathematical model of the kinetics involved in zeolite synthesis is very important in furthering our understanding of the processes occurring and thus our ability to produce efficient industrial syntheses and tailor syntheses for specific products. Several models have been proposed of varying complexity\textsuperscript{62-65, 70-72}, but while these usually fit the experimental data extremely well from a curve fitting point of view, the coefficients utilised are often found to have little or no fundamental chemical significance. This is well illustrated by the use of the Avrami equation to fit experimental data. The approximate form of this equation, describing the early stages of crystallisation only is shown below.\textsuperscript{64, 71}

\[ Z(t) = 1 - \exp(-kt^n) \]  
\(Z(t)\) = the fractional yield of crystalline material.  
\(k\) = a constant.  
\(t\) = time.  
\(n\) = term dependant on the mechanism of nucleation.

The full forms of this equation were developed by Melvin Avrami over fifty years ago principally to describe the solidification of metals after a period of nucleation. While this model provides a qualitative interpretation of zeolite crystallizations, it incorrectly predicts a slowing down and stopping of the crystallisation process due to depletion of the amount of material to be converted i.e. it caters for a phase transformation in a fixed volume. In hydrothermal zeolite crystallizations on the other hand, growth rates become limited by reduced transport rates as solute concentrations decrease. The growth of zeolite crystals occurs from solution with the dissolution of amorphous material replenishing this solution.\textsuperscript{64, 71}
Several other approaches to the problem of modelling zeolite growth have been considered in addition to modified Avrami type equations. These model types were classified by Thompson and Dyer\textsuperscript{73} as empirical, reaction engineering, and particulate population balance based models. They then concluded that the two most important aspects for the future advancement of zeolite synthesis modelling were precise definitions and physical understanding of all process parameters, along with the accurate identification of the kinetics of nucleation and growth.

Current models tend to suffer from one of two problems, first: complexity, with large numbers of parameters all requiring accurate experimental data and thus very prone to inaccuracies. Secondly, as in the case of the Avrami model mentioned above, simpler models tend only to be approximations that model a small part of the complete synthesis with the interpretation of physical parameters being rather unclear.\textsuperscript{64,71,73}

In chapter 2, the use of high quality experimental data gained from EDXRD of zeolite A is described. A subsequent attempt was made to fit the resulting data to a relatively simple quantitative model in order to calculate the activation energy of crystallisation for this material. This quantitative study was performed both to compare our data with similar results produced by others and to illustrate the potential of this technique to generate data for use in creating a superior quantitative model. The rapid data collection available using EDXRD allows large quantities of data to be collected at critical points during the synthesis, a difficult feat using traditional \textit{ex situ} techniques. \textit{In situ} NMR\textsuperscript{66}, light scattering\textsuperscript{67} and SAXS (small angle X-ray scattering)\textsuperscript{74} studies can also be utilised to follow the early stages of zeolite synthesis such as the induction period and nucleation. The latter technique has been successfully combined with wide angle X-ray scattering at the Daresbury SRS.
allowing both nucleation and crystallisation to be observed during zeolite synthesis. A combined approach using such techniques would form the basis of an extremely powerful means of studying the synthesis of microporous materials.

1.5) Synchrotron Radiation for Materials Characterisation

Synchrotron radiation is produced when a beam of electrons fired from a linear accelerator (LINAC) is accelerated to near relativistic speeds (i.e. around 99.999% c) in a booster ring and then injected into a storage ring, where the beam is held at constant energy by means of a constant field from powerful electromagnets. Centripetal acceleration provided by each of these bending magnets can no longer increase the velocity of the electrons so they must lose this energy in the form of electromagnetic radiation.

The beam emits white electromagnetic radiation, with a typical energy range from the infrared to the hard X-ray region, tangentially from the beam orbit into a very small angle called the photon-opening angle. The beam energy needs to be constantly replenished due to this electromagnetic emission, and radio frequency power for this is provided by a klystron. Even with this replenishment, the beam still decays over time due to occasional collisions with gas molecules still present, even in the high vacuum (10^{-9} Torr) environment of the storage ring. For this reason, the beam is shut down and re-injected typically once every 24 hours, depending on the machine.

The beam in the storage ring can be provided in one of two ways: first, and more normally, as a multi-bunch beam where, for example at Daresbury SRS, 160
bunches of electrons a few centimetres long travel through the storage ring with a separation of 2 nanoseconds. An alternative beam type, used for running some time resolved experiments, consists of a single bunch of electrons injected into the storage ring, resulting in a pulsed radiation source, for example at the Daresbury SRS a pulse occurs every 320 nanoseconds.

The distribution of the synchrotron radiation flux can be further altered by the use of magnetic insertion devices known as ‘wigglers’ and ‘undulators’ inserted into the straight sections between the bending magnets. A ‘wiggler’ magnet shifts radiation up to higher energies while an undulator creates a series of very sharp peaks in the spectrum, allowing enhancement at certain frequencies. Stations 16.4 and 9.3, used in this project are both on beamlines equipped with ‘wiggler’ devices.75-76

Synchrotron radiation has several advantages over conventional radiation sources as follows:

1) The very high intensity of the light allows high-speed data collection, measurements of extremely dilute samples and the measurement of in situ experiments taking place within high-pressure cells.

2) The radiation source is both white and tuneable, allowing techniques such as energy dispersive X-ray diffraction (EDXRD) to be used as well as improving element specific techniques such as X-ray Absorption Fine Structure (XAFS) and allowing the use of anomalous scattering effects in XRD experiments.

3) The beam is highly collimated, a fact which, when coupled with the high intensity allows extremely high-resolution measurements to be made. Furthermore the light is almost 100% plane polarised in the orbit plane.

4) The beam is strongly polarised in the plane of the synchrotron – a property which may be of major benefit in studies of magnetic systems.75-78
1.6) X-ray Diffraction

1.6.1) A General Overview of X-Ray Diffraction Techniques

As described above, the microporous materials studied in this project are crystalline solids and are thus very suitable for characterisation by X-ray diffraction. A great deal of information can be obtained from diffraction data, including the parameters required for a complete description of a crystal structure. These factors include the size of the unit cell, the spatial arrangement of the atoms inside the unit cell and the symmetry elements relating them to the final structure. In addition to this structural information, X-ray diffraction data can be used to measure both the purity and crystallinity of a particular phase and more generally as a useful means of routine phase identification.79-82

The work reported herein describes X-ray diffraction experiments carried out using a conventional laboratory powder diffractometer in addition to both energy dispersive and angular dispersive synchrotron radiation diffraction apparatus at the Daresbury SRS. During the course of these experiments, diffraction patterns were used as a ‘fingerprinting’ technique for identifying crystalline phases as they form and also as a means of following changes in the nature of crystalline solids during hydrothermal synthesis and post-synthetic thermal treatment. The structures of the major crystalline phases studied during this work were already known, removing the requirement for structure solution.

The following section therefore concentrates on the basic concepts of X-ray diffraction utilised during this project while avoiding an in depth review of the methodologies used during crystal structure solution. Furthermore, in keeping with
the theme of structural studies with synchrotron radiation, the advantages of such sources over conventional X-ray sources for diffraction experiments are described, with emphasis being placed on powder diffraction techniques such as those used in the course of this work. In addition to discussions of the techniques themselves, the following sections also describe the methods of equipment calibration and sample standardisation that were used when carrying out these experiments.

1.6.1.1) Basic X-ray Diffraction Theory

The scattering of X-rays is relatively weak compared to the diffraction of visible light. Therefore a regularly repeating lattice such as a crystal is required to produce an observable pattern. In reality, while this diffraction is caused by the electrons of the atom, for ease of description it is often considered to be caused by the lattice planes or the atoms themselves. X-rays are diffracted by the crystal lattice because they have a wavelength similar to the inter-atomic separation of ca. 1Å.

X-ray diffraction by crystals is most simply considered using the method produced by William L. Bragg, who, in 1913 first noticed the similarity of diffraction to normal reflection. He deduced a simple equation that treated diffraction as reflection from the lattice planes, with each lattice plane acting as a semi-transparent mirror. This reflection takes place so that all the reflected rays are in phase. From this model, a simple mathematical relationship now known as Bragg’s law was produced as follows:

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

(1.3)
Where \( n \) is an integer, \( \lambda \) is the wavelength of the X-radiation, \( d \) is the d-spacing, the perpendicular spacing between the crystal planes, and \( 2\theta \) is the detector angle.

If this law is obeyed, constructive interference occurs as the reflected beams are in phase, resulting in a strong reflection. At other angles of incidence, reflections will be weak or non-existent because the beams interfere destructively and probably completely cancel out.

In order to derive the Bragg equation, reflections from only two planes are normally considered. However, in crystals there are many thousands of planes, which results in a sharpening of the diffraction maxima, giving easily measurable peaks which occur at clearly defined \( 2\theta \) angles, and, upon analysis, can provide detailed information on the crystal structure.\(^{79-82}\)

### 1.6.1.2) Indexing an X-ray Diffraction Pattern

As stated above, the d-spacing of a set of planes in a crystal is defined as the perpendicular distance between any pair of adjacent planes in the set. For a cubic unit cell, the \((100)\) planes simply have a d-spacing of \( a \), the value of the cell edge, while the \((200)\) plane would have a d-spacing of \( a/2 \) etc. For orthogonal crystals, the d-spacing for any set of planes is given by the formula:

\[
1/d^2_{hkl} = h^2/a^2 + k^2/b^2 + l^2/c^2
\]  

(1.4)

Where \( a, b \) and \( c \) are the lengths of the cell edges and \( h, k \) and \( l \) are integers that together form a Miller index \((hkl)\), which describes a particular lattice plane. All parallel Miller indices for a specific structure are separated by the same d-spacing.\(^82\)
The equivalent formulae for monoclinic and triclinic systems are much more complicated because each of the angles that are not fixed at 90° become additional variables. A knowledge of these relationships and the unit cell parameters will allow the Bragg angle for each set of planes in a given crystal to be calculated for a given wavelength. Conversely, a given set of reflections, recorded at a known wavelength, can be indexed and used to calculate the cell parameters of the crystalline material.\textsuperscript{79-82}

In principle, each set of lattice planes can give rise to a diffracted beam. In practice, however, the intensity of the beam diffracted by a certain set of lattice planes may be zero. These are known as systematic absences and they arise for non-primitive (i.e. body centred, face centred etc.) lattices or if elements of space symmetry such as screw axes or glide planes are present. For each lattice type, there are additional rules determining whether a reflection is present; for example in the case of a body centred lattice, a reflection is present for a specific Miller plane (hkl) if \(h+k+l=2n\), where \(n\) is an integer. Therefore in such a body centred lattice, the (100) reflection will be absent. Such rules follow on from the rules of symmetry.\textsuperscript{79-82}

\textbf{1.6.2) X-ray Diffraction Techniques for the Study of Microporous Structures}

While single crystal X-ray diffraction is an ideal means of solving the structure of inorganic crystalline materials, high quality single crystals of a sufficiently large size have frequently been unavailable for many materials. This has proved to be a problem with many microporous solids, which tend to form as a powder composed of very small crystallites. The recent availability of a new
microcrystalline single crystal diffraction facility on station 9.8 of the Daresbury SRS now allows the structures of many such microporous materials to be investigated in greater detail than ever before as described in a recent paper by Muncaster et al. for microporous aluminophosphates.

However, there is a continuing role for powder X-ray diffraction whereby diffraction from a finely ground (1 - 50 μm crystallite diameter) and randomly orientated crystalline powder is analysed in either a rotating flat plate or capillary configuration. The following sections briefly describe the current situation with regard to powder X-ray diffraction with both conventional and synchrotron sources, highlighting the advantages and limitations of both radiation sources.

1.6.3) The Use of Powder Samples in X-ray Diffraction

As described above, the traditional applications of powder X-ray diffraction were in phase identification, which remains one of the primary uses for powder data collected in the laboratory. However, in the last three decades, powder diffraction has increasingly been used for the refinement of crystal structures. Peak overlap can be a major problem when dealing with powder data, a phenomenon which becomes increasingly prevalent at high angles and is especially problematic with low symmetry structures and large unit cells. Due to this problem, prior to about 1970, structural investigations with powder data were limited to the study of systems with small, high symmetry unit cells.

A major advance was to occur in the early seventies with the study of powder data by high resolution powder diffraction (HRPD) using a neutron source. The
reflections produced in such experiments were found to be almost Gaussian in shape, and if the line shape is accurately known, it becomes possible to de-convolute the overlapping Bragg reflections in the diffraction pattern. To achieve this end, the total profile of the pattern is fitted by employing a point-by-point comparison of the profiles of the experimental and calculated patterns. Refinement is then performed by minimisation of the R-factor at each point of the pattern. As a profile is being fitted to the whole peak, difficulties associated with the loss of individual reflection intensities can therefore be overcome.\textsuperscript{75-78}

The Rietveld refinement technique, however, made little headway with powder X-ray diffraction until the mid 1980’s mainly due to the complex line shapes produced by laboratory X-ray diffractometers. Such shapes are difficult to describe reliably using a simple analytical expression with few parameters. However, the technology of laboratory X-ray diffraction instruments had developed enormously during this period, allowing laboratory powder X-ray diffraction data to be used to solve structures of moderate complexity.\textsuperscript{76} An example of such a development is the use of a primary monochromator to isolate the copper K\alpha\textsubscript{1} X-ray frequency, resulting in the simplification of the reflection profiles compared to those from traditional instruments, especially at low angles. During this period, the dramatic increase in affordable computing power and the development of improved Rietveld refinement software have also had a major impact on the ability to refine structures from laboratory powder data.

Probably the single greatest advance in powder X-ray diffraction, however, came about with the use of synchrotron radiation as an X-ray source in diffraction experiments as described below.
1.6.4) High Resolution Powder Diffraction (HRPD) Using Synchrotron Radiation

With the advent of synchrotron radiation techniques during the 1980s, it became possible to solve complex structures using High Resolution Powder X-ray Diffraction (HRPD).\(^76\) Diffraction from a synchrotron source has the following advantages over laboratory powder diffraction methods:

1) Due to the high intensity of the synchrotron source, recorded peak intensities are much greater resulting in a much improved signal to noise ratio due to reduction of instrumental background.

2) The greater collimation of the synchrotron source results in a typical three to five-fold decrease in peak width from 0.15° to typically 0.04° at full width half maximum (FWHM)\(^76\). Even narrower reflections with FWHM of less than 0.02° can be obtained using third generation synchrotron sources such as the ESRF in Grenoble.\(^76\)

3) Peak shapes are much simpler than those of a laboratory source and can easily be simulated using Pseudo-Voigt functions, a convolution of the Lorentzian and Gaussian functions.\(^76\)

In addition, the tuneable nature of the synchrotron radiation allows for easy access to techniques such as anomalous dispersion. In this technique, the locations of specific elements in a structure can be found by studying the differences between diffraction patterns observed at energies both on- and off-edge for particular elements that have absorption edges within the energy range of the beamline.\(^76\)

These improvements greatly reduce the number of fitting parameters required in any least-squares analysis and also result in, typically, several hundred diffraction lines being available for de-convolution. This means that complex structures can now be successfully solved using a combination of direct methods and refinement.
procedures. Such data is of sufficiently high quality both for Rietveld refinement and \textit{ab initio} solution of completely new structures\textsuperscript{75-78}.

A typical experimental set-up for synchrotron HRPD is schematically shown in \textit{figure 1.4} below. The white radiation from the storage ring is monochromatised, (typically by a channel cut Si(111) monochromator) and the Debye-Scherrer pattern intercepted using a \(0/2\theta\) diffractometer. The long, multiple collimators are matched to the source/monochromator which strictly control the angle of the diffracted beam, allowing for large rotating flat plate samples to be employed with much improved signal\textsuperscript{75 78}.

\textbf{Figure 1.4} – A schematic illustration of a high-resolution powder diffractometer based on the Hart-Parrish design.\textsuperscript{75 78}
1.6.5) EDXRD – Theory, Calibration & Error Analysis

Synchrotron radiation also allows access to another highly useful X-ray diffraction technique allowing fast data collection for in situ experiments even under conditions of elevated temperature and pressure. Energy Dispersive X-ray Diffraction (EDXRD) is especially useful for the study of microporous materials as they are normally synthesised under hydrothermal conditions within a stainless steel autoclave. With EDXRD the whole diffraction pattern, within a limited d-spacing range, is collected simultaneously by fixing the scattering angle and measuring the diffracted intensities as a function of X-ray energy. Only radiation with the correct energy (and hence wavelength) to satisfy the Bragg condition will be reflected.

As: \[ \lambda = \frac{hc}{E} \] (1.5)

substituting into: \[ n\lambda = 2d \sin \theta \] (1.6)
gives: \[ d = \frac{hc}{(2E \sin \theta)} \] (1.7)

Where \( d \) is the d-spacing of the reflection, \( h \) and \( c \) are Planck's constant and the speed of light respectively; \( E \) is the photon energy and \( 2\theta \) is the angle of the fixed detector arm.

The white character of the synchrotron radiation makes it ideal for energy dispersive measurements, while the high intensity of the source allows the X-Rays to easily penetrate through a stainless steel autoclave and PTFE liner to the sample and out the other side without severe and detrimental loss of intensity. The energy of the beam is further boosted by the presence of a 6 Tesla 'wiggler' insertion device on beamline 16. These experiments are carried out in situ using a hydrothermal cell developed by O'Hare et al.\(^1\) at Oxford University and the Daresbury SRS for station 16.4 at the aforementioned facility. This cell was used in conjunction with, initially a
single element solid-state detector and later a new 3-element detector array developed jointly by Barnes et al. at Birkbeck college London and the Daresbury SRS\textsuperscript{34}. A schematic of the experimental set-up with the single element detector is shown in \textit{figure 1.5} overleaf, while the 3-element detector array is described in \textit{figure 1.6}.

In \textit{figure 1.5} we can see that the white beam is collimated directly from the storage ring and incident onto the sample contained within the hydrothermal cell. This cell is composed of a furnace unit designed to hold a modified stainless steel autoclave and a magnetic stirrer unit for experiments where constant agitation of the sample is required. Holes in the furnace walls have been positioned in order to allow passage of the white radiation beam directly through the reaction vessel and out to the detector. Passage of the beam has been further facilitated by machining an area at the bottom of the stainless steel autoclave liner in order to produce a band of thinner steel for the beam to pass through. The incoming beam is typically around 0.1mm in diameter, which is ideal for the measurement of miniature samples within restricted environmental cells.

The fixed detector angle is chosen in order to optimise data collection within an energy range containing strong reflections for the material under study. When using the single element detector array for the study of zeolite A, discussed in \textit{chapter 2}, a detector angle of 1.46°2θ was used, allowing observation of the first four reflections of this material.

Later experiments using the 3-element detector shown schematically in \textit{figure 1.6}, allowed the bottom detector to be set at a lower fixed angle, when necessary, for collection of data at the higher d-spacings typical of large pore microporous materials. Each detector in the array is separated by a fixed angle of \textit{ca.} 2.8°2θ resulting in the middle detector then being at an angle appropriate for observing additional reflections.
at lower d-spacings, including those of any dense phase materials. A typical d-spacing range covered by the 3-element detector is shown in figure 1.7 for the microporous cobalt substituted aluminophosphate structure, CoAlPO-5.

Figure 1.5 – A schematic representation of an experimental configuration used on station 16.4 for EDXRD investigations of microporous materials. This diagram shows the hydrothermal cell design and a single element solid-state detector.

Figure 1.6 – A schematic representation of the 3-element detector array used on station 16.4 for EDXRD investigations of microporous materials.
a) Top Detector
(6.88°2θ)

b) Middle Detector
(4.08°2θ)
Figure 1.7 – Typical d-spacing ranges available using the 3 element detector array for *in situ* observation of synthesis in microporous materials. The sample shown is a standard sample of the microporous cobalt substituted aluminophosphate structure, AlPO-5. The fixed angles for each detector are a) top 6.88°2θ, b) middle 4.08°2θ and c) bottom 1.29°2θ.
1.6.5.1) Calibration of Energy Scale and Detector Angle

The detector is calibrated using an americium radioactive dial source in order to calculate the start (a) and step (b) parameters for each detector as shown in figure 1.8 below for the bottom detector. The graph is calculated using the channel numbers of a set of fluorescence lines of known energy produced for several elements as shown in table 1.1, with the resulting parameters being 6.7757KeV (a) and 0.0320KeV/Channel No. (b).

\[ y = 0.03196X + 6.77573 \]

Figure 1.8 – A calibration plot for the bottom detector of the three element detector array, produced using the channel number positions of a set of fluorescence lines from an americium radioactive dial source as detailed in table 1.1. The resulting calibration parameters are start (a) = 6.7757KeV and step (b) = 0.0320KeV/Chan. No..
Table 1.1 – Calibration data used for calculation of the $a$ (start) and $b$ (step) parameters for the bottom detector of the three-element detector array. Energy values were obtained from the station 16.4 data book.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fluorescence Line</th>
<th>Weighted Energy Value (KeV)</th>
<th>Channel Number (Bottom Detector)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>$\alpha_{12}$</td>
<td>8.041</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>$\beta_{123}$</td>
<td>8.9044</td>
<td>61</td>
</tr>
<tr>
<td>Rb</td>
<td>$\alpha_{12}$</td>
<td>13.376</td>
<td>202</td>
</tr>
<tr>
<td></td>
<td>$\beta_{13}$</td>
<td>14.959</td>
<td>252</td>
</tr>
<tr>
<td>Mo</td>
<td>$\alpha_{12}$</td>
<td>17.479</td>
<td>370</td>
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<td>$\beta_{13}$</td>
<td>19.603</td>
<td>398</td>
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<td></td>
<td>$\beta_{2}$</td>
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<td>478</td>
</tr>
<tr>
<td></td>
<td>$\beta_{13}$</td>
<td>24.934</td>
<td>565</td>
</tr>
<tr>
<td></td>
<td>$\beta_{2}$</td>
<td>25.462</td>
<td>581</td>
</tr>
<tr>
<td>Ba</td>
<td>$\alpha_{1}$</td>
<td>32.194</td>
<td>782</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{2}$</td>
<td>31.817</td>
<td>793</td>
</tr>
<tr>
<td></td>
<td>$\beta_{13}$</td>
<td>36.357</td>
<td>924</td>
</tr>
<tr>
<td></td>
<td>$\beta_{2}$</td>
<td>37.27</td>
<td>953</td>
</tr>
<tr>
<td>Tb</td>
<td>$\alpha_{1}$</td>
<td>44.481</td>
<td>1156</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{2}$</td>
<td>43.744</td>
<td>1179</td>
</tr>
<tr>
<td></td>
<td>$\beta_{13}$</td>
<td>50.338</td>
<td>1364</td>
</tr>
<tr>
<td></td>
<td>$\beta_{2}$</td>
<td>51.709</td>
<td>1406</td>
</tr>
</tbody>
</table>
Using the start and step parameters calculated above it was possible to convert the horizontal scale of the data sets from channel numbers to energy (KeV). However, in order to calculate accurately the angle of the detector, a parameter needed for conversion of the horizontal axis into a d-spacing scale, a pure standard of known structure was required.

While a silicon standard is generally used for this purpose in a conventional laboratory diffraction experiment, it was not suitable for calibration of the bottom detector when set at the shallow angle required for the study of microporous materials, the reason for which is that the silicon reflections are outside the d-spacing range of the detector at such a low angle. For this reason, and as a means of checking the suitability of the detector angle for a particular system, a pure phase of the material under study was usually used as the standard. As the cell parameters and space group of the standard are known, the variations of the reflection positions with changing detector angle could be calculated with the Dragon reflection generation program\textsuperscript{84} available on the Daresbury mainframe computer system. The linear fit equations from each of these reflections could then be used to calculate the actual value of the detector angle. As a check, the resulting angle could be fed back into the Dragon program to produce energy values for the complete set of reflections for comparison with the actual sample. An example of such a calibration is shown below for the middle detector using a pure sample of the large pore microporous aluminophosphate, AlPO-5 as a standard. The linear fits to the data illustrated in figure 1.9 produce the following equations listed in table 1.2, which in turn are used to calculate the detector angle value from the measured reflection positions. In this case the mean value calculated for the detector angle is 4.02°±20.
Figure 1.9 – Plots of detector angle versus reflection position for the AIPO-5 structure as a means of calibrating the detector angle. The numbers in brackets are the Miller indices for each reflection used. The data used to produce these graphs have been produced using the Dragon program.

Table 1.2 – Linear fit equations for the listed AIPO-5 reflections with the resulting calculated detector angles, produced using the measured reflection positions.

<table>
<thead>
<tr>
<th>Miller Index</th>
<th>d-spacing (Å)</th>
<th>Linear Fit Equation</th>
<th>Reflection Position (KeV)</th>
<th>Calculated Detector Angle (°2θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(210)</td>
<td>4.4975</td>
<td>y = -9.88x + 79.026</td>
<td>39.27</td>
<td>4.02</td>
</tr>
<tr>
<td>(002)</td>
<td>4.2370</td>
<td>y = -10.48x + 83.856</td>
<td>41.89</td>
<td>4.00</td>
</tr>
<tr>
<td>(211)</td>
<td>3.9726</td>
<td>y = -11.20x + 89.526</td>
<td>44.47</td>
<td>4.02</td>
</tr>
<tr>
<td>(220)</td>
<td>3.4350</td>
<td>y = -12.94x + 103.486</td>
<td>51.35</td>
<td>4.03</td>
</tr>
</tbody>
</table>

Once the detector angle is known, it is possible to convert the data sets into d-spacing values and then, if required into 2θ values for any desired wavelength. Such conversions are useful when comparing EDXRD data sets with conventional X-ray
diffraction patterns. These conversions can be carried out using a new version of the DL Convert program supplied by CCP14 at the Daresbury SRS.

1.6.5.2) Calibration of Sample Heating In Situ Using an Internal Thermocouple

During the course of the experiments carried out in this project, the temperature of the system was measured by means of a thermocouple attached directly to the furnace body. The temporary availability on loan of a modified ‘spider’ (the system of valves built into the cap of the stainless steel autoclave) enabled the use of a second, internal thermocouple that could be placed directly in contact with the reaction gel. A calibration was carried out over a range of temperatures using a standard fill volume of a fumed silica-water gel mixture of a similar consistency to the actual synthesis gels used during the project. Even though heating was found to be rapid, the gel was left at each temperature for at least 1 hour to achieve a stable reading.

The resulting calibration curve is shown in figure 1.10, below. Where fluctuations were still being observed after an hour, error bars are displayed to give an indication of this fluctuation. One feature of note is the fluctuation in the general upward trend of the internal temperature between 373K and 408K. It is likely that this is due to the sample beginning to boil within the autoclave, with the fluctuation continuing until the pressure had equilibrated. Once this had happened, the general trend in increasing temperature could continue.
Figure 1.10 – Calibration of the internal and external thermocouples with respect to the furnace controller dial reading. Error bars show the level of temperature fluctuation after remaining at that temperature setting for 1 hour.

1.6.5.3) Adjustment for Beam Decay

When describing the synchrotron radiation source it was mentioned that even under ultra high vacuum conditions, the beam slowly decays due to occasional collisions of the electrons in the accelerator with gas molecules. This decay will have an effect on the intensities of reflections observed over time and so must be corrected for when analysing data collected over any time period longer than a few minutes. This correction could be carried out either by using the monitor readings collected in the scalar file accompanying each data set or by using data from the central beam decay monitor for the synchrotron ring, collected continuously during operation. This
data is archived and available from the central computer system at the Daresbury Laboratory.

1.6.5.4) Data Analysis

The PC, Windows 95 based DLconvert package from CCP14 at Daresbury was used in order to convert the data into a form appropriate for use with a graphical curve-fitting package, Xfit also from CCP14. DLconvert has recently been upgraded to convert data from an energy dispersive scale to either a d-spacing or an angular dispersive scale for a specific wavelength. Xfit was used both to visualise the data and to fit the areas under each reflection. A Gaussian function was used to fit each reflection while the background hump created by the presence of water in the gel was fitted to a split Pearson 7 function (asymmetrical) and a Gaussian function (symmetrical). The resulting data were then analysed using the Microsoft Excel package in order to compare the synthesis curves for each crystalline phase as a function of time. Microcal Origin 5.0 was used to display individual data sets. A more detailed description of the data analysis process is given in chapter 2.

1.6.5.5) Treatment of Errors in Crystal Growth Curves

Errors within crystal growth curves can be estimated by obtaining the standard deviation of the data points recorded after completion has been reached. Large deviations in the values of these data, as often observed in the aluminophosphate syntheses, are likely to be due to movement by convection of the crystallites through the unstirred liquid with especially large deviations being caused by ‘bumping’.
1.7) X-Ray Absorption Techniques

In a similar way to X-ray diffraction, absorption techniques such as X-ray absorption fine structure (XAFS) have advanced rapidly since the development of synchrotron radiation sources. The following sections describe the use of Extended X-ray absorption fine structure (EXAFS) during the course of this project to analyse the local environments around a series of elements in microporous systems.

1.7.1) Basic Theory of EXAFS

When X-ray energy is sufficient to excite a core level photoelectron within atoms of a specific element, a characteristic absorption edge is observed for that element. The scattering of the excited photoelectron by atoms neighbouring the excited atom results in the formation of a set of oscillations beginning around 30eV above the absorption edge, known as the Extended X-ray absorption Fine Structure (EXAFS) region. The region immediately above the absorption edge is known as the X-ray absorption near edge structure (XANES) region and is discussed later in more detail. Both regions are illustrated schematically in figure 1.11 below.

The major strength of the EXAFS technique is that it allows us to analyse the local environments around atoms of specific elements within a material. The oscillations are produced by phase differences between outgoing and back-scattered electron waves, resulting in either constructive or destructive interference. From a qualitative point of view, shorter bond distances give larger spaced oscillations while an increase in the number of atoms in a co-ordination sphere results in an increased
amplitude, the scale of which is related to the scattering power and thus to the atomic number of the scattering atom.\textsuperscript{76 80 86-90}

Figure 1.11 – a) A schematic of an XAFS spectrum showing the XANES and EXAFS regions. The oscillations in the EXAFS region are produced by phase differences between outgoing and backscattered electron waves shown in b) as solid and dashed circles respectively. The red circle represents the excited atom while the blue circles represent its four nearest neighbours.
For quantitative analysis of EXAFS data a function must be derived to describe the EXAFS modulation for core level absorption. The full form of equation 1.10 below (i.e. when combined with equation 1.11) is known as the EXAFS plane wave equation.

A photoelectron ejected from an atom as a result of X-ray absorption is characterised by a wave-vector \( k \), which is given by the equation:

\[
  k = \frac{(2mE)^{1/2}}{(\hbar/2\pi)} \tag{1.8}
\]

Where \( m \) is the mass of the electron, \( \hbar \) is Planck's constant and \( E \) is the kinetic energy of the photoelectron, which is equal to the difference between the X-ray energy and a threshold energy associated with the ejection of the electron. The EXAFS function \( \chi(k) \) is defined by the equation:

\[
  \chi(k) = \frac{\mu - \mu_0}{\mu_0} \tag{1.9}
\]

Where \( \mu \) and \( \mu_0 \) are atomic absorption coefficients characteristic of the absorption associated with the ejection of an inner core electron from an atom. The coefficient \( \mu \) refers to absorption by an atom in the material of interest while \( \mu_0 \) refers to absorption by an atom in the free state, both of which are functions of \( k \).

Theories of EXAFS based on the scattering of an ejected photoelectron by atoms in the co-ordination shells surrounding the central absorbing atom give an expression for \( \chi(k) \) of the following form:

\[
  \sum_j A_j(k) \sin[2kR_j + 2\delta_j(k)] \tag{1.10}
\]

Where the summation extends over \( j \) co-ordination shells. In this expression, \( R_j \) is the distance from the central absorbing atom to atoms in the \( j^{th} \) co-ordination shell and \( \delta_j(k) \) is the phase shift. The factor \( A_j(k) \) is an amplitude function for the \( j^{th} \) shell, and is defined by the expression:
\[ A_j(k) = (N_j/kR_j^2)F_j(k)\exp(-2k^2\sigma_j^2) \]  

(1.11)

Where \( N_j \) is the number of atoms in the \( j \)-th shell, \( \sigma_j \) is the root mean square deviation of the interatomic distance about \( R_j \). \( \sigma_j^2 \) is the Debye-Waller factor to account for the smearing out of the EXAFS due to the static disorder of the atoms. This factor is also temperature dependant, being lower at lower temperatures. \( F_j(k) \) is a factor accounting for electron backscattering and inelastic scattering. The factor \( F_j(k) \) is related to the backscattering factor \( f(k) \) and the mean free path \( \lambda \) for inelastic scattering by the expression:

\[ F_j(k) = f(k) \exp(-2R_j/\lambda) \]  

(1.12)

As mentioned previously, the backscattering factor \( f(k) \) describes the amplitude of the EXAFS oscillation and is related to the atomic number \( z \) of the backscattered species. The variation of this term with \( k \) may therefore be used to recognise the species around the emitting atom.

1.7.2) Analysis of EXAFS Data

Refinement was carried out using the suite of codes available at the Daresbury SRS comprising EXCALIB\textsuperscript{91}, EXBROOK\textsuperscript{92} and EXCURVE98\textsuperscript{93}, although alternative codes are available at Daresbury and elsewhere that carry out similar tasks. EXCALIB is a data normalisation code that converts the recorded data into the form of energy vs. absorption coefficient from, in the case of a transmission experiment, the measured values of \( I_0, I_t \) (from the ion chambers) and the monochromator position in milli-degrees. A range of other options allow similar conversions to be carried out for
several other experimental configurations, while summation of scans can also be performed and any glitches or spurious data removed.

The resulting data sets are then processed using EXBROOK, which carries out three main tasks, first of which is pre-edge subtraction as shown in figure 1.12 below, whereby the contributions to the pre-edge slope due to mass absorption, Compton and other scattering are removed by fitting this slope to a polynomial. This subtraction is extrapolated to include the absorption data, yielding the absorption coefficient of the absorber.

Once the pre-edge slope has been subtracted, the background also has to be removed, which is a less straightforward process as the background is complicated by features including detector counting errors and absorption by elements in the sample other than that under investigation. Background subtraction is generally performed by fitting the data to a combination of a simple polynomial and a cubic spline in order to produce a plot of $\chi(E)$, (Figure 1.13) which is the fine structure EXAFS modulation per absorbing atom.
Figure 1.12 – A schematic illustration to show the effect of pre-edge subtraction on the EXAFS spectrum. The dashed line in (a) represents the extrapolated polynomial which is subtracted from the raw data to give the absorption per absorbing atom shown in (b).
The final task of EXBROOK is to convert the data from a $\chi(E)$ to a $\chi(k)$ scale, where $k$ is the photoelectron wave vector space described in equation (1.8) above. If background subtraction has been performed satisfactorily, the EXAFS oscillations in the $\chi(k)$ plot will bisect the zero point of the $\chi(k)$ axis. When carrying out background subtraction, periodic observation of both the weighted $\chi(k)$ plot and the associated Fourier transform help in producing a successful subtraction. A Fourier transform of the function $k^n \chi(k)$, where $n$ is normally an integer from 1 to 3, yields a radial structure function $\phi(R)$, where $R$ is the distance from the absorber atoms. A general rule when observing the Fourier transform is to minimise the 0-1Å region while maximising the first peak.
The normalised EXAFS data is analysed using EXCURV98, which applies curved wave theory, the more complex version of the plane wave theory discussed above, and refinement by least squares methods in order to fit the experimental data to a theoretical model. These calculations are usually performed with reference to a model compound of known structure. For example, CoAl₂O₄ would make a suitable model for the study of the cobalt edge in a material such as a cobalt substituted aluminophosphate as the local structure of cobalt in this spinel material is similar to the tetrahedrally coordinated cobalt seen in the frameworks of such microporous solids.

During refinement, the interatomic distance, denoted R in EXCURV98, the co-ordination number (N), the Debye-Waller factor (A) and the edge position relative to the calculated vacuum zero (E_f), in addition to several other parameters are allowed to vary until a best fit between the observed data and the theoretical model is achieved.

When carrying out the fitting process, Fourier transform techniques can once again be used to assist in analysis by converting the data to obtain approximate distance information from the central atom. An active method of utilising the Fourier transform is with the technique of Fourier filtering in which a section of the Fourier transform is selected, for example around one co-ordination shell and then back transformed to yield EXAFS oscillations for that shell only. The resulting spectrum can, in turn, be used to produce a simpler structural model. This method however is not recommended as it removes all noise, making error analysis meaningless.
1.7.3) Factors to Consider When Fitting EXAFS Data

When fitting data, we need to keep in mind that EXAFS data describe a 1-dimensional curve derived from a 3-dimensional material, with the result that the system is under-determined with more than one model giving a “good fit” to the data. A measure of chemical common sense must also be used when considering the validity of a model while the number of independent data points ($N_{\text{ind}}$) must also be considered compared to the number of parameters used in the refinement ($p$). $N_{\text{ind}} = 2\Delta k \Delta R / \pi + 1$ where $\Delta k$ and $\Delta R$ are respectively the widths in k- and R-space over which substantial data were collected. A value of $N_{\text{ind}} / p$, known as the degree of determinancy, less than 1 cannot be justified as this would mean less than one observation per parameter.\footnote{\textsuperscript{94}}

1.7.3.1) Correlation

A further factor to be considered when analysing EXAFS data concerns the strong correlations that occur between certain parameters, the principal of which are the correlations between the coordination number ($N$) and the Debye-Waller factor ($\Delta$) and also between the bond distance ($R$) and the threshold energy ($E_o$). These correlations, if not accounted for can have the effect of producing false minima and thus incorrect results during refinement. A correlation map can be produced in order to observe the relationship between two such variables, which will show a series of contours displaying the minima between these variables and allowing errors to be detected.\footnote{\textsuperscript{94}}

The R-factor gives a meaningful indication of the quality of the fit to the EXAFS data in k-space. A value of 20% is normally considered to be a good fit while
a value greater than 40% would be considered poor, with values of 15% or less being difficult to obtain with unfiltered data. Higher values will obviously be expected when only attempting a partial fit, for example to only the first coordination shell.

1.7.3.2) Multiple Scattering

In systems where there are central atom-nearest neighbour atom-next nearest neighbour atom bond angles close to 180°, for example in the case of the –Ti–O–Ti– chains in ETS-10 discussed in chapter 5, multiple scattering interactions must be taken into account to achieve a good fit to the data. Such a configuration results in the outgoing photoelectron being strongly forward scattered by the intermediary atom, resulting in a significant enhancement of the EXAFS amplitude, as shown schematically in figure 1.14. The enhancement is greatest at 180° and has largely disappeared by the time the angle is reduced to 150°.

![Figure 1.14](image)

Figure 1.14 – A schematic of the process occurring during multiple scattering, with the outgoing electron waves from an excited atom (red) shown as solid circles and the backscattered waves from a nearby atom (blue) shown as dashed circles. The green atom represents a second neighbour making a linear bond with the immediate neighbour and the absorbing atom. The orange chevrons signify the forward scattering of the photoelectron wave by this linear moiety before being back-scattered.
During data analysis, multiple scattering may be accounted for by setting up a unit for each multiple scattering pathway, describing the positions of the atoms in the pathway and the angle of the bond. The additional forward scattering along the pathway is then calculated during refinement.

1.7.4) The XANES Region

It should also be noted that another region of the X-ray absorption spectrum can provide useful data for the study of materials. This region, situated within about 50KeV of the absorption edge, is known as the XANES (X-ray Absorption Near-edge Structure) and can provide a wealth of useful chemical information, for example, changes from the octahedral to the tetrahedral state of the absorbing species indicated by the appearance of a pre-edge feature due to a forbidden 1s $\rightarrow$ 3d transition. Factors such as multiple scattering effects also show up in this region, but due to the many complex interactions that take place, quantitative interpretation of XANES data is a highly complex task. The EXAFS and XANES regions are grouped together simply as XAFS.
1.7.5) EXAFS Data Collection Procedures

Prior to the availability of synchrotron sources for XAFS analysis, the bremstrahlung output from a rotating anode X-ray tube was used. Unfortunately, to achieve good signal counting statistics and hence a good signal to noise ratio, scans could take up to a week. Using synchrotron radiation, rapid XAFS data collection can be achieved in milli-seconds using a bent monochromator crystal and photodiode array. More usually, EXAFS data sets are recorded over the course of ca. 45-60 minutes at the Daresbury SRS, with the exception of combined QuEXAFS/XRD experimental set-ups, discussed later, which require data sets typically every few minutes. A similar QuEXAFS facility was more recently made available on station 7.1.

There are two ways that XAFS data are routinely collected in scanning mode. The first of these is transmission, where two ion chambers are used to record data from the beam before and after it passes through the sample. A second method is fluorescence, where the sample is tilted at 45° to the incident beam and the fluorescence emissions are typically detected using a solid state detector array. Fluorescence data is collected when the element to be studied occurs in an extremely dilute form within the sample and was not required during the work reported in this project. These experimental configurations are shown in figure 1.15 below. In transmission mode the ion chamber detectors I₀ and Iᵣ record sample transmission while a detector records data in fluorescence mode.
In addition to the conventional scanning mode used throughout this project, it is worth mentioning that an energy dispersive EXAFS (EDE) configuration can also be used when extremely rapid scans are required, for example when studying a fast reacting system *in situ*. In such cases a bent crystal monochromator is used to focus X-rays with a range of energies onto the sample disk, with the transmitted spectrum then being recorded by a position sensitive detector (PSD).
1.8) Combined QuEXAFS/XRD Studies

Station 9.3 at the Daresbury SRS is a versatile instrument developed for materials science experiments. Several different experimental configurations can be used in order to carry out a wide range of experiments as follows:96-97

1. X-ray absorption spectroscopy (XAS) (transmission, fluorescence and electron yield modes) in an energy range from ca. 6KeV to 35KeV.
2. QuEXAFS (quick EXAFS) using either transmission or fluorescence configurations. Data sets can be recorded in five minutes or less.
3. REFLEXAFS (glancing angle reflectivity XAS) for studying surface and near-surface effects.
4. EDE (Energy Dispersive EXAFS) for studying fast chemical systems.
5. *In situ* catalyst research using a range of specially designed cells and combined QuEXAFS/XRD to analyse the formation and reactivity of these materials under realistic elevated temperature and/or pressure systems.

During the course of this project, experiments were carried out on station 9.3 to investigate the thermal stability of the microporous titanosilicate ETS-10 as reported in chapter 5. These experiments were performed using the experimental configuration shown in figure 1.16 below. We can see that this configuration is capable of carrying out combined QuEXAFS and XRD experiments using either a transmission or fluorescence geometry. However for these particular samples we could only collect diffraction data as the titanium K-edge occurs outside the energy range of the station. Successful combined experiments have been carried out by other members of the Davy-Faraday Research Laboratory (DFRL) research group, studying more suitable
systems, such as cobalt substituted aluminophosphate structures, where cobalt K-edge EXAFS could be recorded\textsuperscript{96-99}.

Such combined QuEXAFS/XRD experiments are very useful, allowing both the long and short range ordering of a sample to be studied \textit{in situ} for a sample exposed to a wide range of environmental conditions including temperature, pressure and flowing gas. Data have also been recorded for samples performing as catalysts under operating conditions.\textsuperscript{100} The use of a specially designed high temperature cell allows a sample to be studied at temperatures in excess of 1273K\textsuperscript{8}, which is especially useful for the \textit{in situ} study of solid state transformations including those described in \textit{chapter 5}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{./1.16.png}
\caption{A schematic diagram of the experimental configuration for collecting combined QuEXAFS/XRD data on station 9.3.}
\end{figure}
1.8.1) Calibration of Data Sets Using a Silicon Standard

X-ray diffraction data sets recorded on station 9.3 were calibrated using a silicon standard. In the example below, the channel number positions of the four visible silicon reflections shown in figure 1.17 were noted and, knowing the wavelength at which the experiment was performed (\( \lambda = 1.4062\text{Å} \)) it was possible to calculate the expected 2\( \theta \) positions of these reflections using the Dragon reflection generation program. It was then possible to calculate the a (start) and b (step) correction parameters as follows:

![Intensity vs Channel Number](image)

Figure 1.17 – An X-ray diffraction data set for a silicon standard run on station 9.3 at the Daresbury SRS. This data set is converted into °2\( \theta \) where \( \lambda = 1.4062\text{Å} \) using the procedure described below.
Table 1.3 – Data required for the calibration of station 9.3 data sets using a silicon standard. Reflection positions were calculated using the Dragon reflection generation code.°

<table>
<thead>
<tr>
<th>Miller Index (Silicon Std.)</th>
<th>d-spacing</th>
<th>Reflection position (°2θ) (λ=1.4062Å)</th>
<th>Channel Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>3.1356</td>
<td>25.92</td>
<td>398</td>
</tr>
<tr>
<td>(220)</td>
<td>1.9201</td>
<td>42.96</td>
<td>737</td>
</tr>
<tr>
<td>(311)</td>
<td>1.6375</td>
<td>50.86</td>
<td>888</td>
</tr>
<tr>
<td>(222)</td>
<td>1.5678</td>
<td>53.29</td>
<td>1118</td>
</tr>
</tbody>
</table>

\[ b \text{ (step)} = 2θ_3 - 2θ_1 / \text{Ch}_3 - \text{Ch}_1 = 24.94 / 490 = 0.051 \text{ 2θ/Channel No.} \]  
\[ 0.051 \times 737 = 37.51 \]  
\[ a \text{ (start)} = 42.96 - 37.51 = 5.448°2θ \]

Therefore, in this case, the raw data sets could be converted from a channel number scale to an angular scale at the wavelength \( \lambda=1.4062\text{Å} \) by multiplying each x axis value by 0.051 and subtracting 5.448 from the result. Once this conversion was achieved, the scale for data sets could be converted into d-spacing and then into other wavelengths if required, for comparison with other data sets. This could be done by manipulation of the Bragg equation.
1.9) Summary

This introductory chapter briefly describes various aspects of the work reported in subsequent chapters of this thesis with the aim of providing an overall picture as to the scope of the project described herein. A survey of the scientific and technical background has been performed with the aim of setting this work in context regarding current technical progress and ideas in the field of *in situ* microporous materials synthesis. The following chapter describes a series of such *in situ* synthetic experiments, carried out using EDXRD, during which, both quantitative and qualitative aspects of zeolite formation are discussed for the industrially important aluminosilicate, zeolite A.
1.10) References


85) DLconvert *Collaborative Computational Project 14 – CCLRC Daresbury Laboratory Computer Program.*


91) EXCALIB CCLRC Daresbury Lab. Computer Program.

92) EXBROOK CCLRC Daresbury Lab. Computer Program.


97) Station 9.3 Information Daresbury SRS World-Wide Web-Site (1999) Daresbury SRS.


Chapter 2

An Energy Dispersive X-ray Diffraction Study of the Microporous Aluminosilicate, Zeolite A

2.1 Chapter Overview

This chapter describes a series of in situ energy dispersive X-ray Diffraction experiments carried out on the industrially important aluminosilicate, zeolite A. These studies were performed with the aim of comparing the data obtained using this technique with those from both conventional laboratory studies and in situ studies by myself\(^4\) and others\(^2\)\(^{-6}\), in both open and closed hydrothermal systems.

We show that high quality data with a good degree of time resolution (typically 1 minute per scan) can readily be obtained with the in situ approach. Furthermore, such an approach permits study under realistic synthesis conditions, eliminating many of the problems associated with the majority of conventional techniques. The high-energy 'white' synchrotron radiation beam did not appear to affect the zeolite A syntheses by either inhibiting or accelerating crystal growth as had been observed in certain systems containing organic template molecules.

The synthesis of high quality crystalline samples of zeolite A was first perfected using the in situ cell\(^1\). We then undertook a study of the kinetics of crystallisation for a pre-cursor gel of a standard composition over a range of temperatures, our aim being to perform a quantitative study of the activation energy of crystal growth for zeolite A synthesis under a clearly defined set of reaction conditions. Due to the complications involved in producing a soundly based theory
that accurately models the many processes occurring during zeolite synthesis, a relatively simple formulation based on the Avrami equation was used in order to illustrate the quality of the data obtained\(^8\). It has thus been possible to suggest the EDXRD technique as another avenue from which to gain the high quality kinetic data required as an aid to the formulation of chemically meaningful mathematical models for the processes occurring during zeolite synthesis. The value of the activation energy of crystal growth obtained from our empirical model was found to be in good agreement with those from experimental work by others\(^8\)\(^9\)\(^19\) and also with theoretical studies\(^20\).

A further investigation was carried out over a higher temperature range in order to study the competitive formation of zeolite A with a second smaller pore microporous solid known as hydroxy-sodalite, the formation of which had been previously reported by others\(^8\)\(^9\)\(^12\). The mechanism by which these two phases interacted was then considered based on the resulting observations.

The next part of the investigation involved a study of the effects of altering the pre-cursor gel composition including alteration of the source of silica used in the synthesis and the quantity of water used. These changes were found to alter the kinetics of the system and the nature of the resulting products. The results gained from these studies were then used in order to postulate qualitative models that attempt to explain several of the observed phenomena.

The competitive formation of zeolite A and hydroxy-sodalite was finally investigated in more detail using a novel 3-element solid-state detector array developed by groups at Birkbeck College London and Daresbury Laboratory\(^21\)\(^22\). From the data collected using this detector array, we confirmed that the extra information gained using multiple detectors now allowed the unambiguous
identification of crystalline phases \textit{in situ} by comparison with diffraction data for known phases. A brief study of the effect of altering the NaOH content of the precursor gel was also carried out using this modified experimental set-up.

2.2) Zeolite A as a Candidate for Energy Dispersive X-ray Diffraction Studies of Crystallisation in Microporous Materials

Zeolite A is a widely investigated microporous aluminosilicate zeolite. It was discovered in 1956 by Milton$^{23}$ and has the formula \{Na$_{12}$[Al$_{12}$Si$_{12}$O$_{48}$].27H$_2$O\}$_8$, hence with a Si/Al ratio of 1. In terms of the standard nomenclature for microporous materials, zeolite A has the structure type LTA (Linde Type A). It is composed of a network of sodalite or $\beta$ cages joined together in a primitive cubic arrangement by double 4-ring (D4R) linkages. The resulting structure has the cubic space group Fm-3c, with cell dimensions of length 24.61\AA.

The sodalite structural sub-unit is shown in figure 2.1 below, together with an illustration of how these cages link to form zeolite A, sodalite and another industrially important microporous solid, faujasite. Each line on the figure represents two T atoms (silicon or aluminium) linked by a bridging oxygen atom. The charges on the structure are balanced by extra-framework cations, these being typically, sodium, potassium or calcium, while the cages can also contain water molecules when in the hydrated state.
Zeolite A is a widely used industrial material with a variety of uses in laboratory, commercial and industrial processes due to its ion exchange, sorption and catalytic properties, one of the most important of which is as a *detergent builder* in soap powders where it acts as a safe, essentially non-toxic, water softener and replaces environmentally damaging phosphates. Other microporous aluminosilicates such as the sodium form of zeolite X are often mixed with the zeolite A to facilitate more efficient removal of Mg$^{2+}$ ions. The annual demand for zeolite A in the detergent industry has been estimated at over 500 million tons per annum.
The synthesis conditions by which zeolite A is produced have a marked influence on the crystal morphology and size of the product. Precise control of these parameters is important for the detergent industry in order to produce a product with the desired properties. These specifications include crystallites with bevelled edges as opposed to the sharp edged cubic crystals more commonly associated with zeolite A. Such crystals are more easily removed from fabrics during the rinse cycle\textsuperscript{24}.

Zeolite A is also widely used as a general-purpose molecular sieve. Changing the nature of the cation results in a range of pore size. For example, zeolite A samples containing K\textsuperscript{+}, Na\textsuperscript{+} and Ca\textsuperscript{2+} form molecular sieves with internal pore diameters of around 3, 4 and 5Å respectively. These materials are often pelletized for general laboratory and industrial use and sold as Molecular Sieves 3A, 4A and 5A.

Zeolite A was chosen as a candidate for investigating the suitability of energy dispersive X-ray Diffraction in order to study zeolite synthesis for several different reasons. It is a well-studied material, the synthesis of which has been investigated with a variety of both \textit{in situ} and \textit{ex situ} techniques. These studies include an early, qualitative \textit{in situ} EDXRD study of zeolite A and sodalite synthesis from kaolinite carried out by Munn et al\textsuperscript{11}.

In addition, Zeolite A is a relatively easy zeolite to synthesise and one which, unlike many other such materials, also has a relatively short crystallisation time, with syntheses taking typically 30 minutes to 3 hours depending on the reaction conditions. Materials with short crystallisation times were important in this work for two reasons. Firstly, ‘beam-time’ on a central synchrotron X-ray facility is very expensive. In order to maximise the productivity during a synchrotron ‘beam-time’ allocation, it is therefore advantageous to have a situation where relatively large numbers of experiments can be carried out during a scheduled period of only a few days.
Secondly, zeolites with short synthesis times are exactly the sort of materials that would be the most difficult to gain useful, high quality data from in a conventional ex situ laboratory synthesis and diffraction experiment. An additional consideration was that zeolite A can be synthesised from a thick gel at relatively low temperatures, typically 353K-393K, thus avoiding any added complications that could be caused by excessive movement of the sample within the reaction vessel during heating. Such effects have become apparent in other systems, as discussed in later chapters.

Finally, it was known that the high-energy radiation beam used in these experiments could noticeably affect the synthetic system. These effects can be observed in the radically reduced synthesis times exhibited over traditional syntheses for the aluminophosphate systems discussed in chapter 3. It was also discovered during trial experiments that some zeolite systems containing organic template species would not form in the beam, possibly due to damage to the organic species. It was therefore desirable to carry out initial work with a zeolite that did not require such an organic template species in order to form. It was subsequently found that the zeolite A system was indeed largely unaffected by the synchrotron radiation beam.
2.3) Experimental

2.3.1) Preparation of Zeolite A

Conventional laboratory syntheses of zeolite A were initially carried out in order to optimise synthesis conditions and obtain a gel composition capable of repeatable production of well crystalline zeolite A samples from a relatively thick gel suitable for in situ EDXRD studies. The resulting composition was then used as the basis for a series of in situ experiments as described below.

Zeolite A, like many zeolites is normally synthesised by a hydrothermal route, using a pre-cursor gel containing soluble sources of silicon and aluminium, water and a strong, soluble alkali such as NaOH. Typical source materials include alkali metal silicates and aluminates, fumed silica, colloidal silica in stabilised solutions e.g. Ludox, aluminium hydroxide and also organic sources such as tetra-alkyl orthosilicate and aluminium isoalkoxide. The alkali acts as a mineralising agent, breaking down the silicon and aluminium species and as a source of extra-framework, charge balancing cations.

Other synthetic routes include the use of a combined silica and alumina source such as metakaolinite with an Si/Al of 1.5 8 9 11 18 25 Metakaolinite is formed by calcining china clay (kaolinite) in air at high temperatures, typically, 773-1173K, in order to form a reactive, X-ray amorphous source material. Calcination is required as uncalcined kaolinite tends to produce sodalite.8 In addition, the degree of calcination can influence the crystallinity and morphology of the crystalline product.8

As previously mentioned, unlike many synthetic microporous materials such as the large pore aluminosilicate, zeolite beta, and the aluminophosphate structures
discussed in later chapters, the zeolite A pre-cursor gel does not require the addition of an organic ‘template’ molecule to act as a shape directing agent. It should however be noted that triethanolamine\textsuperscript{7}\textsuperscript{26} has been used as a means of halting nucleation, for example in a seeded system in order to produce large single crystals of product.

2.3.1.1) Laboratory Synthesis of Zeolite A

2.3.1.1.1) A Conventional \textit{ex situ} Synthesis Investigation of Zeolite Kinetics

Prior to the research conducted for this thesis, I performed a brief study of the crystallisation kinetics of zeolite A as a standard laboratory preparation\textsuperscript{27}. I shall briefly describe the method used and results obtained from this work as a means of comparison between a traditional \textit{ex situ} experiment and the \textit{in situ} studies carried out during the course of later work.

A gel of composition 4.0 \( \text{Na}_2\text{O} : 1.0 \text{Al}_2\text{O}_3 : 1.5 \text{SiO}_2 : 160 \text{H}_2\text{O} \) was used and the synthesis carried out as described below on a 0.1M scale. The raw materials used were sodium aluminate (Aldrich), Ludox-HS40 (Fluka), NaOH (Aldrich) and distilled water. The experimental apparatus is shown in figure 2.2 overleaf.
Figure 2.2 – Experimental apparatus for an *ex situ* study of the kinetics of crystallisation of zeolite A.

1) NaOH pellets were added to half of the H₂O and the solution was stirred until all the pellets had dissolved. The sodium aluminate was then added over a period of 10 minutes and the mixture stirred thoroughly. This solution was then placed in the three-neck flask and stirred with the water bath at a constant temperature of 368K.

2) Adding 22.5g of LUDOX HS-40 to 80g of H₂O and then thoroughly stirring the solution, produced a second solution. This solution was added drop-wise via the Hersch funnel over the course of several minutes.

3) The stirred mixture was kept at a constant 368K for two hours and samples were removed to a microscope slide for later XRD analysis at regular, recorded intervals using a glass rod.
4) Removed samples were subsequently analysed using a Philips 1710 powder X-ray diffractometer. A strong zeolite A reflection at 24°20 (622) was isolated and its intensity plotted as a function of time to produce a synthesis curve.

2.3.1.1.2) Laboratory Synthesis of a Zeolite A Gel Suitable For in situ EDXRD Studies

A Zeolite A pre-cursor gel with the composition Al₂O₃:2SiO₂:1.0Na₂O:17.5H₂O was prepared using the standard synthetic method below.¹ The starting materials for this gel were sodium hydroxide pellets (Aldrich), aluminium hydroxide hydrate (Aldrich), Cab-O-Sil M5 fumed silica (Fluka) and distilled water.

1) 2.67g of sodium hydroxide pellets were dissolved in 10.50ml of distilled water in a PTFE beaker with stirring.
2) 2.60g of Aluminium Hydroxide (Aldrich) was added to the NaOH solution, the resulting mixture being thoroughly stirred.
3) 2.00g of fumed silica (Cab-O-Sil) M5 were then added slowly and the resulting paste was mixed thoroughly with a spatula.
4) The resulting pre-cursor gel was a translucent white paste with a highly alkaline pH (pH=14). X-ray diffraction patterns of this material reveal an amorphous nature. This gel was then sealed within a polypropylene screw-top bottle and placed in an oven at ca 368K for periods between 30 minutes and 4 hours.
5) Upon removal from the reaction vessel, the sample was analysed using a Siemens D500 X-ray diffractometer fitted with a pre-sample monochromator, using Cu-Kα₁ radiation in order to confirm the formation of zeolite A.

2.3.1.2) **In situ synthesis of Zeolite A on station 16.4 of the Daresbury Synchrotron Radiation Source**

Experimental work on zeolite A was carried out on station 16.4 of the Daresbury Synchrotron Radiation Source that operates at 2GeV. A schematic of the experimental arrangement for these *in situ* hydrothermal studies can be seen in figure 1.5 of *chapter 1*, the details of which have been published elsewhere. The bulk of the work discussed here was carried out utilising a Canberra single-element Ge solid state detector array. However, some later experiments were carried out using an advanced three element detector array developed jointly by Birkbeck College London and the CCLRC Daresbury laboratory, see figure 1.6. The angle of the detector was set at a fixed value of 20 chosen to allow several of the major reflections expected during the formation of zeolite A to be seen. With a relatively large pore microporous material such as zeolite A, these reflections would be expected to occur at relatively large values of d-spacing, typically 8-12Å, giving rise to the requirement for a low detector angle, typically in the region 1.0-1.8°. The data were collected under isothermal conditions and scans had durations of either 1 or 2 minutes.

Data for zeolite A were recorded over several periods of ‘beam-time’, each with slightly different instrument settings. Each experimental series has therefore been reported separately for the sake of simplicity.
2.3.1.2.1) Experimental Series 1 - Determination of the Activation Energy of Crystallisation for Zeolite A

(Synthesis and data collection for experimental series 1 was carried out by Dr. G. Sankar and Dr. F. Rey prior to my joining the research team. Subsequent data analysis and interpretation of results was carried out by myself.)

Zeolite A syntheses were performed using the following gel composition, $\text{Al}_2\text{O}_3:2\text{SiO}_2:1.0\text{Na}_2\text{O}:17.5\text{H}_2\text{O}$ and the synthesis was carried out in a similar manner to that described above (section 2.3.1.1.2), resulting in the production of a thick, translucent gel. This gel was then placed within a PTFE autoclave liner to a fill volume of 50% and sealed within the \textit{in situ} hydrothermal cell. This cell was placed in a preheated furnace and hydrothermal syntheses were performed at 357K, 363K, 367K and 378K for selected time periods.

For this series of experiments, the detector angle was set at a constant angle of $1.46 \pm 0.01 \degree$. A diffraction pattern was recorded every 2 minutes. Data analysis was carried out as described in section 2.3.2

2.3.1.2.2) – Experimental Series 2 – Investigations of Changing Experimental Conditions on Kinetics and Phase Formation

a) The Competitive Formation of Hydroxy-Sodalite During Zeolite A Synthesis

A further investigation of the zeolite A system was conducted in order to study the processes occurring during the competitive formation of the small pore
microporous material, hydroxy-sodalite (structure type SOD). This phenomenon occurs at higher temperatures than normally used for the synthesis of pure zeolite A. Batches of pre-cursor gel having the standard composition Al$_2$O$_3$:2SiO$_2$:1.0Na$_2$O:17.5H$_2$O were produced using the method described in synthesis 2. A 50% constant fill volume was used and syntheses were carried out in the temperature range 373-430K, this being a considerably higher thermal range than that studied in experimental series 1. The detector for experimental series 2 was set at a constant angle of 1.84±0.01°2θ. The data recorded were again analysed as described in section 2.3.2 in order to study the thermal stability and kinetics of formation of both the zeolite A and hydroxy-sodalite phases.

b) Studies of the effect of altering the initial gel composition of zeolite A.

i) Studies of the effect of silica source on the synthesis of zeolite A.

A range of pre-cursor synthesis gels were prepared at 385K, in each case using a pre-cursor gel based on the standard composition Al$_2$O$_3$:2SiO$_2$:1.0Na$_2$O:17.5H$_2$O but changing the silica source. Synthesis of gels using Cab-O-Sil M5 fumed silica were compared to gels prepared using Ludox-HS40* stabilised colloidal silica and a sample of the mesoporous silica material known as MCM-41. This final silica source was considered after it was discovered that using this material in the preparation of the large pore aluminosilicate, zeolite beta produced a more crystalline compound in the same synthesis time. The preparations of MCM-41 and zeolite beta are described in Appendices 1 and 2 respectively.
The synthesis curves produced were then analysed for any differences in kinetics, crystallinity and shape that may indicate different synthesis mechanisms for the resulting crystalline phases.

* When preparing gels using Ludox HS-40, the quantity of water added in step 1 was adjusted to accommodate the water in the Ludox thus keeping the final gel composition consistent.

**ii) Studies of the effect of changing water content on the synthesis of zeolite A**

A brief study was made of the effect on the crystallisation kinetics of increasing the water content of pre-cursor gels containing both Cab-O-Sil M5 and Ludox HS40 silica sources as described in the table below.

Table 2.1 – Changes in pre-cursor gel composition for a range of zeolite A synthesis experiments.

<table>
<thead>
<tr>
<th>Gel No.</th>
<th>SiO₂ Source 1.0</th>
<th>Al(OH)$_3$</th>
<th>NaOH</th>
<th>H₂O</th>
<th>Synthesis Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cab-O-Sil M5</td>
<td>1.0</td>
<td>1.0</td>
<td>17.5</td>
<td>385</td>
</tr>
<tr>
<td>2</td>
<td>Cab-O-Sil M5</td>
<td>1.0</td>
<td>1.0</td>
<td>25.8</td>
<td>385</td>
</tr>
<tr>
<td>3</td>
<td>Ludox HS-40</td>
<td>1.0</td>
<td>1.0</td>
<td>17.5</td>
<td>421</td>
</tr>
<tr>
<td>4</td>
<td>Ludox HS-40</td>
<td>1.0</td>
<td>1.0</td>
<td>34.2</td>
<td>421</td>
</tr>
</tbody>
</table>
2.3.1.2.3) Experimental Series 3 – Use of a New 3-Element Detector Array

The recent availability of a 3-element detector array$^{21, 22}$ on station 16.4 provided the opportunity to study the formation of zeolite A over a larger d-spacing range. This enabled a further, more detailed investigation of the competitive formation of LTA and SOD. The possibility of being able to identify accurately crystalline phases \textit{in situ} could now also be investigated. To this end, two separate experiments were performed as described below. The 3-element detector was set with the bottom element at a fixed angle of $1.70 \pm 0.01^\circ\theta$, resulting in the middle detector being set at $4.35 \pm 0.01^\circ\theta$. No measurable peaks were observed on the top detector in this case, therefore it was not calibrated. However, due to the way in which the array was constructed, having a separation of \textit{ca} $2.8^\circ\theta$ between each detector, the top detector would have been set at an angle of \textit{ca} $7.1^\circ\theta$.

\textbf{i) The formation of dense phases at higher synthesis temperatures}

Syntheses were carried out with the standard synthesis gel composition and preparation method (see \textit{section 2.3.1.1.2}) at a range of temperatures (363K, 393K and 413K) chosen in order to study the formation of LTA, SOD and any denser phases such as analcime.

\textbf{ii) The effect of NaOH content on the synthesis of zeolite A}

Gels were prepared based on the standard composition $2\text{SiO}_2:\text{Al}_2\text{O}_3:x\text{NaOH}:17.5\text{H}_2\text{O}$ using three different NaOH compositions where $x=0.5, 1.0$ and $1.5$ in order to observe the effects of both increasing and decreasing the standard quantity of NaOH used in the synthesis of zeolite A.
2.3.2) Data Analysis

As described in chapter 1, the Windows 95 based DLconvert and Xfit packages from CCP14 at Daresbury\(^{28}\) were used in order to convert the data to an appropriate format and then fit the areas under each reflection. A Gaussian function was used to fit each reflection while the background hump created by the presence of the gel and the PTFE liner was fitted to a split Pearson 7 (asymmetrical) and a Gaussian (symmetrical) function. The resulting data were then analysed using the Microsoft Excel package in order to compare the synthesis curves for each crystalline phase as a function of time.

For the higher temperature studies carried out after experimental series 1, scans were recorded every minute instead of every 2 minutes as in previous syntheses, due to the faster crystallisation rates. This resulted in less well-defined reflections being recorded especially during the early stages of crystal growth. The main effects of this reduction in definition were large fluctuations in the full width half maximum (FWHM) value during the early stages of observed crystallisation. It was found that by using peak intensity (i.e. peak area divided by FWHM) as opposed to peak area when plotting crystallisation curves these fluctuations could be largely removed as shown in figure 2.3 below. However, it should be noted that when carrying out a quantitative study of the kinetics of crystallisation, the area under the reflection is the more chemically meaningful measure and therefore the measure generally reported in the literature. The area under the reflection represents the change in the overall quantity of crystalline material present in the system during the period of a scan. For this reason, peak area was the measure best used to estimate the activation energy of crystallisation. However, as described later (section 2.4.3) crystallisation curves
produced with intensity measurements could be considered for purposes of qualitative comparison.

![Graphs showing crystallisation curves for LTA](image)

**Figure 2.3** – Crystallisation curves for LTA synthesised at 385K showing the difference in data quality between plots using a) peak area and b) peak intensity. The differences at early stages of crystal growth can be clearly seen. Plots were produced from the LTA (220) reflection at 44KeV on a detector with the angle 2θ fixed at 1.84±0.01°.

Phase identification was carried out by comparing the data with standard data sets from the ‘Collection of Simulated Powder Patterns for Zeolites’ in addition to laboratory powder diffraction patterns. Initial data were adjusted to account for the fixed detector angle and converted to KeV using the Dragon program available on XRDSV1 at Daresbury Laboratory. In later experiments, such as those using the 3-element detector array, the data sets have been converted to a d-spacing (Å) scale for ease of comparison with conventional diffraction data and to avoid confusion, due to all 3 detectors having a similar energy range.
2.4) Results & Discussion

2.4.1) Comparison of data collected by conventional means and EDXRD

The synthesis curve resulting from the *ex situ* laboratory study of zeolite A described previously can be seen below. In this case, the number of points recorded on the synthesis curve was unfortunately limited by time available on a heavily used X-ray diffractometer. The resulting plot (*figure 2.4*, below), however, gives an idea of what can be achieved by such a study. These data show that it is possible to plot the sigmoidal synthesis curve characteristic of zeolite crystal growth, using a conventional *ex situ* method, especially when studying slower forming zeolites that can often take several days to form.

![Figure 2.4 - The Synthesis Curve Obtained from Data Collected During a Conventional *ex situ* Study of Zeolite A Synthesis.](image-url)
It should however, be considered that the time resolution of this type of conventional study is limited by the time required to remove a sample manually from the synthesis mixture. Carrying out such a task carefully would realistically limit the time resolution of such a study whereas, depending on the crystallinity of the material under study, the in situ EDXRD technique can allow the collection of a useable data set automatically every 30 seconds in a well crystalline sample. Figure 2.5 shows a typical synthesis curve obtained for zeolite A synthesis at 367K, obtained during an in situ EDXRD experiment. In this case, data were collected at the rate of 2 minutes per diffraction pattern.

![Graph showing synthesis curve](image)

Figure 2.5 – The Synthesis Curve Produced from in situ EDXRD Data Obtained During the Synthesis of Zeolite A at 367K

While the improvement in time resolution is the obvious difference between figure 2.4 and figure 2.5, this is not the major advantage of in situ EDXRD. In fact, the use of an automated sample removal system in an ex situ study could greatly improve matters in this respect.
A more important consideration is that the ability to study a closed system allows us to follow what is actually happening under realistic hydrothermal synthesis conditions. It has been reported that the very act of removing and cooling samples when tracking the progress of a synthesis can result in the destruction of unstable intermediate phases. Also when working with other zeolitic systems that require even higher temperatures and therefore elevated pressures, it becomes increasingly impractical to carry out *ex situ* experiments as described above. Instead, in such cases, a large number of separate autoclaves are required, leading to the inconsistencies and errors in gel composition and heating resulting from a study using multiple, separate syntheses.

In certain microporous systems, particularly those requiring an organic template in order to produce the desired phase, the intense white radiation beam has been found to affect the synthesis in one of two ways. Firstly, the beam may inhibit the formation of any crystalline phase as observed in the attempted synthesis of faujasite with 15-Crown-5 crown ether. Secondly, the energy of the beam can appear to cause a speeding up of the reaction as is the case for the templated aluminophosphates discussed in chapters 3 and 4.

However, the beam appears to have very little if any effect on the synthesis of zeolite A. This would seem to indicate that the beam is interacting with the organic species in the gel, with the nature of the effect being governed by the nature of the template.
2.4.2) Laboratory Synthesis of a Sample of Zeolite A with a Composition Suitable for \textit{in situ} EDXRD Studies

Initial laboratory syntheses were carried out to confirm the suitability of a chosen gel composition for subsequent \textit{in situ} studies. Pure batches of zeolite A were produced from pre-cursor gels of the composition $\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot1.0\text{Na}_2\text{O}\cdot17.5\text{H}_2\text{O}$ (Made using the method described in synthesis 2. (section 2.3.1.2.2)) after synthesis in a sealed polypropylene screw-cap bottle at 368K for \textit{ca} 45-50 minutes. The thick translucent gel was observed to change colour to opaque white and become much less viscous at \textit{ca} 40 minutes, roughly corresponding to the start of crystal formation. The resulting white solid was repeatedly washed with distilled water then filtered before finally being dried. The pH of the gel was found to remain constant at 14 throughout the synthesis.

![Figure 2.6 - The Cu-Kα₁ laboratory powder XRD pattern produced for zeolite A synthesised at 368K for 1 hour in a sealed polypropylene bottle. The 2 reflections marked by asterisks relate to the presence of a small quantity of hydroxy-sodalite impurity. The pattern was collected on a Siemens D500 diffractometer with pre-sample monochromator over \textit{ca} 13 hours.](image-url)
The resulting diffraction patterns were compared to that of a standard sample of molecular sieve 4A (Aldrich) and also with data obtained from the ‘Collection of Simulated XRD Powder Patterns for Zeolites’\textsuperscript{29}. Syntheses taking place over periods longer than 50 minutes were found to contain a progressively increasing proportion of hydroxy-sodalite as shown in figure 2.6. A four-hour synthesis resulted in the formation of pure hydroxy-sodalite.

2.4.3) Calculation of Activation Energies from EDXRD Data

![3D stack plot of an in situ EDXRD zeolite A synthesis at 363K, with the detector angle fixed at 1.46±0.01°. The 4 observed zeolite A reflections have been indexed.](image)

Figure 2.7 – A 3-dimensional stack plot of an in situ EDXRD zeolite A synthesis at 363K, with the detector angle fixed at 1.46±0.01°. The 4 observed zeolite A reflections have been indexed.
Figure 2.7 above shows a stack plot of a typical EDXRD data set recorded under isothermal conditions during the synthesis of zeolite A at 363K. After an induction period of ca. ninety minutes, the reflections associated with the zeolite A structure start to appear. Comparison of the EDXRD pattern of the final product with that of a sample prepared in the laboratory confirmed the formation of a pure zeolite A phase.

The area under each reflection was calculated by fitting it with a Gaussian function. The resulting data for each reflection, when plotted as a function of time and normalised, could be superimposed as shown in figure 2.8, suggesting that uniform growth had taken place along each of the crystallographic directions as would be expected from a cubic system such as zeolite A. It was therefore deemed acceptable to use only the most intense reflection, this being the (220) reflection at 57KeV, in order to carry out the subsequent kinetic studies.

Figure 2.8 – Synthesis curves for each of the 4 zeolite A reflections observed in figure 2.6. Each curve has been normalised against its final area value in order to account for differences in peak intensity. The superimposition of each curve indicates uniform crystal growth in each crystallographic direction.
As can be seen in figure 2.8, plots of peak area as a function of time produced characteristic sigmoidal curves, where an initial period of induction/nucleation, during which no peaks were discernible is followed by a period of rapid increase in the area under the peak. This increase occurs for a period of ca. 30 minutes, corresponding to the main phase of crystal growth: A constant value indicating the completion of the crystallisation process is then observed. Figure 2.9 shows the synthesis curves for zeolite A, measured at 357K, 363K, 367K and 378K. These curves were found to exhibit a clear trend where increasing the synthesis temperature resulted in both a reduction in the induction/nucleation period before crystallisation began and an increase in the rate of crystallisation. The observed induction period is between 50 and 100 minutes depending on the synthesis temperature. The curves shown in figure 2.9 have been corrected for beam decay.

Errors that arise during the EDXRD experiment and subsequent data analysis can be estimated by calculating the standard deviation of the final part of each data set after crystallisation is complete. In this case, small values in the range 11-29 were obtained for synthesis curves produced using both the peak area and intensity. Considering that the overall peak intensities/areas upon completion have values between 1000 and 2000, the high quality of these data sets once again becomes apparent. This is however not always the case, as can be seen with the more liquid aluminophosphate based gels discussed in chapters 3 and 4 where large variations in the post crystallisation data can occur.
Figure 2.9 – Plots of a) the area and b) the intensity under the zeolite A (220) reflection, as a function of time for syntheses carried out at over a range of temperatures (357-378K) under hydrothermal conditions. The data were corrected for beam decay.
Separate consideration was made for each of the two components that make up the peak area, i.e. the peak intensity and the full width at half maximum (FWHM). It was found that for each sample, the FWHM decreased steadily over the main period of crystal growth from a value of \( ca \ 1.7 \text{KeV} \) to a value of \( ca \ 1.3 \text{KeV} \) where it became constant as can be seen in figure 2.10. From a consideration of the Scherrer formula, this trend would appear to indicate a steady growth in the average crystal size during the main growth phase. The constant FWHM values at completion between samples appears to indicate that within the temperature range of the investigation, changing the temperature has a negligible affect on the final size of the crystallites.

![Figure 2.10](image)

*Figure 2.10 – A plot of the full width at half maximum (FWHM) as a function of synthesis time for the zeolite A (220) reflection synthesised at 363K under hydrothermal conditions.*

Comparisons of the peak area under the reflections at each temperature with values for the intensity of the reflections produced very similar trends as shown in (figure 2.9a-b). Furthermore, calculations of the activation energy using both the area and the intensity values were found to be virtually identical (section 2.4.3). These results were due to the very small variations in the values of FWHM compared to the intensity over the same time span, meaning that intensity is by far the dominant
component of the area under a reflection. While, as discussed previously, it is chemically more meaningful to use the peak areas in order to carry out calculations of activation energies, the similarities in the curves meant that these area/intensity values are essentially interchangeable as an approximate measure of the degree of crystallinity. For qualitative comparisons, using the peak intensity has the added advantage that the large errors in FWHM values often generated by the curve-fitting program during the early stages of crystallisation could be removed.

From a comparison of the intensities at the completion of crystallisation it was additionally possible to conclude that the optimum temperature for the zeolite A synthesis in this case was between 257K and 367K, with higher temperatures resulting in a smaller quantity of zeolite A being synthesised.

**2.4.3.1) Avrami-Erofeev Treatment**

If the data in *figure 2.9* are normalised against the peak area or intensity upon completion, it is possible to obtain directly an approximation of the rate constant associated with the crystallisation process. As described by others, the normalised area ($\alpha$) in the range of values between 0.1 and 0.9 was used in order to consider data only from the main period of crystal growth. A common procedure for estimating the rate constant uses the Avrami-Erofeev approximation which gives $\alpha$ (the fraction of crystalline product) according to:

$$\alpha = 1 - e^{(-kt)^n},$$

(2.1) Yielding,
\[- \ln (1 - \alpha)^{1/n} = kt. \quad (2.2)\]

Figure 2.11 shows one of the plots thus obtained, of the mean value of 
\(-\ln (1 - \alpha)^{1/n}\) versus \((t-t_0)\), where \(t\) is the time for each scan, where \(\alpha=0.1-0.9\) and \(t_0\) is the induction period which describes the time at which the reflections start to appear.

The time exponent \(n\) is thought to depend on the mechanism of nucleation and in cases such as these, typical values of \(n\) are 3 or 4, although larger values have been used. A value of \(n=3\) has been suggested to represent a system with 'zero' nucleation, i.e. where all nuclei have formed and no further nucleation takes place. On the other hand \(n=4\) has been similarly suggested to represent a system undergoing constant nucleation. A value of \(n=4\) was chosen in this case as it is believed that...
nucleation actually continues to occur for at least the initial period of crystallisation.\textsuperscript{18}

The gradient of the resulting approximate linear fit shown in figure 2.11 gives the rate constant $k$, which was subsequently calculated for each synthesis temperature. Using the Arrhenius equation it was then possible to plot $-\ln(k)$ versus reciprocal temperature, $T^{-1}$, in order to estimate the value of the activation energy of crystallisation for the zeolite A synthesis, as shown in figure 2.12. Using this analysis, we obtain $E_{A(Cryst.)} \approx 53 \text{kJmol}^{-1}$ using the area under the reflection and. $E_{A(Cryst.)} \approx 55 \text{kJmol}^{-1}$ using the equivalent peak intensity.

This calculation was originally carried out for the same data sets using the ABFFIT curve-fitting program\textsuperscript{33} on an Apple Macintosh computer. In this case a less complex treatment of the background meant that peaks were best fitted to a more complex asymmetric mixed function described by the authors of the code as ‘Gumbel+’. The activation energy resulting from use of this method was $E_{A(Cryst.)} \approx 58 \text{kJmol}^{-1}$.

![Graph](image)

**Figure 2.12 – An Arrhenius plot of the rate constant $k$ for the synthesis of zeolite A.**
These values are close to those reported in previous studies of the kinetics of hydrothermal silicate synthesis\(^8\)\(^9\). Moreover, they accord well with calculated values of \(~60\text{kJmol}^{-1}\) calculated by Pereira (1997)\(^20\) for the activation energy for condensation reactions forming Si-O-Si bridges in silicate systems. Differences between our estimated value and those obtained by others\(^8\) can be largely explained by the use of different starting materials, especially silica source materials.

When considering the Avrami-Erofeev treatment for calculating the activation energy of crystallisation as illustrated above, it quickly becomes apparent that it is at best a good approximation of the summation of a number of different processes occurring during this period of zeolite formation. The approximate nature of this approach is made especially apparent by the curved nature of the Avrami-Erofeev plot. While this type of empirical approach is popular among those requiring a relatively simple gauge of the energies involved in the crystallisation of one zeolite compared to another, it is much too simple to describe the fundamental processes actually occurring. In fact, the Avrami model was originally designed for describing the solidification of metals and is really more suited to phase transformations in a confined volume.

In order to produce a more realistic model of zeolite synthesis, a range of theoretical approaches of widely varying complexity have been advanced\(^8\)\(^13\)\(^31-32\)\(^34-40\) as mentioned in the introductory chapter. However, there is still no single approach that accurately models all of the observed phenomena and thus gives a complete insight into the processes occurring during zeolite formation. It is considered therefore, that the relatively simplistic approach described above would fulfil the aim of the early stages of this study. This being to show that the \textit{in situ} EDXRD technique makes an excellent addition to the tools available for collecting the high quality data
required for detailed studies of the kinetic processes occurring during zeolite synthesis. This experimental approach could prove even more valuable when coupled with others such as SAXS/WAXS \(^{41-43}\), light scattering \(^{44}\), solid state NMR \(^{45}\), electron microscopy \(^{46}\) and combined QuEXAFS/XRD. \(^{46}\) Such a combinatorial study would enable zeolite formation to be investigated beginning at the early stages of nucleation. The picture could be further augmented with the use of theoretical computational approaches to model the behaviour of the very building blocks of the synthetic processes. \(^{20,47-48}\)

### 2.4.4 A Kinetic Study of The Competitive Formation of Zeolite A (LTA) and Hydroxy-Sodalite (SOD) at Elevated Synthesis Temperatures

Heating batches of zeolite A pre-cursor gel of standard composition at increasingly higher temperatures at first results in the progressively faster formation of the crystalline product as previously discussed. However, as temperatures increase still further, the resulting zeolite A becomes increasingly more unstable and in addition, a second, more dense microporous phase known as hydroxy-sodalite (structure type SOD) begins to form competitively. The series of experiments described in this section were carried out at significantly higher temperatures than previously used in order to investigate this phenomenon.

In order to carry out this high temperature study, six samples were synthesised, each from a precursor gel of the following standard composition, \(\text{Al}_2\text{O}_3:2\text{SiO}_2:1.0\text{Na}_2\text{O}:17.5\text{H}_2\text{O}\) using Cab-O-Sil M5 amorphous fumed silica. The pre-cursor gels were prepared as described previously in synthesis 2 (section
2.3.1.1.2) In situ hydrothermal syntheses were carried out over a temperature range of 373-430K. The lowest temperature synthesis was therefore just inside the upper range of temperatures used in the previous synthesis series. This was considered as a suitable starting point having previously observed that a single, stable crystalline phase corresponding to LTA would form at this temperature.

Figure 2.13 shows a typical pattern obtained during these studies with the reflections due to the LTA and SOD phases at the fixed detector angle $1.84\pm0.01\degree$ being labelled. The reflections observed at this angle correspond to the d-spacing values listed in the table 2.2 below, with the reflections in the region ca 40-70KeV being most strongly recorded due to the nature of the experimental set-up. For the purposes of these experiments, the kinetics of zeolite A were followed using the (220) reflection while hydroxy-sodalite kinetics were followed with the (110) reflection.

![Figure 2.13](image.png)

Figure 2.13 – The diffraction pattern obtained after 50 minutes from a standard zeolite A pre-cursor gel heated at 417K. All of the observed zeolite A peaks and the single hydroxy-sodalite (SOD) peak are labelled. Other small peaks are constant and due to fluorescence from the materials of the cell. The detector angle was fixed at $1.84\pm0.01\degree$.
Table 2.2 – Comparison of zeolite A diffraction data with calculated values.

<table>
<thead>
<tr>
<th>Crystal Phase</th>
<th>Miller Index</th>
<th>Energy (KeV)</th>
<th>d-Spacing (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Exptl/Calc)</td>
<td></td>
</tr>
<tr>
<td>LTA (200)</td>
<td></td>
<td>31.16/31.44</td>
<td>12.31</td>
</tr>
<tr>
<td>LTA (220)</td>
<td></td>
<td>44.01/44.46</td>
<td>8.70</td>
</tr>
<tr>
<td>LTA (222)</td>
<td></td>
<td>53.92/54.45</td>
<td>7.10</td>
</tr>
<tr>
<td>SOD (110)</td>
<td></td>
<td>60.31/61.83</td>
<td>6.26</td>
</tr>
<tr>
<td>LTA (422)</td>
<td></td>
<td>74.91/77.01</td>
<td>5.02</td>
</tr>
<tr>
<td>LTA (442)</td>
<td></td>
<td>93.23/94.31</td>
<td>4.10</td>
</tr>
<tr>
<td>LTA (622)</td>
<td></td>
<td>103.61/104.27</td>
<td>3.71</td>
</tr>
</tbody>
</table>

It can be seen from figure 2.14 below that as the temperature increases, the induction periods for LTA synthesis become shorter as would be expected from the previous results. However, the situation is now complicated by the competitive formation of the SOD phase that is first observed to appear in the sample synthesised at 410K (figure 2.15d). This results in the trend of decreasing induction/nucleation period being non-linear, with the time at which crystallisation is first observed appearing to approach a minimum value of ca. 16 minutes at higher temperatures. It was also noted (figure 2.15) that the formation of the SOD phase appeared to be linked to decomposition of the LTA phase.
At 410K (figure 2.15d) the SOD phase begins to crystallise at the same point that the LTA phase begins to decompose, which would initially appear to indicate that the SOD phase is a breakdown product of the LTA phase. Both phases are composed of sodalite cages (figure 2.1.) and essentially differ by the type of linkages connecting these cages, these being double 4 ring (D4R) linkages for LTA and single 4 ring (S4R) linkages for SOD. Such a re-arrangement could possibly occur due to breakdown of D4R linkages and subsequent reformation of S4R linkages.
However, this initial picture changes when the results are observed for even higher temperature syntheses at 417K and 430K (figure 2.15 e-f). Here it can be seen that a further increase in synthesis temperature also brings the starting points for the
crystallisation of LTA and SOD closer together, with the crystal growth periods for both phases overlapping. This would therefore indicate another possible mechanism in which the breakdown of LTA is governed purely by thermal factors and thus the formation of hydroxy-sodalite is unconnected and does not require a structural rearrangement. If this is the case, the SOD nucleates separately from the pre-cursor gel and merely takes advantage of the nutrient species released into the gel by the breakdown of LTA to continue crystallising. In this case SOD crystallisation occurs simply because we have crossed over into a region of the phase diagram for a gel of this composition in which SOD crystallisation is favoured and LTA crystallisation is not.

As was previously noted in figure 2.14, there is a point after which further increasing the synthesis temperature does not appear significantly either to reduce further the induction period before LTA formation or to increase the rate of crystallisation. This observation probably corresponds to the approach of an upper temperature limit for LTA formation in a system with this starting composition. Further increases in temperature merely cause the crystallisation of the LTA phase to become increasingly unfavourable. It can be postulated from these results that further increasing the temperature above 430K will lead to a situation in which only the SOD phase forms. In turn, further temperature increases may result in the SOD phase becoming itself unstable, resulting in the formation of a phase such as analcime, which is the most stable and dense common zeolite, in a continuing cycle leading eventually to the formation of a dense phase such as quartz.

Such cycles have frequently been reported in previous studies. For example, Lechert reports that synthetic zeolites tend to be thermodynamically unstable under synthesis conditions with zeolite A transforming into either hydroxy-sodalite as
observed in this case or alternatively into zeolite Na-P (GIS), which tends to form at higher Si/Al ratios and lower alkalinites. These observations are in agreement with Ostwald’s Law of successive transformations (see Chapter 1) which states that an initial metastable phase will be transformed successively into one or more phases of higher stability.

When comparing the synthesis curves for the formation of SOD (figure 2.16), it can be seen that, in addition to a decrease in induction period with increasing temperature, there is also a marked steepening in the gradient of the curves, indicating an increasing rate of crystallisation. However, neither this trend nor that for the LTA can be studied quantitatively to gain chemically meaningful results in this case, owing to the simultaneous formation of the other phase, which will have an effect on the kinetics. In order to calculate the energy of activation for SOD crystallisation, synthesis conditions would need to be altered, for example, by further increasing temperature, in order to produce a pure SOD phase over a range of temperatures.
Figure 2.16 – A comparative plot of the crystallisation curves for hydroxy-sodalite (SOD) from the (110) reflection at 60KeV, illustrating the trends in decreasing induction/nucleation period and increasing reaction rate (gradient) with increasing synthesis temperature. The data was corrected to account for beam decay.

Table 2.3 below contains a summary of the induction periods, relative maximum degrees of crystallinity and mean full width half maxima (FWHM) values for both the LTA and SOD phases at the various temperatures.
Table 2.3 – Summary of data gained from EDXRD investigations for the LTA (220) and SOD (110) reflections recorded for pre-cursor gels of a standard composition over a range of synthesis temperatures.

<table>
<thead>
<tr>
<th>Synthesis Temp (K)</th>
<th>Phase</th>
<th>Induction Period (Mins.)</th>
<th>Proportion of crystalline material on completion*</th>
<th>Mean FWHM (KeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>LTA</td>
<td>47</td>
<td>84</td>
<td>0.92</td>
</tr>
<tr>
<td>376</td>
<td>LTA</td>
<td>40</td>
<td>52</td>
<td>0.94</td>
</tr>
<tr>
<td>385</td>
<td>LTA</td>
<td>22</td>
<td>72</td>
<td>0.94</td>
</tr>
<tr>
<td>410</td>
<td>LTA</td>
<td>20</td>
<td>80</td>
<td>0.94</td>
</tr>
<tr>
<td>410</td>
<td>SOD</td>
<td>79</td>
<td>Synthesis incomplete</td>
<td>2.42</td>
</tr>
<tr>
<td>417</td>
<td>LTA</td>
<td>16</td>
<td>58</td>
<td>1.00</td>
</tr>
<tr>
<td>417</td>
<td>SOD</td>
<td>22</td>
<td>Synthesis incomplete</td>
<td>2.46</td>
</tr>
<tr>
<td>430</td>
<td>LTA</td>
<td>16</td>
<td>52</td>
<td>0.97</td>
</tr>
<tr>
<td>430</td>
<td>SOD</td>
<td>20</td>
<td>Synthesis incomplete</td>
<td>2.34</td>
</tr>
</tbody>
</table>

* Estimated from the average intensity values of the plateau area of the synthesis curve after completion of crystallisation.

⊗ This synthesis was not performed to the point of completion but stopped after the first phase of crystal growth.

From this table the trends in the nucleation/induction periods for both phases can be seen as discussed previously. Other trends of note are a gradual increase in the FWHM values for LTA with increasing temperature indicating a decrease in average crystal size as would be expected for a faster reaction. It was also noted that, while the FWHM values for LTA quickly reach a constant value (figure 2.17a), the values for
SOD in each case show a trend with a negative gradient that gradually shallows with time as crystal growth begins to approach completion. (figure 2.17b).
The shape of the FWHM plot for SOD is a result of the continuing crystal growth process as the reaction rates for hydroxy-sodalite are much slower than those for LTA and do not reach completion during the period of the experiments. The mean FWHM values for SOD in these cases can therefore only tell us that in the time-scale over which these experiments were performed the SOD crystallites never became anywhere near as large as the LTA crystallites.

2.4.5) The Effects of Altering the Pre-Cursor Gel Composition

2.4.5.1) Effect of silica source

Zeolite A pre-cursor gels produced using Cab-O-Sil M5 fumed silica, Ludox HS-40 stabilised colloidal silica and MCM-41 (see Appendix 1) as silica sources were used in a series of syntheses at 385K. As shown in figure 2.18, the use of different silica sources does indeed affect the overall kinetics of the resulting LTA synthesis. While zeolite A was successfully synthesised in each case, the crystallisation kinetics, quantities of crystalline material formed and average sizes of these crystallites were found to vary considerably. The overall shapes of the resulting synthesis curves were also found to vary, giving an insight into the processes occurring in each case.
It can also be seen from figure 2.18 that Cab-O-Sil produced the greatest degree of crystallinity and therefore the largest quantity of crystalline material as defined by the intensity of the peaks after correction for beam decay. MCM-41 was the next most productive while the use of Ludox HS40 resulted in the lowest degree of crystallinity. However, a comparison of the average full width half maxima (FWHM) reveals significantly higher values for the MCM-41 synthesis as shown in the table below. This would appear to indicate that the use of MCM-41 results in the formation of significantly smaller crystallites of zeolite A than those produced by the more traditional silica sources studied.
Table 2.4 – Crystallinity and FWHM data for LTA samples produced with a range of silica sources.

<table>
<thead>
<tr>
<th>Silica Source</th>
<th>Proportion of Crystalline Material on Completion</th>
<th>Mean FWHM (KeV) of LTA Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cab-O-Sil</td>
<td>72</td>
<td>0.94</td>
</tr>
<tr>
<td>Ludox-HS-40</td>
<td>35</td>
<td>0.99</td>
</tr>
<tr>
<td>MCM-41</td>
<td>57</td>
<td>1.12</td>
</tr>
</tbody>
</table>

2.4.5.1.1) Cab-O-Sil M5 Amorphous Fumed Silica.

When the amorphous fumed silica source, Cab-O-Sil M5 was used, a thick, ‘waxy’, translucent greyish gel was produced. This gel was so viscous as to require tapping of the autoclave liner against the bench when filling it in order to get an even and accurate fill level.

Upon performing hydrothermal synthesis at 385K, reflections due to zeolite A were first observed after 22 minutes. Growth of these reflections proceeded rapidly for ca. 8 minutes and then slowed in a manner characteristic of other gels of this composition. After this slowdown, growth then accelerated until another gradual rate decrease began to occur 10 minutes later as the nutrient gel was used up, leading to an eventual plateau at completion. This 2-stage growth curve is more pronounced at lower temperatures as can be seen below in figure 2.19. At 385K, the LTA product was found to remain stable, with no sign of secondary crystal phase formation after scanning for 81 minutes, at which time the experiment was stopped. The final product
in this case was a damp, opaque white solid which when washed and filtered produced a fine white zeolite A powder.

![Synthesis curve for LTA](image)

Figure 2.19 – The synthesis curve for LTA formed at 373K from a pre-cursor gel of standard composition, illustrating the 2 stages of crystallisation characteristic of the thick gel produced with Cab-O-Sil M5. The curve was produced from the (220) reflection at 44KeV and the data was corrected for beam decay.

2.4.5.1.2) Ludox HS-40 Stabilised Colloidal Silica.

Pre-cursor gels made using the stabilised colloidal silica source, Ludox-HS40 were found to have the consistency of a runny, semi-transparent gel. A gel of this consistency resulted despite the extra water in the colloidal source (60% wt.) having been compensated for by reducing the quantity of distilled water added to the gel, thus ensuring a constant gel composition. In this case the liquid gel could be easily poured into the autoclave to achieve the desired 50% fill level.

Comparison of the zeolite A synthesis curve for the Ludox HS-40 preparation with that for the Cab-O-Sil preparation shows that LTA reflections appear only 2
minutes later than for the Cab-O-Sil preparation. The gradients of the synthesis curves also indicate a similar crystallisation rate in the initial growth phase for each source. However, at the point where the synthesis curve for the Cab-O-Sil preparation displayed a temporary decrease in crystal growth rate (ca. intensity 3.5), the synthesis curve for the Ludox preparation reaches a maximum. At this point the synthesis curve reaches a plateau and then begins to decrease. This decrease corresponds to the beginnings of formation of the competing hydroxy-sodalite phase as can be seen in figure 2.20 below. The resulting products are a white, opaque solid and a small volume of supernatant liquid. Washing and filtration resulted in a white powder product containing a mixture of LTA and SOD.

**Figure 2.20** – The synthesis curve for LTA synthesised at 385K from a pre-cursor gel made using Ludox HS-40 illustrating the crystallisation and subsequent slow decomposition of LTA and the competitive crystallisation of SOD. These curves were produced from the LTA (220) reflection at 44KeV and the SOD (110) reflection at 60KeV. The data was corrected for beam decay.

The Ludox-HS40 syntheses appear to produce a relatively unstable crystalline zeolite A product when compared to Cab-O-Sil equivalents at equal temperatures. The
zeolite A formed using Ludox HS-40 has a greater tendency to collapse, resulting in formation of hydroxy-sodalite.

2.4.5.1.3) MCM-41 Mesoporous Silica

Using MCM-41 as a silica source produced an opaque white gel with a moderately runny consistency. The MCM-41 appeared to dissolve rapidly in the strongly alkaline environment, during which time a small quantity of noxious smelling fumes similar to ammonia evolved. These fumes may have originated from the breakdown of trace quantities of nitrogenous species remaining within the MCM-41 after calcination.

From figure 2.18 it can be easily seen that the MCM-41 source requires a considerably longer synthesis period to produce zeolite A than either Cab-O-Sil or Ludox. Indeed, no reflections were observed before 51 minutes, a doubling of the induction/nucleation period. The MCM-41 curve again had a distinctive shape, with a period of relatively slow growth from 51 to ca. 64 minutes being observed, followed by a period of more rapid growth until a plateau was reached at completion ca. 76 minutes. This plateau was observed to remain stable until completion of scanning at 100 minutes.

After a synthesis period of 90 minutes, several other peaks began to form. These peaks can not be attributed to either zeolite A or hydroxy-sodalite. Unfortunately, the experiment was stopped before these reflections became large enough for accurate phase identification using laboratory powder X-ray diffraction. Upon repeating this experiment in the laboratory, it was found that different batches
of MCM-41 appeared capable of producing different secondary crystal phases. In one case the zeolite A was found to collapse making way for the formation of hydroxy-sodalite while in another case, the product, under the same synthesis conditions, was found to be a stable mixture of zeolite A and zeolite X. However, it is also possible that the observed reflections marked the beginnings of zeolite Na-P formation. This zeolite has been previously reported as a product of prolonged heating during zeolite A syntheses\textsuperscript{6,49}.

MCM-41 was considered as a possible, although rather expensive silica source for zeolite A after a rather surprising result was obtained in an unrelated experiment. It was discovered that the use of MCM-41 in the synthesis of aluminium rich zeolite beta produced a considerably more crystalline material in the same time compared with a Cab-O-Sil preparation under the same reaction conditions (see appendix 2). Hamdan et al.\textsuperscript{10} have also reported the formation of crystalline Na-A by alumination of purely siliceous MCM-41 and subsequent hydrothermal conversion.

However, while MCM-41 used in the zeolite A synthesis does indeed produce a well crystalline zeolite A sample, it appears from a comparison of intensities (figure 2.18) to be slightly less crystalline than the corresponding Cab-O-Sil preparation. However, as discussed above, the use of MCM-41 does appear to produce LTA with a noticeably smaller particle size than the other sources as indicated by the larger FWHM. The possible mechanisms resulting in these observations are discussed in section 2.4.6.
2.4.5.2) Effect of Water Content

Two different comparative experiments were carried out in order to investigate the effect of changing the water content of the pre-cursor gel on the kinetics and final products of the zeolite A synthesis. Differences in the growth kinetics were noted for both the Cab-O-Sil and Ludox syntheses when extra water was added to the system.

2.4.5.2.1) Cab-O-Sil M5 Fumed Silica

![Graph showing synthesis curves for LTA synthesised at 385K from pre-cursor gel made using Cab-O-Sil M5 and 2 separate water compositions, these being 17.5 H₂O (standard) and 25.8 H₂O (Dilute). These curves were produced from the LTA (220) reflection at 44KeV and the data was corrected for beam decay.](image)

Comparison of two Cab-O-Sil preparations at 385K, one with the standard gel composition (17.5 H₂O) and the other with extra water (25.8 H₂O) resulted in several differences being noted as shown in figure 2.21 above. Firstly, the induction period is longer as would be expected for the more dilute system, although the initial gradients of the growth curves appear similar, indicating that once growth commences it does so at a similar rate for each system. However, when, as described previously, there is
a temporary decrease in the reaction rate and a mini plateau for the standard gel composition, the more dilute sample continues to crystallise at a constant rate until reaching a final plateau at completion. A possible explanation for this two stage versus single stage synthesis will be discussed later in more detail.

Upon reaching completion, it can be seen that the proportion of crystalline material produced during the synthesis with dilute gel is only ca 75% that of the sample with standard composition, which would also be expected as the proportion of nutrients available in the dilute gel for conversion to crystalline material will of course be lower. Comparison of the FWHM reveals virtually identical values, indicating no significant difference in crystallite size between the samples.

2.4.5.2.2) Ludox HS-40 Stabilised Colloidal Silica

In the case of the two Ludox HS-40 syntheses at 421K, it was similarly observed that crystal growth in the dilute system (34.2 H₂O) occurred later than for the standard preparation (17.5 H₂O). In addition, figure 2.22 shows that the dilution of the system inhibited the almost immediate collapse of the zeolite A phase to hydroxy-sodalite observed in the standard preparation. The time gap between formation of the LTA and SOD phases also widened in the dilute system, allowing LTA to form a single phase for several minutes before competitive SOD formation began.
In the preparation with a gel of standard composition, the hydroxy-sodalite phase can be seen to have 2 growth phases. The reduction in SOD growth rate observed between ca 50 and 60 minutes may coincide with the point just after which all of the gel nutrients have been used up in the form of LTA and SOD. Hydroxy-sodalite growth can then proceed at a faster rate once the LTA begins to collapse, enriching the gel with fresh nutrients for SOD crystal growth. As a result of the wider separation between the onset of crystal growth for LTA and SOD in the dilute system, a single growth phase is observed for SOD as the LTA is already in the process of collapsing before the nutrients from the gel can be exhausted.

The rapid collapse of the LTA phase in the standard Ludox synthesis results in there being much less LTA formed than with the dilute prep as indicated by the lower maximum degree of crystallinity shown in the table below. For the SOD phase,
growth was still in progress when the scan ended so it is not possible to compare the final crystallinity of this phase between standard and dilute samples.

**Table 2.5 – Comparative data for hydroxy-sodalite (110) reflections from samples produced using gels containing differing quantities of water.**

<table>
<thead>
<tr>
<th>Water Content</th>
<th>Rel. Deg. of Crystallinity LTA</th>
<th>FWHM (KeV) LTA</th>
<th>Rel. Deg. of Crystallinity SOD</th>
<th>FWHM (KeV) SOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.5</td>
<td>22</td>
<td>1.53</td>
<td>*</td>
<td>2.35</td>
</tr>
<tr>
<td>34.2</td>
<td>49</td>
<td>1.03</td>
<td>*</td>
<td>2.39</td>
</tr>
</tbody>
</table>

* Crystal growth did not reach completion during the period of the *in situ* experiment.

As can be seen from the table above, some interesting information can be gained by comparing the FWHM for each phase. While these values for the SOD phase in each synthesis appeared similar, the FWHM for the LTA phase showed considerable variation. The average FWHM for the sample of standard composition was approximately 50% greater than that of the dilute sample, indicating the formation of much larger crystallites in the dilute gel. It is interesting to note that the FWHM values for the dilute system were found to be very similar to those of the Ludox sample prepared at 385K and discussed earlier. This appears to indicate that by increasing the temperature and thus speeding up the reaction, the formation of smaller crystallites is favoured.

In the hydrothermal synthesis of zeolites, water is not only a solvent. It also stabilises the porous lattices of the zeolite by acting as a space filler. In addition, water molecules are involved in the hydrolysis and reformation of the T-O-T bonds. In a
sense water can, as described by Yang et al.\textsuperscript{50}, be considered to act as a solvent, a reactant and a catalyst during zeolite formation.

The longer synthesis periods of dilute pre-cursor gels and the resulting increase in average crystallite size have been widely reported in the literature\textsuperscript{15}. The larger crystal size is due to a dilute gel having a lower concentration of nuclei. Dilution of gels is a useful strategy when wishing to carry out a detailed study of a normally fast synthesis and when large, single crystals are required. Dilute gels are also required when using techniques such as dynamic light scattering\textsuperscript{44} and solid state NMR\textsuperscript{15} to gain information about the species formed during nucleation.

Yang et al.\textsuperscript{50} carried out a series of studies of zeolite synthesis with controlled quantities of water in essentially non-aqueous systems. They reported that a minimum water content is required in order to initiate crystallisation, while the quantity used can influence the type of zeolite formed. Small quantities of water in a glycerol system act so as to facilitate the hydrolysis of T-O-T bonds and regenerate the hydroxide ions by hydrolysis of the Na-O-R species in the non-aqueous medium. These effects coupled with a decrease in viscosity resulted in an enhancement of the crystallisation rate. However, it was also reported that further increasing the water content of a system resulted in a similar effect to a reduction in alkalinity, i.e. a slowdown in crystallisation rate and an increase in the induction/nucleation period.
2.4.6) Possible Mechanisms for Growth of Zeolite A

This section summarises the observations from the previous 2 sets of experiments dealing with altering aspects of the standard gel composition. Models are postulated for the formation of zeolite A under the different circumstances described above.

2.4.6.1) Cab-O-Sil M5 Fumed Silica

In the case of Cab-O-Sil, the 2-stage growth curve observed could be due to the extremely thick nature of the synthesis gel. The viscous nature of the gel would result in any nuclei that form being trapped within the gel matrix. These nuclei would subsequently grow by using nutrients from the gel immediately adjacent to them until such nutrients became exhausted, resulting in only excess water remaining and the crystallite being temporarily starved. However, as this process continues and more free water become available, the water will mix with and dissolve unreacted gel thus providing a dilute nutrient gel for the nuclei to use for further growth. The growing crystallites would therefore now exist in a less viscous environment and would be transported throughout the gel matrix by the convection currents from heating. These crystallites would thus have access to all the available nutrients until completion. The slower second stage of crystal growth observed during these syntheses can be explained by the more dilute nature of the resulting gel.

Further support for this proposed mechanism of formation comes from the observation that the Cab-O-Sil prep does not exhibit a second growth phase when the
gel is diluted by a factor of around 50%. In this case, the gel is again liquid enough for nuclei to move within it in a reasonably free manner, thus having access to a constant supply of nutrients until completion.

Antonic et al.\textsuperscript{2} discussed the evidence for the formation of quasi-crystalline nuclei formed in the gel and/or at the gel/liquid interface. It was suggested that these nuclei cannot grow within the gel matrix. However, they can grow after release from the gel dissolved during the early stages of crystallisation into the liquid phase. This is a process known as autocatalytic nucleation. The rate of this autocatalytic nucleation and the particulate properties of the resulting LTA depend on the rate of gel dissolution and the number of nuclei inside the gel matrix.

2.4.6.2) Ludox HS-40 Stabilised Colloidal Silica

The pre-cursor gels produced using Ludox HS-40 are very runny compared to those made with Cab-O-Sil, resulting in a single phase of LTA crystal growth. However, these gels form relatively unstable LTA compared to Cab-O-Sil preparations, with the LTA collapsing to form SOD even in comparatively low temperature syntheses. It is possible that both the nature of the gel and this instability are due to the different pH of the colloidal silica compared to fumed silica in water.

To further study the effect of the silica source, several more syntheses were carried out in the laboratory. In the case of the colloidal source, the pH was found to be basic (9-10) while the pH for an equivalent solution of fumed silica and water was found to be mildly acidic (5-5.5). While the large quantity of NaOH used in these syntheses mean that the overall pH of the gel remains unaffected at pH=14, the initial
difference in pH does appear to affect the solubility of the gel components. While Cab-O-Sil is easily mixed to form a uniform gel, the addition of the strong NaOH solution to the Al(OH)$_3$/Ludox HS-40 mixture produces a lumpy, non-uniform gel. This gel only becomes uniform after being heated at the synthesis temperature (368K) for at least 20 minutes. It is possible that the initial non-uniform nature of the Ludox HS-40 gel results in local variations of gel composition, for example where the NaOH does not get uniformly distributed, resulting in a range of pH conditions.

2.4.6.3 MCM-41 Mesoporous Silica

In the case of MCM-41, crystal growth begins much later than for the amorphous silica sources. Hamdan et al.\textsuperscript{10} have reported the synthesis of zeolite A from MCM-41 when attempting to aluminate the MCM-41 sample using a >1 molar solution of NaAlO$_2$ at elevated temperatures (353-393K). At lower temperatures and concentrations of NaAlO$_2$, alumination of the MCM-41 framework occurred. However, while increasing the temperature increased the efficiency of alumination, increasing the NaAlO$_2$ concentration at constant temperature resulted in the progressive disruption of the MCM-41 framework. It may therefore be the case that during the initial stages of the long induction period the MCM-41 became progressively aluminated in the aluminium rich, alkali environment. At a critical point in this process, the framework structure would begin to collapse. The aluminosilicate species thus formed would be expected to take time to decompose to a sufficient extent to provide the building blocks for LTA nucleation, unlike the other silica sources, which are composed of very fine particles and would quickly break down to
monomeric species. The smaller crystallites observed to form in the MCM-41 synthesis may be due to the alumination and decomposition of MCM-41, resulting in the formation of a greater number of nuclei than either the Cab-O-Sil or Ludox HS-40 sources. Such collapses have been observed during the first 10-15 minutes of \textit{in situ} capillary syntheses of LTA with MCM-41 during \textit{in situ} XRD experiments on station 9.3 at the Daresbury SRS as shown in \textit{figure 2.23a}. \textit{Figure 2.23b} shows the diffraction pattern obtained from a capillary containing only the MCM-41 source material for comparison.

It was also noted that some remnant of the template may remain within the MCM-41 even after calcination (See \textit{Appendix 1} for preparation method.). The synthesis of LTA with MCM-41 produces an almost classic sigmoidal growth curve (\textit{figure 2.18}). However, the early slow growth period prior to the main rapid phase of crystal growth appears rather prolonged, which may be a result of the large number of nuclei in the system growing relatively slowly until they reach a size with a large enough surface area for growth to occur at an optimum rate.
Figure 2.23 – a) A stack plot illustrating the decay of MCM-41 when used as the silica source for the \textit{in situ} synthesis of zeolite A on station 9.3 at the Daresbury SRS. b) The diffraction pattern from a capillary containing only the MCM-41 source material. Data were recorded at $\lambda=1.803\text{Å}$. 
2.4.7) Use of a Novel 3-Element Detector Array

A novel 3-element solid state detector array, developed by Birkbeck College London and Daresbury Laboratory\textsuperscript{21-22} enabled the phase transitions occurring at high temperatures to be studied in much greater detail than could be achieved previously with the single element detector. The effects of altering the NaOH content of the gel were also investigated. When, for the single detector, a typical d-spacing range studied would be \textit{ca.} 14-4.5\AA\ (30-90KeV) at \(1.7^\circ\theta\), the middle detector simultaneously allowed extra reflections to be observed in a d-spacing range \textit{ca.} 4.5-2.0\AA\ (30-90KeV) allowing the nature of resulting phases to be ascertained \textit{in situ}. This capability could be vital in the case of a transitory intermediate phase, as it may often prove very difficult to isolate such materials and even if this could be achieved, the act of removing them from the synthesis environment for conventional study could result in their transformation or destruction. Such a transitory intermediate phase has been reported by Francis et al.\textsuperscript{51} in a similar EDXRD study on the oxyfluorinated gallophosphate, ULM-5, using the same \textit{in situ} hydrothermal cell\textsuperscript{17} on station 16.4.

2.4.7.1) Confirming the Nature of Metastable Crystalline Species During Phase Transitions at Elevated Temperatures

An LTA precursor gel of standard composition was heated at a temperature range appropriate to following the crystallisation of zeolite A and hydroxy-sodalite. There had been only one observable hydroxy-sodalite reflection in the previous
experiments but using the 3-element detector allowed \textit{in situ} observation of SOD formation in greater detail. This detector array would also allow recording of the formation of any dense phases such as analcime, which would have exhibited reflections outside the d-spacing range of a single detector experiment.

For this series of experiments, the detector array was set-up with the bottom detector element at $1.70 \pm 0.01^\circ \theta$, resulting in the middle detector being at $4.35 \pm 0.01^\circ \theta$. No reflections of note were seen on the top detector so calibration was not carried out in this case. For the purposes of plotting the growth curves in \textit{figure 24}, the LTA (220) reflection at 48KeV/8.68Å and the SOD (110) reflection at 66KeV/6.52Å were used from the bottom detector. \textit{Figures 2.25 and 2.26} show the indexed diffraction patterns produced by both the bottom and middle detectors for LTA and SOD respectively. At this point in the thesis it becomes convenient to convert the energy dispersive diffraction patterns from an energy scale (KeV) to a d-spacing scale (Å). This avoids any confusion when discussing the different detectors of the three-element detector array as they each operate in a similar energy range but at different fixed angles, thus having unique d-spacing ranges. Such a conversion also makes for easier comparison with conventional diffraction data.
Figure 2.24 – Plots a-c show the results of syntheses carried out at 363, 393 and 413K respectively for a standard LTA pre-cursor gel. Curves were produced using the LTA (220) reflection at 48KeV/8.70Å and the SOD (110) reflection at 66KeV/6.26Å. The data was corrected for beam decay.
The results shown in figure 2.24 a-c are for syntheses performed with gels of standard composition at 363, 393 and 413K. The synthesis at 363K produced a single crystalline phase corresponding to LTA, reflections of which were first observed after 32 minutes. The crystallisation curve exhibited the 2 phases of growth described previously and the LTA remained stable up to 82 minutes when scanning was stopped. Upon increasing the temperature to 393K, zeolite A began to crystallise after 22 minutes and had reached a maximum after 40 minutes, after which it began to slowly collapse. Hydroxy-sodalite began to form at 31 minutes and was still crystallising steadily when the scan was stopped after 90 minutes, at which point both phases were still observed to coexist. Further increasing the temperature to 413K for a third batch of pre-cursor gel resulted in rapid formation of LTA, with reflections first observed at 16 minutes and intensity reaching a maximum five minutes later before collapsing back to almost zero over a period of 24 minutes. Hydroxy-sodalite began to crystallise simultaneously with LTA and was found to be stable when scanning was stopped after 60 minutes. The dominantly SOD diffraction pattern remaining after 60 minutes was found to still exhibit some very weak LTA reflections upon detailed analysis. No other, denser phases were observed to crystallise during the period of the experiment.

Patterns for the LTA and SOD phases produced on both the bottom and middle detectors during the 363K and 413K experiments respectively have been indexed and are shown in figures 2.25 and 2.26 below. Also shown for comparison is the LTA/SOD phase mixture produced during the 393K experiment (figure 2.27). The 'L' symbols in figure 2.26b mark peaks associated with the remnants of the LTA structure.
Figure 2.25 – Indexed diffraction patterns recorded after 39 minutes over a period of 1 minute for the synthesis of LTA at 363K on a) the bottom detector and b) the middle detector of the 3-element detector array at fixed 2θ angles of 1.70±0.01° and 4.35±0.01° respectively. A reflection from the PTFE autoclave liner can be seen on the bottom detector.
Figure 2.26 – Indexed diffraction patterns recorded after 71 minutes over a period of 1 minute for the synthesis of SOD at 413K on a) the bottom detector and b) the middle detector of the 3-element detector array at fixed 2θ angles of 1.70±0.01° and 4.35±0.01° respectively. L indicates remnant LTA peaks in figure 2.26b. A reflection from the PTFE autoclave liner can be seen on the bottom detector.
Figure 2.27 – Energy dispersive diffraction patterns recorded after 90 minutes over a period of 1 minute for the synthesis at 393K, producing a mixture of LTA and SOD as indicated. Data is shown for a) the bottom detector and b) the middle detector of the 3-element detector array at fixed 2θ angles of 1.70±0.01° and 4.35±0.01° respectively. A reflection from the PTFE autoclave liner can be seen on the bottom detector.
2.4.7.2) NaOH – The Effects of Sodium Concentration and Alkalinity

It was found that reducing the NaOH content of the gel by 50% from the standard composition (1.0 NaOH) resulted in the formation of a thicker, more viscous pre-cursor gel. No crystalline material was observed to form after this gel was subjected to hydrothermal conditions for 90 minutes at 363K. In comparison, increasing the NaOH content of the gel by 50% resulted in a ‘soapy’ gel with a less viscous texture than a gel of the original composition. It can be seen in figure 2.28 below, that the presence of the extra NaOH had a marked impact on the kinetics of the system. The LTA phase only exists very briefly, breaking down after less than 5 minutes while SOD begins to crystallise almost simultaneously. This is similar to the effect that would be expected by conducting the synthesis at a much higher temperature for a gel containing the standard quantity of NaOH. The pattern of reflections on the middle detector confirmed the formation of hydroxy-sodalite although no dense phase material was observed after 60 minutes.
Figure 2.28 – Plots a and b show the results of syntheses carried out at 363K for a) the standard LTA pre-cursor gel containing 1.0NaOH and b) a gel with 1.5 NaOH. Lines have been plotted between the points in (b) for reasons of clarity. Curves were produced using the LTA (220) reflection at 48KeV and the SOD (110) reflection at 66KeV. The data was corrected for beam decay.
As would be expected with such a fast reaction, the mean FWHM for the NaOH enriched gel (2.58KeV) was noticeably larger than that for the gel of standard composition (2.08KeV) indicating that the faster reaction produced smaller crystallites as would also occur at higher temperatures.

It is well known that increasing the NaOH content\textsuperscript{14,52} increases the speed of nucleation and crystallisation in a zeolite gel system. NaOH can also affect the yield and even the type of zeolite phase formed. There are two factors to consider when studying these effects. Firstly the influence of the sodium cations on the system and secondly the influence of the alkalinity.

Schoeman et al.\textsuperscript{52} found that varying the NaOH content of a pre-cursor gel influenced the final product, with zeolite Na-Y being formed below a certain critical level and zeolite A being formed above this level. Further increasing the NaOH content of the gel resulted in shorter crystallisation times and a higher yield of product as indicated by an increase in the ultimate crystallinity. However, upon investigating hydroxy-sodalite formation, they found that the amount of alumina and not sodium was the crystal growth-limiting nutrient.

Yang et al.\textsuperscript{50} discuss the structure directing role of sodium ions, whereby the Al and/or Si species are drawn together on the interface of the solvated cations. These species polymerise under the continuing influence of the cations and form the pre-cursor structures of the zeolite framework. They found that increasing the Na content of a pre-cursor gel while keeping the alkalinity constant (using NaCl) could favour the formation of analcime in a zeolite omega pre-cursor gel. Similar structure directing properties were also found for K, Rb and Cs. They also report that the Si/Al ratio of the zeolite product tends to decrease with increasing molar Na\textsubscript{2}O concentration. This influence is primarily attributed to the variation in the alkalinity of the synthesis
mixture. The increasing alkalinity causes dissolution of silica to a greater extent than alumina, resulting in an Al-enriched product. This would explain the observation of Schoeman et al.\textsuperscript{52} that zeolite A (Si/Al \textasciitilde 1) is favoured over zeolite Y (Si/Al > 1.5) with increasing NaOH.

Antonic et al.\textsuperscript{2} reported that the presence of hydroxyl ions in the reaction mixture determines the concentrations of reactive aluminate, silicate and aluminosilicate species in the liquid phase, as well as their chemical and structural characteristics. The constant Si/Al ratio of the reaction mixture, the Si/Al ratio in the initial amorphous aluminosilicate gel and the Si/Al ratio in the final product of crystallisation respectively depend on the concentration of hydroxyl ions in the reaction mixture.

In many cases even the type of zeolites crystallised from the reaction mixture with a constant Si/Al ratio strongly depends on the alkalinity of the system. On the other hand the increase in alkalinity causes an increase in the crystallisation rate via an increase in the crystal growth rate and/or nucleation rate consequent to an increased concentration of reactive silicate, aluminate and aluminosilicate species in the liquid phase of the crystallising system. In that case it can be assumed that the influence of alkalinity on the nucleation of zeolites is related to its influence on the formation and distribution of nuclei in the gel matrix.
2.5) Further Changes to Pre-cursor Gel Composition

As can be seen from the examples in this chapter, there are a great many interesting comparative experiments possible using the \textit{in situ} EDXRD technique to study the zeolite A system. It was however considered unnecessary to carry out a comprehensive survey of the effects of varying all the major parameters in the synthesis of zeolite A. We therefore decided that, due to the large amount of data already available in the literature for this system and the constraints of limited beam-time, this work was best extended to other more challenging systems such as the aluminophosphates and titanosilicates described in the following chapters. A brief summary of the effects of varying a range of other synthesis parameters follows, based mainly on a review of current literature.

2.5.1) Other Silica Sources

As previously mentioned, metakaolin can be used to prepare zeolite A. This source has provoked much interest as a means of producing LTA by a stoichiometric method therefore cutting down on waste during production, which would have positive effects for both the economics of LTA production and the environment\textsuperscript{16}. Other possible sources of silica include sodium silicate and also organic sources such as tetra-ethyl orthosilicate\textsuperscript{14}. However, it was found that the use of such organic sources resulted in the slow formation of poorly crystalline LTA which had a tendency to transform to zeolite P.
2.5.2) Aluminium Sources

In addition to the Al(OH)$_3$ used throughout these experiments and metakaolin with an Si/Al ≈ 1, other inorganic aluminium sources including sodium aluminate can be employed in addition to organic sources such as aluminium isopropoxide. Round et al.$^{14}$ found that the aluminium source had a major effect on the crystal morphology of the resulting LTA crystals, while Na Aluminate tended to produce sharp edged, cubic crystals, the use of aluminium isopropoxide produced crystals with the chamfered edges favoured in industrial production.

2.5.3) Silicon/Aluminium Ratio

The Si/Al ratio has a profound effect on the resulting crystal phase. For a zeolite A gel with an Si/Al less than 1.5, LTA tends to form, while increasing the Si/Al ratio above this level results in the formation of zeolite Y.$^{52}$ Increasing the Si/Al in conjunction with reducing the alkalinity tends to produce zeolite Na-P.$^{49}$ Within the Si/Al range for LTA formation, increasing the Al concentration results in the formation of progressively smaller crystals that increasingly depart from the sharp edged cube morphology toward a truncated octahedral morphology as the edges of the cube become increasingly chamfered.$^{3}$
2.5.4) Use of Organic Compounds

While an organic template molecule is not required for the crystallisation of zeolite A, several studies have been carried out with this system, using organic compounds for a variety of purposes. Basaldella et al.⁴ and Fulcher et al.⁷ used triethanolamine in the synthesis of LTA from metakaolinite. This acted to slow down the LTA synthesis and produce larger product crystals. The triethanolamine was believed to have caused the slower reaction both by complexing with the Aluminium and acting to reduce the pH of the gel. The triethanolamine thus acted to control nucleation in the gel. Other organic amines have also been found to act as complexing agents with aluminium and they act to influence significantly both the size and morphology of the zeolite A crystals.²⁶

Yang et al.⁵⁰ used glycerol as an alternative solvent in order to investigate the effects of using only very small, controlled quantities of water in a mainly non aqueous zeolite pre-cursor gel. LTA was successfully synthesised with only a very small proportion of the water normally used.

2.6) Zeolite A Synthesis – The Accepted Model

This section summarises in the light of the results presented in this chapter, the current generally accepted mechanisms by which zeolite A is synthesised from an amorphous pre-cursor gel. Prior to any crystallisation being observed, there is a period of induction/nucleation during which time the silicon and aluminium sources undergo dissolution possibly to species as small as the basic Si(OH)₄ and [Al(OH)₄]⁻ units. In
**situ** solid state NMR evidence from Shi et al.\textsuperscript{15} indicates that no NMR observable quantities of more complex soluble aluminosilicate or silicate species, indicative of possible secondary building units are observed. The only species observed in these studies were amorphous Al(OSi)\textsubscript{4} units, a small amount of Si(OH)\textsubscript{4}, [Al(OH)\textsubscript{4}]\textsuperscript{−} and the growing zeolite phase.

The evidence gained by Shi et al.\textsuperscript{15} further indicated that crystallisation occurred by a solution mediated mechanism. Si(OH)\textsubscript{4} and [Al(OH)\textsubscript{4}]\textsuperscript{−} ions formed by rapid dissolution of the gel are rapidly deposited on the growing zeolite surface. It was postulated that much of this transformation occurs in the vicinity of the solid gel phase.

The solution-mediated mechanism appears to be generally accepted and Cizmek et al.\textsuperscript{6} describe the chain of events occurring in this process as follows. Firstly the gel undergoes dissolution in the hot alkali solution. This results in super-saturation of the liquid phase with soluble silicate, aluminate and/or aluminosilicate species. Nuclei of the stable crystalline phase begin to form in this supersaturated solution. Crystal growth can then occur from these nuclei.

The results presented in this chapter are fully compatible with these models. In particular we recall that our measured activation energy was close to that calculated for condensation of two silicate monomers\textsuperscript{20}, a result which is clearly in line with a mechanism involving addition of silicate monomers to the growing nucleus.
2.7) Summary and Conclusions

*In situ* EDXRD is a valuable technique for the study of metastable systems such as the zeolite A – hydroxy-sodalite system under realistic synthesis conditions. The high quality of data obtained from such a study can be used in an attempt to model quantitatively the processes occurring during crystallisation. However, the current limiting factor in this regard is the lack of a single model that accurately accounts for the various processes occurring during crystallisation. In lieu of such a model, a relatively simple but commonly used empirical approach has been used in order to gain a measure of the energy of activation for zeolite crystallisation. As noted, the results agree with those achieved by others experimentally and with theoretical studies. The theoretical study suggests that the activated process relates to the condensation reaction involving formation of Si-O-Si bridges.

Higher temperature studies of the zeolite A system showed that the LTA phase was metastable, breaking down and being replaced by hydroxy-sodalite. Analysis of this competitive formation indicated that hydroxy-sodalite nucleated and grew independently of the zeolite A, while the destabilising factor for zeolite A appeared to be the synthesis temperature.

Qualitative studies of the effect of using a range of different silica sources showed differences in the stability of the resulting crystal phases as well as in the yields of the products and average crystal sizes. Furthermore, the different shapes of the synthesis curves appear to suggest differences in the processes occurring during crystallisation. Models have been proposed based around these observations in order to link these observations with plausible mechanisms of crystallisation.
The effects of altering the water and NaOH contents of the pre-cursor gel agree with the observations of others reported in the literature. Dilution of the gel results in slower zeolite formation with an increase in particle size. Increasing the NaOH content causes a speeding up of the synthesis with LTA rapidly decomposing and being replaced by hydroxy-sodalite.

The replacement of the single detector with a new 3-element detector array allowed a much wider d-spacing range to be studied at one time. This allowed any crystalline phases to be identified in situ with much more accuracy. It would also have allowed the formation of any dense phases such as analcime to be observed in the high temperature studies. However, in this case no such phases were observed.

The high-energy white radiation beam on the zeolite A system was not found to noticeably speed up syntheses compared to experiments outside the beam, unlike for certain other microporous materials as described later. However, it is important to consider carefully the possible effects of radiation and take account of these in such studies especially when considering comparison with standard laboratory synthesis methods.
2.8) References


28) Collaborative Computational Project 14 – CCLRC Daresbury Laboratory.


32) Budd P.M., Myatt G.J., Price C., Carr S.W., Zeolites (1994) 14, 198-204.


Chapter 3

An In Situ Structural Study of the Competitive Crystallisation of Microporous Aluminophosphates and their Cobalt Substituted Derivatives with Changing Synthesis Conditions

3.1) Chapter Overview

Since the initial discovery of a range of novel microporous aluminophosphate structures by Union Carbide in 1982\(^1\), there has been a great deal of interest in the structures and properties of these materials and their catalytically active, heteroatom substituted, derivatives. The basic classification of these materials is as AlPO\(_4\)-n where n denotes the structure type, however they are normally referred to simply as AlPO-n. This chapter describes a systematic study of the synthesis of these AlPOs and their cobalt substituted derivatives which was carried out using in situ EDXRD as described in the previous chapters to monitor their crystallisation over a wide composition range: all of the syntheses are variants of a standard recipe for AlPO-5\(^2\,^3\).

As described later in more detail, the neutral aluminophosphate framework is not suitable for use as a heterogeneous catalyst. However, addition of divalent or tetravalent heteroatoms such as cobalt, manganese or silicon produces a negatively charged framework capable of acid catalysis in the protonated form\(^4\,\ldots\,11\). Additionally, for transition metals with multiple oxidation states, redox properties allow oxidation reactions to be catalysed \(^12\,\ldots\,13\). These heteroatom-substituted materials are classified as MeAPOs, SAPOs and MeAPSOs where Me refers to a divalent heteroatom such as cobalt and S refers to tetravalent silicon. Due to the wide range of framework
architectures formed by these materials, combined with the possibility of introducing catalytic properties, there is a great deal of interest in MeAPOs as shape selective catalysts with a wide range of potentially novel applications in the petroleum and fine chemical industries.

A study of the synthesis of the aluminophosphate AlPO-5 (AFI) was initially carried out over a range of temperatures using the triethylamine (TEA) template in order to observe the effect of altering the synthesis temperature on the crystallisation kinetics. This work was later extended to consider the effects of using a range of other organic template molecules on the kinetics and stability of the resulting crystal phases.

Varying quantities of cobalt were subsequently substituted for aluminium in the pre-cursor gels and these CoAlPO (or CoAPO) gels were also investigated in situ with several different template molecules over a range of reaction conditions. The addition of cobalt was found to have a profound effect both on the crystallisation kinetics and the nature of the resulting products. The relationship between the nature of the template molecule and the cobalt was also found to be fundamental in determining the nature of the resulting phases as was the concentration of cobalt used and the synthesis temperature. Both the size and basicity of the templates were considered when proposing mechanisms for these observations. Our data were compared to studies carried out by others using a variety of experimental and theoretical approaches. Various mechanisms for template heteroatom-framework interactions proposed from these studies have subsequently been discussed.

These in situ EDXRD investigations were once again performed using the energy dispersive diffractometer on station 16.4 of the Daresbury SRS, using the modified hydrothermal cell described in previous chapters. Initial studies were carried out using a single element detector array, however, the subsequent availability of a multi-
element detector\textsuperscript{15-16} proved extremely useful for distinguishing between a range of different cage structures found to crystallise competitively with the AlPO-5 (AFI) channel structure. In some cases these phases were found to have only subtle structural differences, requiring data collected over a wide d-spacing range in order to distinguish between them. Such differences were made even more difficult to detect owing to the relatively dilute nature of the gel producing a broad hump due to water absorption.

Further work on these systems is reported in chapter 4, involving substitution of a range of heteroatoms into the aluminophosphate gels. For these latter studies, \textit{in situ} EDXRD will once again be used to investigate the kinetics of crystallisation of the MeAPOs. In addition, an investigation of the local environment of many of the heteroatoms within the product frameworks will be described, using Extended X-ray Absorption Fine Structure (EXAFS) to ascertain the extent of framework substitution. These systems are then compared to the AIPO and CoAIPO systems discussed in the present chapter.
3.2) AlPO-5 Structure & Properties

Aluminophosphate molecular sieves have general compositions based on the formula, \( x\text{R}:\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:y\text{H}_2\text{O} \) where \( \text{R} \) is generally an amine or quarternary ammonium species added to the pre-cursor gel as a template molecule. The quantity \((x+y)\) represents the total amount of template and water molecules required in order to fill the microporous void of the final framework. These structures are composed of a strict 3-dimensional alternation of \( \text{AlO}_4 \) and \( \text{PO}_4 \) tetrahedra resulting in the formation of a neutral framework. Most such aluminophosphates have 3-dimensional structures but some are layer compounds while others occur as dense phases\(^{17}\).

AlPO-5 has a large pore structure with the hexagonal space group \( \text{P6cc} \) and cell dimensions \( a=b=13.740\text{Å} \) and \( c=8.474\text{Å} \) where \( \alpha=\beta=90^\circ \) and \( \gamma=120^\circ\). This structure consists of columns of twisted 4- and 6-rings forming a one dimensional 12-ring cylindrical channel system parallel to the \( c \)-axis. These channels have a diameter of \( 7.3\text{Å} \) and can be seen in figure 3.1 below\(^{19}\).

![Figure 3.1 - The AlPO\(_x\)-5 (AFI) structure illustrating the large unidirectional 12-ring channels. The aluminate and phosphate tetrahedra are coloured in pink and purple while bridging oxygen atoms are red.](image-url)
The pore size of AFI is comparable with those for the large pore aluminosilicates such as faujasite (FAU) and zeolite L (LTL). AlPO-5 has been synthesised with several different organic template molecules, while samples have also been produced incorporating a range of heteroatoms including cobalt, discussed in this chapter and a range of other elements such as manganese, zinc, magnesium, iron and silicon, discussed in chapter 4. In addition, combinations of these heteroatoms can produce materials such as CoAPSO-5, which contains both cobalt and silicon. These heteroatoms introduce a negative charge imbalance which, when compensated by a proton upon removal of the template molecule by calcination, produces Brønsted acid sites which are responsible for giving MeAPO-5 acid catalytic properties. Additionally, substitution of metal ions such as cobalt and manganese allow the additional possibility of redox catalysis where the ions can be raised to a higher oxidation state, for example $\text{Cu}^{2+} \leftrightarrow \text{Cu}^{3+}$, and subsequently easily reduced. Such MeAPOs therefore have the ability to catalyse oxidation reactions.

As a result of the relatively recent discovery of the MeAPO materials in comparison to the aluminosilicates and the need for often expensive organic template molecules, the industrial exploitation of these materials has so far been on a much smaller scale than for traditional aluminosilicate zeolites. However, materials such as CoAlPO-18 have demonstrated high levels of catalytic activity for the conversion of methanol to light alkenes such as ethylene and propylene, while both SAPO-18 and SAPO-34 (silicon substitution) have proved to be effective acid catalysts for methanol to olefin (MTO) reactions.
3.3) The Synthesis of Microporous Aluminophosphates

Microporous aluminophosphates are generally synthesised under hydrothermal conditions at a neutral to mildly acidic pH in the presence of an amine or tetraalkyl ammonium species. A commonly used source of phosphate is concentrated (typically 85%) phosphoric acid, which is generally diluted and then mixed with an aqueous solution of an aluminium source such as aluminium hydroxide, aluminium triisopropoxide or a powdered mineral source such as the hydrated aluminium oxide, pseudo-boehmite.¹⁹

When heteroatom substitution is required, a soluble source such as the metal acetate or in the case of silicon, fumed silica, is usually dissolved to form an aqueous solution and then added to the aluminium source. The final step in the production of a pre-cursor gel is the addition of the organic template.

Alternatively, very large pore aluminophosphates such as VPI-5, JDF-20 and gallophosphates such as cloverite are often produced in a non-aqueous environment. Such structures are difficult to synthesise and tend to collapse or transform to another microporous phase, for example VPI-5 \( \Rightarrow \) AlPO-8 and AlPO-H2 \( \Rightarrow \) Tridymite upon calcination to remove the template species.³²
3.4) Experimental

3.4.1) Synthesis

The preparation of a standard aluminophosphate pre-cursor gel is described in addition to the subsequent modification of this gel by changing the nature of the organic template molecule and substituting small quantities of aluminium by cobalt. Subsequent synthesis conditions are also described, with samples being treated hydrothermally over a range of temperatures.

3.4.1.1) An In Situ Study of the kinetics of AlPO-5 Synthesised with a Range of Different Organic Template Molecules

Batches of AlPO-5 pre-cursor gel with the composition $\text{Al(OH)}_3:1.5\text{H}_3\text{PO}_4:0.8\text{R}:30\text{H}_2\text{O}$ were produced using a standard synthesis procedure\textsuperscript{2-3} as described below (where R represents triethylamine (TEA), tetraethylammonium hydroxide (TEAOH), tripropylamine (TPA) and tetrapropyl-ammonium hydroxide (TPAOH)).

1) Appropriate quantities (see table 3.1) of distilled H$_2$O were added to 3.46g of 85% H$_3$PO$_4$ (Aldrich) in a PTFE beaker and the mixture was stirred thoroughly.

2) 1.56g of Al(OH)$_3$ (Aldrich) were then slowly added to this mixture and the resulting mixture stirred until the ‘fizzing’ had stopped.

3) An appropriate quantity (see table 3.1) of the template was then added dropwise to the mixture with stirring. Where necessary, as described in the table below, the
quantity of H$_2$O used in step 1 was modified to account for the differing dilution of the templates in their commercially available forms. In each case, a temporary thickening of the gel was observed upon addition of the template with the gel subsequently thinning with continued stirring.

Table 3.1 – Template and water contents for a range of aluminophosphate gels containing different template molecules.

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<thead>
<tr>
<th>Template Used</th>
<th>Conc. in H$_2$O (Wt. %)</th>
<th>Template Required</th>
<th>H$_2$O Required in Step 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA (Aldrich)</td>
<td>&gt;99%</td>
<td>1.56g</td>
<td>10.8g</td>
</tr>
<tr>
<td>TEAOH (Aldrich)</td>
<td>35 Wt.% in H$_2$O</td>
<td>6.74g</td>
<td>6.41g</td>
</tr>
<tr>
<td>TPA (Aldrich)</td>
<td>&gt;99%</td>
<td>2.29g</td>
<td>10.8g</td>
</tr>
<tr>
<td>TPAOH (Aldrich)</td>
<td>25 Wt.% in H$_2$O</td>
<td>13.02g</td>
<td>1.04g</td>
</tr>
</tbody>
</table>

4) The resulting gels were poured into a PTFE autoclave liner and sealed within the modified in situ cell$^{14}$ on station 16.4 at the Daresbury SRS. Samples were subsequently heated at several temperatures in the range 423-475K, during which time in situ Energy Dispersive X-ray Diffraction data were collected as described in greater detail below.
3.4.1.2) The Effect of Cobalt Substitution on the *In Situ* Synthesis of CoAlPO-5 Over a Range of Cobalt Concentrations and with Several Different Template Molecules

The above procedure for the synthesis of aluminophosphate gels was modified as described below in order to substitute aluminium for a range of cobalt compositions.

1) An appropriate quantity of cobalt (II) acetate (Aldrich) calculated as shown in *table 3.2* below was dissolved in the minimum amount of H$_2$O. The remaining H$_2$O was then added to the H$_3$PO$_4$.

*Table 3.2 – Modifications to the standard pre-cursor gel recipe required for various levels of cobalt substitution.*

<table>
<thead>
<tr>
<th>Cobalt Conc. (Mole fraction)</th>
<th>Wt. Of Co(II) Acetate</th>
<th>Aluminium Conc. (Mole fraction)</th>
<th>Wt. Of Al(OH)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00g</td>
<td>1.00</td>
<td>1.56g</td>
</tr>
<tr>
<td>0.02</td>
<td>0.10g</td>
<td>0.98</td>
<td>1.53g</td>
</tr>
<tr>
<td>0.03</td>
<td>0.15g</td>
<td>0.97</td>
<td>1.515g</td>
</tr>
<tr>
<td>0.04</td>
<td>0.20g</td>
<td>0.96</td>
<td>1.50g</td>
</tr>
<tr>
<td>0.06</td>
<td>0.30g</td>
<td>0.94</td>
<td>1.47g</td>
</tr>
<tr>
<td>0.08</td>
<td>0.40g</td>
<td>0.92</td>
<td>1.44g</td>
</tr>
<tr>
<td>0.10</td>
<td>0.50g</td>
<td>0.90</td>
<td>1.40g</td>
</tr>
</tbody>
</table>
2) The resulting red solution was added to the aluminophosphate mixture in the 
PTFE beaker with stirring prior to the final addition of the template. This resulted 
in the liberation of acetic acid as indicated by a 'vinegary' smell.

3) Upon addition of the template the gel thickened and then thinned again upon 
stirring, resulting in the formation of a pink or purple gel.

4) Gel samples were again treated hydrothermally over a range of temperatures and 
\textit{in situ} EDXRD data were recorded.

3.4.2) Data Collection

EDXRD data were recorded on station 16.4 at the Daresbury SRS as described 
in previous chapters. These data were collected using both a single element solid-state 
detector and subsequently a 3-element detector \textsuperscript{15,16} described in more detail in \textit{chapter} 
1. In both cases, the detector array was set at a fixed angle in the range 1.2-1.8° 20. 
Scans were recorded every 60 or 120 seconds over a typical period in the range 40- 
180 minutes.

Conventional X-ray diffraction patterns of the final products were recorded on 
a Siemens D500 diffractometer with a pre-sample monochromator set for Cu-K\textalpha_1 
radiation. Scans were collected over an angular range 5-50°20 and typically recorded 
over 10-12 hours.
3.4.3) Data Analysis

Using a similar methodology to that previously described for zeolite A in chapter 2, the DLconvert and Xfit packages from CCP14 at Daresbury were used first to convert the EDXRD data into an appropriate format and then to fit the areas under each reflection. The resulting data were then analysed using the Microsoft Excel package in order to compare the synthesis curves for each crystalline phase as a function of time. Scans were recorded every 60 or 120 seconds and the peak intensity was used as a gauge of the changing crystallinity of each crystal phase. Throughout this chapter, where individual diffraction patterns are shown, the energy scale of the data has been converted to d-spacing using DLconvert for ease of comparison between different experiments. These patterns have been plotted with Microcal Origin 5.0.

Conventional laboratory X-ray diffraction data were compared with standards from both the JCPDS crystal structure database and the Collection of Simulated XRD Powder Patterns for Zeolites. A direct comparison between these data and the EDXRD data was enabled using the Dragon program available on XRDSV1 at the CCLRC Daresbury Laboratory.
3.5) Results and Discussion

3.5.1) Aluminophosphates

3.5.1.1) The Crystallisation of AlPO-5 Using the Triethylamine Template Molecule Over a Range of Synthesis Temperatures

Synthesis of AlPO-5 (AFI) with the precursor gel composition Al(OH)$_3$:1.5H$_3$PO$_4$:0.8NEt$_3$:30H$_2$O was attempted over a wide range of temperatures. It was found that, in agreement with the observations of others$^{19}$, at temperatures below *ca.* 423K, no crystalline phase formation was observed. AFI formation was observed to crystallise above *ca.* 433K as can be seen in figure 3.2a and b, which show data from the bottom and middle detectors respectively.

Further increasing the temperature resulted in a decrease in the induction periods prior to the observation of crystal growth and a corresponding increase in the crystallisation rate as shown in figure 3.3 below. However, above *ca.* 473K, the AFI phase becomes increasingly unstable and tends to collapse, forming a range of dense phases such as berlinite, cristobalite or tridymite, the nature of the resulting phase being dependant on the reaction conditions. Such dense phases have also been reported in aluminophosphate syntheses where no template was added to the precursor gel$^{19}$. 
Figure 3.2 – Indexed data sets collected for the synthesis of AlPO-5 with triethylamine (TEA) template at 443K after 40 minutes. Data sets are from a) the bottom detector at a fixed angle of $1.29^\circ$ and the middle detector at a fixed angle of $4.08^\circ$. Scan duration was 1 minute.
Figure 3.3 – Comparative crystallisation curves for AlPO-5 synthesised over a range of temperatures using triethylamine (TEA) as the organic template molecule. The induction period is observed to decrease in an approximately linear fashion as a function of increasing temperature. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.

Under the chosen reaction conditions, the optimum temperature range for synthesis of stable AlPO-5 samples lies between ca. 433-473K. For samples formed within this temperature range, such as shown in figure 3.3, a comparison of the intensity data corrected for beam decay indicates a similar degree of crystallinity for the final products. A similar comparison of the mean FWHM values at completion of crystallisation as an indication of average crystallite size also produces very similar values in the range 1.14-1.17KeV, indicating that within this temperature range the crystallites formed were of similar dimensions.

Quantitative kinetic investigations of the activation energies of crystallisation have previously been reported by Christensen et al.\textsuperscript{35} for similar aluminophosphate systems, including MnAPO-5 (AFI), using \textit{in situ} powder X-ray diffraction. Calculations were carried out using a simple empirical treatment based on the Avrami equation, in a similar way to that described for Zeolite A in chapter 2. Their reported
result for MnAPO-5 (ca. 81 kJmol\(^{-1}\)) was of a similar order to the activation energy that we obtained for zeolite A (ca. 55 kJmol\(^{-1}\)). However, they also reported, as we too found, that the Avrami expressions did not give a good fit to their data. We refrained from carrying out a similar study due partly to the problems discussed in chapter 2 for activation energy values obtained using relatively simple models, but mainly due to a reduction in data quality obtained for the aluminophosphates compared to the zeolite A samples. This reduction in data quality was believed to be due to the much more liquid nature of the aluminophosphate gels, resulting in the formation of convection currents within the reaction vessel that caused periodic perturbations in the intensity of reflections.

3.5.1.2) The Kinetics of AlPO-5 Formation with a Range of Organic Template Molecules

Template molecules, typically amines or tetraalkyl ammonium salts are generally required for the successful synthesis of microporous aluminophosphates. If template is omitted, a dense phase such as tridymite normally forms, while slowly increasing the quantity of template results in a gradual increase in the proportion of microporous material up to an optimum value. However, most syntheses including those described in this chapter use an excess of template.

It has been well established that AlPO-5 can be synthesised with a range of organic template molecules\(^2\) 19 20 22. However, little work has been carried out on a comparison of the crystallisation kinetics of AlPO\(_4\)-5 formed with these different templates. Hence, a systematic \textit{in situ} study was carried out for a range of templates in
order to compare the formation kinetics with the structure of the template under otherwise identical synthesis conditions. To this end, a series of pre-cursor gels were prepared using the standard method\(^2\)\(^-\)\(^3\) described previously. The templates used in this case were, triethylamine (TEA), tetraethyl ammonium hydroxide (TEAOH), tripropylamine (TPA) and tetrapropyl ammonium hydroxide (TPAOH). The addition of each of these templates to an aluminophosphate pre-cursor gel had previously been reported to produce the AFI structure\(^2\)\(^,\)\(^19\)\(^,\)\(^20\)\(^,\)\(^22\)

![Graph showing comparative crystallisation curves for the synthesis of AlPO\(_4\)-5](image)

**Figure 3.4** - Comparative crystallisation curves for the synthesis of AlPO\(_4\)-5 carried out at 443K with a range of organic template molecules and illustrating the differences in kinetic behaviour and stability of the resulting AFI. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.

*Figure 3.4* above, shows what appears to be a distinct correlation between the size of the template molecule and both the kinetics of crystal formation and resulting stability of the crystalline AFI product. Increasing the size of the template molecule both slows down the crystallisation rate and increases the induction period before crystallisation is observed. Additionally, we see that increasing the template size also
decreases the stability of the resulting AFI phase. TEA forms a stable product while the use of TPAOH results in a rapid collapse of the AFI structure to an amorphous phase.

A comparison of the degrees of crystallinity with each template indicated by the intensity may be suggested to indicate differences between the template types, with the trialkyl-amine templates producing a product with a similar level of crystallinity and the tetraalkyl-ammonium hydroxide tending towards a higher degree of crystallinity. This is a somewhat tentative observation because of the collapse in each case of samples made with TPA and TPAOH, but it does appear that prior to a rapid collapse, the TPAOH sample was still undergoing rapid growth and had surpassed the maximum intensity reached by the TEA and TPA samples. As discussed below, this may be due to the different basicities of the two different types of template. However, a similar comparison of the values of the full width of the (100) reflection at half-maximum in each case as an indication of average particle size did not exhibit a trend with FWHM values being in the range 1.83-1.94KeV in each case. Therefore, considering the organic template molecules in this study, the nature of the template does not appear to affect the particle size of the AFI product.

It was additionally found that the use of TEAOH resulted in the formation of a small quantity of a second crystal phase later identified as AlPO-18 (AEI) and shown in figure 3.5a. This pure aluminophosphate AEI phase has previously been reported to form with the TEAOH template only when aluminium isopropoxide has been used as a source. AEI is a medium pore (3.8Å) cage structure related to the chabazite structure (CHA) and is described later in detail.

The crystallisation curves of these two competitive phases can be seen in figure 3.5b. The minority AEI phase began to crystallise several minutes after the AFI
phase at a point when formation of the majority phase was approaching completion. This observation suggests that the conditions for AEI formation become favourable only after the initial gel composition has been largely depleted of aluminate and phosphate species. Such a gel would contain proportionately less aluminate and phosphate and proportionately greater quantities of template and water and will also have a higher pH. This hypothesis is supported by the observation that a gel of uniform consistency separates during hydrothermal synthesis to form a solid precipitate and a transparent liquid containing both excess organic and water, as was expected from the initial gel composition.

It should also be noted that the FWHM value upon completion of crystallisation for the minority AEI phase (2.8KeV) was found to be considerably broader than the associated AFI phase (1.9KeV). This indicates a smaller average particle size for the AEI phase.
Figure 3.5 - a) An in situ EDXRD pattern recorded after 60 minutes at 443K illustrating the formation of a small quantity of AlPO-18 (AEI) in addition to AlPO-5 (AFI) as a secondary phase. b) Comparative crystallisation curves for the competitive crystallisation of AFI and AEI carried out at 443K using a standard pre-cursor gel with tetraethyl-ammonium hydroxide (TEAOH) as the template molecule. Data were plotted from the AFI (100) and AEI (110) reflections and have been corrected for beam decay and intensity.
An investigation of the differences between the organic template molecules illustrates some of the differences in both physical properties and chemistry that may account for the observed differences in the aluminophosphate syntheses. Their size increases from the smallest, TEA through TEAOH then TPA to the largest TPAOH. The size factor alone may have a major influence on the stability, with TEA and TEAOH being accommodated comfortably within the channel system of AFI. However, TPA and TPAOH may be large enough to put increasing strain on the channels, causing the collapse of the ordered AFI structure shortly after crystallisation in the case of TPA and during crystallisation in the case of TPAOH. However, the use of a larger template molecule may be expected to produce a correspondingly larger framework structure, for example with a 14-Ring channel system. The reason this does not happen could be that such a structure, if it can exist, is inherently unstable under these synthesis conditions, or that the increase in template size is not sufficient to allow a larger framework structure to crystallise around it.

A second factor to consider is the basicity of the template molecules. Tertiary amines such as TEA and TPA are weak bases, with TPA being slightly the stronger of the two. In comparison, quaternary ammonium hydroxides such as TEAOH and TPAOH are strong bases equivalent in strength to sodium or potassium hydroxide. However, in aqueous solution, the aminium ions stabilised from primary and secondary amines are stabilised by solvation much more effectively than are the ions formed from tertiary amines. Therefore, in aqueous solution tertiary amines are less basic than the corresponding secondary ions.

These basicity differences may also be factors influencing the differences observed during the aluminophosphate syntheses. The TEAOH and TPAOH will react
with the excess H$_3$PO$_4$ in solution, increasing the pH of the gel slightly and forming large quaternary ammonium phosphate complexes $[(CH_3)_4N\]^3P_04^3$. This pH increase and corresponding alteration in the gel chemistry may have the effect of producing conditions suitable to the formation of the AlPO-18 secondary crystal phase seen for TEAOH. No such phase was observed in the case of TPAOH which may have been due to the rapid collapse of the AFI well before the equivalent stage at which AEI was first observed in the TEAOH experiment.

There has been a great deal of interest in the role of the template in the formation of aluminophosphates and the closely associated role of gel pH.$^{19,22,37-40}$ Such studies have provoked much debate as to whether the template molecule is mainly a vehicle for increasing the gel pH to a suitable level for crystallisation of a specific microporous phase, or alternatively acts mainly in a shape directing capacity. Current thinking tends towards a dual effect, where small quantities of the template act in a shape directing capacity, while increasing the template levels to an excess mainly acts to increase the overall pH of the system, thus tending to affect the crystallisation kinetics.$^{22}$ It should also be noted that the pH of an aluminophosphate system increases significantly during the main phase of crystallisation, possibly producing appropriate conditions for competitive phase formation such as the AEI phase described above.$^{19,22,39}$ It is known that many AlPO and MeAPO phases are extremely sensitive to pH and can only exist in a small pH range, for example SAPO-5 only tends to form a stable, well crystalline material between pH 4.0 and 7.0.$^{19}$

In a recent paper, Garcia-Carmona et al.$^{37}$ have discussed in detail the effects that changing pH has on the nature of the aluminate and phosphate species in the reaction gel. They report that the gel pH is fundamental, determining the number of ionic species through the dissociation products of H$_3$PO$_4$ and also the state of
aluminium ion hydrolysis. These effects become especially important in short-duration experiments. They discuss a critical pH range originally reported by Merino et al.\textsuperscript{41} within which the predominant aqueous aluminium species changes from octahedral $[\text{Al(H}_2\text{O)}_6]^{3+}$ to tetrahedral $[\text{Al(OH)}_4]$\textsuperscript{3}. This pH range is dependent on temperature, being 5.5-6.5 at 298K and dropping to 4-5 at 373K. This relationship between temperature, pH and aluminium co-ordination is advanced as a means of influencing or predicting the formation of specific aluminophosphate phases.

3.5.2) Cobalt Substituted Aluminophosphates

The substitution of cobalt into microporous aluminophosphate structures such as AFI has been the subject of much interest due to the possibility of synthesising catalytic materials with both acid and redox catalytic properties. However, the substitution of such heteroatoms into the pre-cursor gel can actually alter the nature of the phases formed\textsuperscript{2 3 20 40}. These heteroatoms are known to interact with the organic template molecules in such a way that the concentrations of both template and heteroatom become critical to the nature of the crystalline products,\textsuperscript{2 3 20 40} in addition to other factors such as synthesis temperature\textsuperscript{40}. In the sections below, these effects for \textit{in situ} syntheses are considered when performed over a range of cobalt concentrations and with several different template molecules.

This work has been carried out with the aim of directly comparing the cobalt substituted system with the pure aluminophosphate system and with previous experimental data from other sources. Additionally, we compare our findings with those for a theoretical study of the competitive formation of the CoAlPO-5 (AFI) and
CoAlPO-34 (CHA) for triethylamine templated systems carried out by Lewis et al.\textsuperscript{42}

Finally, this work has been extended to consider the differences produced by using other template molecules in cobalt substituted systems.

3.5.2.1) The Effect on the Crystallisation Kinetics of Substituting a Small Quantity of Cobalt (Co/P=0.04) into the AlPO-5 Gel Using TEA as the Template

A comparison of the synthesis curves for AlPO-5 with CoAlPO-5, produced when some of the aluminium is substituted by an equivalent quantity of cobalt, allows a useful insight into the kinetic behaviour of these systems. AlPO-5 was previously seen (figures 3.3 and 3.6a) to crystallise after an induction period that decreases in an approximately linear fashion with increasing temperature.

When a small quantity of cobalt (Co/P=0.04) was substituted for aluminium, this linear relationship no longer appeared to hold as shown in figure 3.6b. In this case the differences in induction periods prior to AFI formation become irregular over similar temperature increases, with samples synthesised over a relatively wide temperature range (436-449K) crystallising out in the AFI phase at approximately the same time.

This behaviour appears to be due to the disruption of the crystallisation kinetics of the AFI phase in the cobalt substituted synthesis by the simultaneous formation of a secondary chabazitic (CHA) crystal phase previously identified as CoAlPO-34\textsuperscript{2} 40, the crystallisation curves of which are shown in figure 3.6c. The formation of the secondary phase can also be seen in figure 3.7 where time-resolved 3-dimensional stack plots compare the synthesis of a pure aluminophosphate gel and
an otherwise identical gel in which 6% of the aluminium has been substituted for cobalt. The reflection attributed to the CHA phase is marked by an asterisk in figure 3.7b. The slight drop in background intensity in figures 3.7a and 3.7b as crystallisation begins is due to the settling of material at the bottom of the autoclave into the line of sight of the synchrotron beam as crystallisation occurs.
Figure 3.6 – Comparative crystallisation curves for a) the crystallisation of AlPO-5 from an aluminophosphate gel. b) the crystallisation of CoAlPO-5 from a gel containing a 0.04 molar proportion of cobalt substituted for aluminium. c) the crystallisation of the AlPO-34 (CHA) phase formed in competition with the AFI in (b). In each case, samples were synthesised using a standard pre-cursor gel with TEA as the template molecule. Data were plotted from the AFI (100) and CHA (100) reflections and have been corrected for beam decay and intensity.
Figure 3.7 – Time resolved EDXRD stack plots for a) AlPO-5 synthesised from a pure aluminophosphate gel. b) CoAlPO-5 synthesised from a gel containing a 0.06 molar proportion of cobalt substituted for aluminium. Data were recorded at a fixed detector angle of 1.46°2θ. The extra peak in (b) marked by an asterisk was attributed to the (100) reflection of CoAlPO-34. Syntheses were carried out at 363K. An extra reflection at 98KeV due to the PTFE line has been removed for reasons of clarity.
The CoAlPO-34 phase has a very different structure to the large pore (7.3 Å diameter) uni-dimensional channel structure of AFI (See figure 3.1). In comparison, CoAlPO-34 has a medium pore (3.8 Å diameter) cage structure similar to that of the natural mineral chabazite as shown in figure 3.8a below. The structure is composed of a 3 dimensional arrangement of double six-rings linked together by four-rings arranged in such a way as to produce 8-ring windows of size 3.8 Å x 3.8 Å. Figure 3.8b is a schematic diagram showing the dimensions of the cages, which can be seen to have an elongated shape.

We also observed, as previously reported by both Uytterhoeven and Rey, that the formation of the CHA phase is not only influenced by the presence of cobalt but also by the synthesis temperature, increasing which has been found to favour the
formation of AFI over CHA. For the temperature range of our study, CHA is observed in each case. However, as can be seen in figure 3.9(a-c), CHA was observed to become increasingly unstable as the temperature increased with the CHA in the 467K sample having completely re-dissolved ca. 35 minutes after it first forms. In contrast, the AFI remains stable at this temperature and even appears to continue growing slowly as indicated by gradually increasing intensity after the main phase of crystal growth. Lewis et al.42 postulated that the greater stability of AFI over CHA with increasing temperature may be due to the CHA not being able to crystallise as fast as AFI. It has been reported by others that the CHA phase re-dissolves over extended periods of crystallisation, leaving a pure CoAlPO-5 product and the speed of this dissolution increases as synthesis temperature increases.45 However, we have found CHA to be stable after synthesis periods of several days. Additionally, Navarro et al.45 have reported the formation of a further, unidentified phase after prolonged syntheses. It is also worth noting that Norby et al.46, upon recently performing an in situ angular dispersive diffraction study of CoAPO-5 formation, observed the slow formation of a dense cubic aluminophosphate (PDF 31-0028) beginning after ca.2 hours when synthesis temperature is ramped up to 498K.

Figure 3.9 shows that no clear trend is observable between the relative maximum crystallinities of each crystal phase formed and the synthesis temperature as indicated by the relative intensities at completion. A comparison of the full width at half maximum (FWHM) values for both phases also failed to show a clear trend, with the mean FWHM values upon completion for AFI being in the range 1.0-1.1KeV and the mean values for CHA being in the range 1.2-1.3KeV. As expected, a decrease in the FWHM indicating an increase in crystallite size, was initially observed during the main stage of crystallisation with values becoming constant on completion. These
results broadly agree with those for the pure aluminophosphate with triethylamine template where no significant variation in either intensity or FWHM was observed.

Figure 3.9 – Comparative crystallisation curves for the competitive formation of CoAlPO-5 (AFI) and CoAlPO-34 (CHA) at a) 436K, b) 449K and c) 467K. In each case samples were synthesised using a standard pre-cursor gel with TEA as the template molecule and a cobalt concentration of 0.04 was used. Data were plotted from the AFI (100) and CHA (100) reflections and have been corrected for beam decay and intensity.
3.5.2.2) The effect of Altering the Concentration of Cobalt in the CoAlPO-5 System Synthesised with Triethylamine Template

In order to investigate further the phenomenon of competitive phase formation in the triethylamine CoAlPO-5 system, samples were synthesised at constant temperature with a range of cobalt concentrations (Co/P=0.00-0.10). Crystallisation of the chabazitic phase was first observed between cobalt concentrations of 0.03 and 0.04. The proportion of CHA was found to increase in proportion to AFI as the cobalt concentration was increased as illustrated in figure 3.10(a-d) and figure 3.11. However, an increase in the molar quantity of triethylamine from 0.8 to 1.5 was required in order to produce a purely chabazitic phase even at cobalt concentrations above 8 mol %. This resulting chabazitic phase was always found to be poorly crystalline in comparison to AFI as seen in figure 3.10d.
Figure 3.10 – EDXRD data sets illustrating the variation in the proportions of AFI and CHA with increasing levels of cobalt substitution. a) pure aluminophosphate b) Co/P=0.04 c) Co/P=0.08 and d) Co/P=0.10 with extra template. Data sets (a)-(c) were recorded for a standard gel composition xCoAc2:1-xAl(OH)3:1.5H3PO4:0.8Net3:30H2O while 1.5Net3 was used for preparation (d). Data sets (a) and (b) were recorded at 1.29°20, (c) at 1.28°20 and (d) at 1.42°20. Intensities have been normalised for beam decay.

Figure 3.11 – Graph illustrating the increase in the proportion of CHA formed as a proportion of the AFI phase with increasing levels of cobalt substitution. Data in each were recorded for a gel of standard composition xCoAc2:1-xAl(OH)3:1.5H3PO4:0.8Net3:30H2O. Data are not directly comparable with figure 3.10 above.
No definite trends were noted when a comparison of the crystallisation kinetics of these samples with changing concentrations of cobalt was carried out as can be seen in figure 3.12 below. It is known that the CHA phase forms more slowly than the AFI phase (Lewis et al.\textsuperscript{42}), but for this system, it may be the case that the quantities of the CHA phase formed are too small to have any significant effect on the kinetics of the system overall. However, it should be noted that the quantity of template used during these experiments was kept constant as cobalt content increased, which may have resulted in a change in the overall pH of the system, masking any trend in the kinetics.

Figure 3.12 – Comparative crystallisation curves for the synthesis of the AFI phases in a system containing increasing quantities of cobalt. Syntheses were carried out at 363K in each case. Data were recorded for the AFI (100) reflection and normalised for beam decay and intensity.
3.5.2.3) The Mechanism and Consequences of Cobalt Substitution into an Aluminophosphate Pre-cursor Gel with the Triethylamine Template

Current ideas on the processes occurring during the substitution of cobalt into an aluminophosphate gel for a system with triethylamine as the organic template molecule are now reviewed below. Observations made during the series of experiments described above will be compared with the experimental and theoretical results of others.

Incorporation of divalent cobalt in the aluminophosphate framework introduces a charge imbalance to the aluminophosphate framework. The template molecules act to balance this charge and the resulting cobalt-template interaction acts to anchor the template within the pores. These template molecules in turn act as shape directing agents allowing the CHA cages to form around them. In comparison, the channel structures of AFI appear less favourable in supporting the presence of the large numbers of template atoms required to charge balance a high cobalt concentration as indicated by the preferred formation of CHA over AFI at high cobalt and template concentrations. In support of our observations, several studies\textsuperscript{2, 32, 35, 40, 42, 45-46} have reported that AFI crystallises at low levels of cobalt substitution compared to chabazitic phases.

Some of these investigations are quantitative and appear to indicate that AFI can crystallise with levels of template that are significantly lower than one organic molecule per unit cell. For example, Urbina de Navarro et al.\textsuperscript{45} using SEM and EDX techniques have investigated the cobalt concentrations of the competing phases. They found that in a mixture of AFI and CHA produced at an intermediate cobalt concentration (Co/P=0.05), the AFI phase would contain 0-4 mol % cobalt while the
CHA phase would contain up to 10 mol % cobalt. However, a pure AFI phase formed in a gel with a lower cobalt concentration (Co/P=0.02) could contain up to 8 mol % cobalt. Additionally, in a high cobalt concentration gel (Co/P=0.10) a pure CHA phase would still contain 10 mol % Co. These observations indicate that the CHA phase in a mixture will preferably take up the available cobalt over the AFI phase. Additionally, strong cobalt concentration gradients were seen in crystals with the concentration being highest in the centre. These observations would suggest that uptake of Co into the frameworks is rapid as also suggested by Uytterhoeven et al., with the bulk of cobalt incorporation occurring during nucleation and the early stages of crystallisation. The mixed phase was also found to contain significantly more cobalt than the pure AFI phase, supporting the idea of there being more than one template molecule per CHA cage.

Our measurements of FWHM indicating the particle size of the phases, combined with observations of the products using an optical microscope indicated that while AFI produced large, well formed crystals, CHA appeared as darker blue clumps of material in which individual crystallites could not be identified. In support of these observations, Urbina de Navarro et al. also report from their SEM study that the AFI tended to form large hexagonal prismatic or needle shaped crystals while the CHA crystallises as tiny stacked plates and large spherical aggregates of crystallites.

Newalkar et al. used thermogravimetric analysis to study the weight loss corresponding to the occluded amine in A1PO-5 and achieved results consistent with the calculated value expected for one molecule per unit cell.

Uytterhoeven et al. investigated the chemistry of the cobalt species over a range of pre-cursor gel pH conditions using the Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS) technique, in order to assess the role of the
template in the competitive formation of AFI and CHA. They found that at low pH and thus low template concentrations, cobalt was mainly detected as a soluble $\text{Co(H}_2\text{O)}_6^{2+}$ complex along with smaller quantities of a $[\text{CoO}_4.2\text{H}_2\text{O}]$ complex described as a structural entity with 4 framework oxygens and 2 additional water ligands. Washing and drying the sample showed this second phase to be the dominant species attached to the gel surface. However, at high pH and thus high template concentration, adsorption of $\text{H}_2\text{PO}_4^-$ onto the aluminium source takes place resulting in the release of the hydroxyl group, which in turn results in the generation of negative surface charges. These charges can react with the positively charged cobalt species, producing a tetrahedral surface complex that cannot be removed by washing.

At intermediate pH, both of these mechanisms are believed to operate. The tetrahedral cobalt species that are important as the pre-cursors for CoAPO-n formation can therefore be generated by two different mechanisms. From these studies Uytterhoeven et al.\textsuperscript{40} concluded that nucleation can take place on the surface of the particles and that the organic molecules regulate the pH but are not part of the cobalt coordination sphere and hence not an essential part of the nuclei. Furthermore, two models were proposed whereby AFI forms via a solution phase reaction with cobalt being taken up as a soluble aquo-complex while CHA may be formed via a solid-solid transformation with the cobalt being associated with the solid phase even in the early stages of mixing. This idea would fit with the observation of high cobalt gradients as noted by Urbina de Navarro et al.\textsuperscript{45}.

Lewis et al.\textsuperscript{42} carried out a series of calculations using energy minimisation methods to investigate the packing energies of the triethylamine template into both the AFI and CHA structures. They reported that the CHA structure is energetically favoured when two template molecules (and thus two framework Co (II) ions for
charge neutrality) occupy each CHA cage providing a much greater stabilisation than for just one template. In contrast, template-template interactions in the AFI structure are much less prominent than for CHA indicating that AFI can form at much reduced levels of template as observed both by ourselves and others.40

They also reported that the template-framework interactions in the CHA structure were considerably higher than in AFI. This meant that the template concentration had a much greater effect on the stability of the CHA framework than on AFI. The consideration that templating effects for AFI are not as critical as for other frameworks can be coupled with the results from lattice energy calculations indicating AFI to be slightly more thermodynamically stable than CHA (Lewis et al.42). It is therefore possible to see why AFI appears to be the preferred crystal phase even at higher cobalt concentrations, when the CHA eventually breaks down to AFI. Another consideration is the added complication of the interactions between two template molecules in a CHA cage, where only certain stacking configurations may be stable. This would go some way to explaining the slower crystallisation rates of CHA formation over AFI formation.

In conclusion, it appears that two major factors influencing the competitive phase formation of AFI and CHA in a system synthesised at a constant temperature are the template and the concentration of cobalt. At low cobalt concentrations, AFI is favoured while increasing the cobalt concentration promotes the formation of CHA. However, as we discovered during our in situ studies, in order to produce a pure CHA phase, the concentration of template had to be further increased in addition to increasing the concentration of cobalt. This observation was backed up by Uytterhoeven et al.40 who found that the quantity of template retained in the framework was dependant on the template concentration. At lower cobalt
concentrations, there is an excess of template available in the pre-cursor gel but more template is required at higher levels of cobalt substitution in order to allow continued CHA formation. Additionally, in mixtures of the two phases, CHA has been reported to take up the bulk of the cobalt, with AFI being able to crystallise with comparatively little or no cobalt uptake.45

Mechanisms have been suggested to explain these observations, based on the template-cobalt interaction.40-42. These rationalise the experimental observations using approaches such as considering that the template acts to regulate pH and thus the chemistry of cobalt incorporation40 and also considering the template interactions with cobalt species in the proto-framework in a shape directing capacity42. It appears likely that some combination of these mechanisms actually occurs and consideration of such a combined approach would be a significant step towards producing a model to fit the observed results. However, there are likely to be further factors to be considered before a truly accurate model can be produced. For example, using TEA as a template in a non aqueous gel where water is replaced as the solvent by triethylene-glycol was found by Cheng et al.46 to produce the novel microporous aluminophosphate, CAM-1 under otherwise similar synthesis conditions. Further work is clearly needed on this intriguing problem.
3.5.2.4) The Effect of Altering the Type of Organic Template Molecule Used in the Synthesis of CoAlPO-5

As discussed above, the use of a range of different organic template molecules in otherwise identical aluminophosphate gels produced changes in both the types of crystalline phase formed and the crystallisation kinetics of the resulting phases. After considering the changes to the kinetics of the AlPO-5 system produced by the substitution of some of the aluminium with a small quantity of cobalt, a further study was carried out into the combined effects of changing the template molecule and substituting cobalt. This study was implemented for TEA as previously described and subsequently extended to include TEAOH, TPA and TPAOH. A range of cobalt concentrations were investigated, with more comprehensive studies being carried out for TEA and TEAOH.

3.5.2.4.1) Tetraethyl-Ammonium Hydroxide

Use of TEA, as reported above, produced only AFI when the proportion of substituted cobalt was below ca 0.03. The proportion of CHA was then found to increase slowly with increasing cobalt concentration. However, with TEAOH, the observed results were rather different as was to be expected considering that very small quantities of a secondary phase, AlPO$_4$-18 (AEI) have been observed (figure 3.5) even without cobalt substitution. Subsequent substitution of a small quantity of cobalt (Co/P=0.02) resulted once again in the competitive formation of AFI and AEI but with a significantly greater proportion of the product being AEI as can be seen by
comparing figure 3.5 with figure 3.13 below. Figures 3.13a and 3.13b respectively show the effect of increasing synthesis temperature on the crystallisation kinetics of the AFI and AEI phases respectively. A general decrease in the induction period and increase in the reaction rate was observed for both phases with increasing temperature. However, no clear trend in maximum crystallinity as indicated by the mean maximum intensity was observed nor was any trend in mean particle size as indicated by the mean FWHM at completion. In each case, AFI had a FWHM in the range 1.34-1.38KeV while AEI was in the range 1.66-1.76KeV indicating a smaller mean particle size for the AEI phase. Figure 3.13c shows an interesting difference in the kinetics upon substituting even a small quantity of cobalt into the pre-cursor gel. While it was observed for the pure aluminophosphate synthesis (figure 3.5), that the AEI phase began to crystallise a significant time after the AFI phase, the CoAlPO gels at each temperature produced both phases approximately simultaneously, with the AEI phase often being observed just before the majority AFI phase. This would indicate that as well as increasing the stability of the AEI phase, the addition of small quantities of cobalt actually promote its growth with respect to AFI. Variations in the data quality are a factor of the synchrotron beam intensity at the time of data collection.
Figure 3.13 - Comparative crystallisation curves for a) the crystallisation of AFI from a precursor gel containing a small quantity of cobalt (Co/P=0.02) and using the TEAOH template over a range of temperatures. b) Shows the AEI phase that crystallises competitively with AFI under the same synthesis conditions and c) shows the comparative kinetics of the two competing phases, in this case at a synthesis temperature of 464K. Data were plotted from the AFI (100) and AEI (110) reflections and have been corrected for beam decay and intensity.
Increasing the concentration of cobalt to $\text{Co/P}=0.04$ resulted in a further increase in the proportion of AEI. However, increasing the cobalt concentrations to $\text{Co/P}=0.06$ resulted in a change in the nature of the secondary phase from AEI to CHA. Observation of this change was made easier by the extra d-spacing range made available by using the 3-element detector array\textsuperscript{15,16} as the major low angle reflections for AEI (110) and CHA (100) have very similar d-spacings.

The structures of AEI and CHA are related: the pore sizes are identical but the structures have different geometries produced by differences in the stacking of the structural sub-units. The main structural difference between AEI and CHA lies in the orientation of the six-membered rings of which both are built up. In AEI alternate rings of double six-membered rings (D6R) parallel to the $ab$ plane are related by a $c$-glide and therefore possess different orientations. In CHA they are related by a simple translation and therefore have the same orientation as can be seen in figure 3.14, below\textsuperscript{5,10}. These minor structural differences, as described later, appear to produce important differences in the catalytic properties of AEI and CHA phase MeAPOs, making a detailed study of the factors causing this phase change potentially important from an industrial point of view.
Figure 3.14 - A schematic diagram of the CHA and AEI structures to illustrate that the structures are related but have different geometries due to different orientations of the double six-ring (D6R) structural sub-units (Wendelbo et al.)

Figure 3.15 shows the changing proportions of the primary (AFI) and secondary (AEI/CHA) phases as the cobalt concentration is increased. We can see that, unlike with the TEA syntheses, the formation of a purely chabazitic phase with TEAOH can be achieved with cobalt concentrations above Co/P=0.08 without the requirement for extra template. However, once again, the resulting chabazitic phase is found to be poorly crystalline in comparison to the AFI phase. More crystalline CHA has subsequently been produced in laboratory syntheses using increased quantities of TEAOH template.
Figure 3.15 – A graph of cobalt concentration versus corrected intensity for the synthesis of aluminophosphates and cobalt aluminophosphates. Pre-cursor gels with a range of cobalt concentrations Co/P = 0-0.1 were used. Syntheses were carried out at 443K using TEAOH as the template molecule. The changing proportions of the primary (AFI) and secondary (AEI and CHA) phases can be seen as well as the decrease in the gradient of the AFI curve between Co=0.04-0.06 where the transition from AEI to CHA occurs, as approximated by dashed lines.

While the exact cobalt concentration at which this phase change occurs has not been ascertained, it is interesting to note the reduced gradient of the AFI curve in figure 3.15 within the region Co=0.04-0.06, where upon increasing the cobalt concentration, CHA replaces AEI as the preferred secondary phase. Such a step in the dissolution curve of AFI may indicate a form of equilibrium-state in the 3-phase (AFI-AEI-CHA) system within this range of cobalt concentrations. A further reduction in the proportion of AFI only occurs in gel compositions with a sufficient quantity of cobalt to produce only CHA as the secondary phase. This area of reduced gradient may therefore indirectly indicate the range of cobalt concentrations in which both AEI and CHA exist.

Figure 3.16 uses the same data to illustrate the effect of increasing cobalt concentration on the overall proportion of secondary phase (AEI or CHA) with
respect to AFI. This plot highlights the difference between the TEA system (Figure 3.11) where CHA is always the minority phase and the TEAOH system where CHA quickly becomes the dominant phase above Co=0.06. It is also interesting to note the dramatic increase in the proportion of the secondary phase after the AEI-CHA phase change, which appears to confirm the observations of others that AEI has a significantly smaller capacity for incorporating heteroatoms into its structure than the CHA phase. Relatively pure AEI phases have been reported using TEAOH template but only at low heteroatom (Mg, Zn, Si) loadings. However, similar syntheses carried out with the N,N-diisopropylamine template have been reported to produce pure AEI with increased levels of heteroatom substitution (Si, Co) than can be achieved with TEAOH.

Figure 3.16 – A plot of cobalt concentration versus the percentage proportion of the secondary phase (AEI or CHA) with respect to AFI. This plot highlights the dramatic increase in the rate of replacement of AFI with the secondary phase after the conversion from AEI to CHA between Co=0.04 and 0.06. Samples were synthesised at 443K with TEAOH as the template molecule. Data were plotted from the AFI (100), AEI (110) and CHA (100) reflections.
The larger size of the TEAOH template compared to TEA may explain the differences in the proportions of AFI and secondary phase formed. The relatively small AEI/CHA cage may exhibit a higher stability with one TEAOH molecule than for two molecules, unlike in the case of TEA where two molecules per CHA cage are preferred as discussed by Lewis et al. Such a difference would fit the observation that no increase in the quantity of TEAOH template is required to produce products that are dominantly composed of CHA unlike for TEA. This hypothesis could be confirmed by computer modelling studies of the interactions between the CHA cage and TEAOH in a similar way to those carried out for TEA by Lewis et al.

An alternative approach would be to consider the AFI channel framework, which may be even less favourable to increasing levels of TEAOH acting to charge balance the increasing levels of cobalt than it would be for the smaller TEA molecules. A combination of these two size effects would tend to favour the formation of the secondary phases even at relatively low cobalt concentrations.

Due to the structural similarities of the AEI and CHA phases it is difficult to assign a reasonable explanation to the change of phase at higher levels of cobalt substitution. Increasing the cobalt concentration with a corresponding increase in the quantity of template being encapsulated in the framework may bring about a change of stacking of the sub-units producing CHA instead of AEI in order to accommodate better the template molecules. The different shape of N,N-diisopropylamine may allow larger amounts of template to enter the framework without forcing a change of stacking and thus producing AEI with a higher cobalt concentration as has been reported. Such an explanation would neatly explain why AEI only forms with low cobalt concentrations while CHA only forms at high cobalt concentrations.
Alternatively, it is possible that changing the concentration of cobalt while keeping the template constant results in an overall change in the gel pH, altering conditions to favour the formation of either AEI or CHA. These pH changes could occur as cobalt interacts with the template, changing the gel chemistry and at the same time releasing acetic acid into the gel from the decomposition of the cobalt acetate salt.

*Figure 3.17a and b* show that the most intense reflections for AEI and CHA occur in almost identical positions. We therefore hoped that use of the three element detector would greatly ease the *in situ* identification of the two phases. There were, however, some problems with this approach as can be seen in *figure 3.18*. Due to the poor crystallinity of the secondary phases in these experiments, combined with the water absorption hump and the presence, in the case of AEI, of the AFI phase, the differences between the phases are somewhat obscured, even though dry standard samples of these materials can easily be distinguished using the data from the middle detector (*figure 3.19*). For this reason, confirmation of the change in preferred crystal phase from AEI to CHA was achieved using a conventional laboratory X-ray diffractometer (*Figures 3.20a and b*) where reflections from the two phases were matched to standard patterns from the JCPDS data base AEI (45-0118) and CHA (34-137) and the *‘Collection of Simulated Powder XRD Patterns for Zeolites’*. 
Figure 3.17 – *In situ* EDXRD data sets from synthesis experiments carried out with TEAOH template at 442K and varying the levels of cobalt substitution as a) Co/P=0.02 and b) Co/P=0.10. These data sets were recorded after 40 minutes and the scan duration was one minute. The data were recorded at a fixed angle 1.28°26.
Figure 3.18 — *In situ* EDXRD data sets from synthesis experiments carried out with TEAOH template at 442K and varying the levels of cobalt substitution from Co/P=0-0.10. These data sets were collected after 40 minutes and the scan duration was one minute. The data were recorded at a fixed angle 4.018°20. Data sets have been normalised for beam decay.

Figure 3.19 — EDXRD patterns of standard samples of AEI and CHA placed within the *in situ* hydrothermal cell. Data were recorded at 298K at a fixed detector angle of 4.05°20. Two reflections due to the stainless steel cell have been manually removed after comparison with an empty cell and liner, for reasons of clarity.
Figure 3.20 - Laboratory powder X-ray diffraction patterns of the products of the *in situ* synthesis experiments carried out with TEAOH template at 442K and varying the levels of cobalt substitution as a) Co/P=0.04 and b) Co/P=0.10. Scans were carried out over *ca*.12 hours with Cu-Kα1 radiation.
In addition to considering the effects of the TEAOH template on the crystal phases formed over a range of cobalt concentrations, we can also observe the crystallisation kinetics to see how the concentration change affects the reaction rate. We see in figures 3.21a and b that at low cobalt concentrations, where Co/P=0-0.02 the AFI phase forms more quickly than at higher cobalt concentrations. However, the opposite trend is observed for the secondary phase, either AEI or CHA which forms most quickly at higher concentrations, where Co/P=0.08-0.10. Such an observation suggests that the kinetics of formation are slower for each individual phase in a mixture than when one phase dominates. In other words, the effect of the competitive formation is to slow down the overall kinetics of the system.
Figure 3.21 - Comparative crystallisation curves illustrating the effects of increasing cobalt in a system templated with TEAOH for a) the AFI phase and b) the secondary phases AEI and CHA. Samples were synthesised at 443K. Data were plotted from the AFI (100), AEI (110) and CHA (100) reflections.

The effect of changing cobalt concentration on the proportions of AFI and secondary phase has been discussed above, but the effect of these changes on the particle size of the resulting materials can also be estimated from the FWHM data as shown in figure 3.22 below. It can be seen that for the AFI phase, the variation in mean FWHM with increasing cobalt concentration is small, in the range 1.31-1.38KeV, but there is a general downward trend indicating a small increase in mean crystal size. The corresponding trend for the secondary phase is more pronounced in
the opposite direction, with values ranging from 1.69 KeV at low cobalt (Co/P=0.02) concentration up to 2.04 KeV at high cobalt concentrations (Co/P=0.08). We can compare these data with the mean FWHM data for the AFI and AEI phases discussed previously for Co/P=0.02 over a range of temperatures, where values were observed to fall in the ranges 1.34-1.38 KeV for AFI and 1.66-1.76 KeV for AEI, with no apparent trend. From such a comparison, it is probable that the trends seen with increasing cobalt concentration are more than just statistical variations. The standard deviations from the mean FWHM for each point have been plotted to give an indication of the likelihood of the apparent trend being significant. From this and the previous data it appears that AEI forms larger crystallites than CHA. A comparison of the two trend lines shows equal but opposite FWHM variations for AFI and the secondary phases between 0.02 and 0.08, with a rise in FWHM for AEI/CHA being matched by a drop in the value for AFI. Such a trend is possibly indicative of a relationship between the mean size of crystallites of the AFI and secondary phases during competitive formation. The end members of each set i.e. AFI where Co/P=0.10 and AEI where Co/P=0 have not been used due to the large fluctuations in FWHM values for very small reflections.

![Figure 3.22 - A plot of FWHM for the AFI (100) and AEI(110)/CHA(100) reflections versus proportion of cobalt in the pre-cursor gel.](image)
Considering the structural similarities between the AEI and CHA structures\textsuperscript{10}, it was generally expected that the MeAPO analogues of these materials would have similar catalytic properties. SAPO-18 has however been found to have a lower efficiency of acid site generation than SAPO-34\textsuperscript{5}. This is due to the AEI structure taking up smaller quantities of silica than CHA, as also occurs for cobalt. Additionally, Sankar et al.\textsuperscript{49} have carried out EXAFS studies of the cobalt environment in a variety of CoAPO frameworks and found large variations in the redox behaviour of the cobalt in these different structures. Lower concentrations of acid sites are known to increase the lifetime of a catalyst before coking in the cavities causes deactivation\textsuperscript{50,51}. It may therefore be possible that, by optimising the synthesis of AEI to gain pure samples with a desired quantity of framework cobalt, a highly selective catalyst with novel properties could be produced with the additional advantage of a long lifetime. \textit{In situ} EDXRD studies can be a valuable tool in carrying out such an optimisation of the synthesis conditions.

\textbf{3.5.2.4.2) Tripropylamine}

The tripropylamine (TPA) template was found to produce an unstable AFI phase with a pure aluminophosphate gel as previously discussed and shown in \textit{figure 3.4}. Substitution of part of the aluminium with a 0.02 molar proportion of cobalt was also found to produce a similarly unstable AFI phase. However, increasing the synthesis temperature from 442K to 464K resulted in the formation of a small quantity of a secondary phase in addition to the unstable AFI phase. This secondary phase appeared to remain stable after the AFI had collapsed. Doubling the proportion
of substituted cobalt to 0.04 results in the formation of unstable AFI and the stable secondary phase as the dominant product at 443K. A cobalt concentration of Co/P=0.08 also forms mainly the secondary phase with a small proportion of unstable AFI. The secondary phase was identified as the cobalt analogue of the MAPO-36 (ATS) structure, the corresponding aluminophosphate framework of which is shown in figure 3.23.

Figure 3.23 – The CoAlPO-36 (ATS) structure showing views from the three perpendicular directions. The structure shown is that for a pure aluminophosphate analogue. The aluminate and phosphate tetrahedra are coloured in pink while bridging oxygen atoms are red.
CoAlPO-36 is a large pore molecular sieve consisting of a unidirectional, elliptical 12-ring system with staggered annular side pockets. The magnesium substituted form of ATS (MAPO-36) is known to be particularly catalytically active compared to many other AIPO frameworks.\textsuperscript{52}

A comparison of the synthesis curves over a range of synthesis temperatures for samples with a low level of cobalt substitution (Co/P=0.02) are shown in figure 3.\textsuperscript{24a}. The competitive formation of the AFI and ATS phases at moderate (Co/P=0.04) and high (Co/P=0.08) levels of cobalt substitution are shown in figures 3.\textsuperscript{24b} and 3.\textsuperscript{24c} respectively. The bottom and middle detector data sets for the high cobalt loading sample are shown in figure 3.\textsuperscript{25}, the major reflections attributed to the ATS structure having been compared to a standard pattern for MAPO-36 (JCPDS code 46-559). All other reflections were attributed to the AFI structure.
Figure 3.24 - Comparative crystallisation curves for the syntheses using tripropylamine (TPA) as the template of a) AFI where Co/P=0.02 over a range of temperatures. b) and c) The competitive formation of AFI and ATS where Co/P=0.04 at 443K and Co/P=0.08 at 442K respectively. Data were plotted for the AFI (100) and the sum of the ATS (110) and (020) reflections and have been corrected for beam decay and intensity.
Figure 3.25 – In situ EDXRD data sets from synthesis experiments carried out at 443K. The red plot shows the results after 40 minutes of a synthesis where TPA is the template and Co/P=0.08, producing a mixture of AFI and ATS. In comparison, the black plot shows the equivalent synthesis carried out with TEA template and Co/P=0.02, producing a pure AFI phase. Data were recorded on a) the bottom detector at a fixed angle 1.283°20 and b) the middle detector at a fixed angle of 4.018°20.
A comparison of the crystallisation curves for pre-cursor gels with increasing quantities of cobalt indicates that the amount of ATS produced increases as the quantity of AFI decreases. This increase in the proportion of ATS with increasing cobalt is even more pronounced than that of TEAOH, with the secondary phase becoming dominant at a cobalt concentration between Co/P=0.02 and 0.04 (Figure 3.26). A small quantity of ATS was even observed in the synthesis at 464K where Co/P=0.02 although lower temperature syntheses produced only the unstable LTA phase.

![Graph](image)

**Figure 3.26** – A graph of cobalt concentration versus corrected intensity for the synthesis of aluminophosphates and cobalt aluminophosphates using the TPA template at 443K. The graph illustrates the changing proportions of the AFI and ATS phases with changing cobalt concentration.
3.5.2.4.3) Tetrapropyl-Ammonium Hydroxide

TPAOH was found to produce an AFI phase even more unstable than that of TPA in the pure aluminosilicate preparation. However, substitution of a 0.04 molar proportion of cobalt appears to stabilise the AFI phase after partial breakdown as illustrated in figure 3.27. The data from the middle detector confirmed that only the AFI phase was present after this stabilisation. It can also be seen that the crystallisation kinetics have been considerably accelerated by the addition of cobalt, manifested both as a decrease in the induction period and a steepening of the crystallisation curve in the main crystal growth region. The incorporation of cobalt in the framework may act to hold the large template molecules in position, stabilising the structure, which would imply that for a pre-cursor gel using TPAOH as the template, CoAlPO-5 is a more stable phase than AlPO-5.

![Figure 3.27](image)

Figure 3.27 – Comparative crystallisation curves for syntheses using tetra-propylammonium hydroxide (TPAOH) as the template of AFI where Co/P=0.00 and 0.04. Data were plotted for the AFI (100) reflection and have been corrected for beam decay and intensity.
In this chapter we have described a systematic study of the synthesis of a range of AlPO and CoAlPO materials produced by varying the components of a standard pre-cursor gel composition. It was found that while changing the template could alter the stability and kinetics of AlPO-5 (AFI) crystallisation, these changes could also result in the formation of secondary phases such as AlPO-18 (AEI). In addition to altering the template type, it was found that a combination of using different templates and substitution of small proportions of aluminium in the pre-cursor gel by cobalt resulted in major changes in the chemistry of the system, producing a range of secondary phases in addition to or completely replacing the AFI phase. These phases were CoAlPO-34 (CHA) and CoAlPO-36 (ATS) as well as increasing proportions of AEI. Small variations in the amount of cobalt substitution were found to alter the nature of the resulting phases in the case of the TEAOH template where AEI crystallised when Co/P=0-0.04 and CHA formed at higher cobalt concentrations. A trend was also observed whereby changing the template type altered the degree of cobalt substitution that could be achieved before AFI became the minority phase. Triethylamine produced a majority AFI phase over CHA even with 10% cobalt substitution, unless more template was added to the pre-cursor gel. However, with TEAOH, CHA became the dominant phase over AFI at cobalt concentrations above ca. 6% substitution. Tripropylamine produced a dominant ATS phase with cobalt concentrations above ca. 2-3%. Many of the results for this chapter are summarised in figure 3.28 below.
Figure 3.28 – Summary of the crystal phases produced using a range of different template molecules (R) over a range of cobalt concentrations for a pre-cursor gel with the standard composition $x\text{CoA}_2:1-x\text{Al(OH)}_3:1.5\text{H}_3\text{PO}_4:0.8\text{R}:3\text{H}_2\text{O}$.

It was possible to propose reasons for our observations based on differences in both the physical size and basicity of the different templates and the interaction with the substituted cobalt. Additionally, a survey of current literature found several models using a variety of approaches in order to explain the interaction between the template and cobalt. It appears from our results and those reported by others that the template-cobalt interaction is a complex one, with the template acting in a charge balancing, structure directing and pH controlling role, while cobalt species act to anchor the template molecules within the growing framework by electrostatic
interactions. The concentration of both cobalt and template species therefore dictate the nature of the resulting crystalline phases.

We have shown that the EDXRD technique can make a valuable contribution to understanding the complex interactions occurring in metal substituted aluminophosphate systems. The collection of such data with a high degree of time resolution allows us to study both the kinetics and relative thermodynamic stabilities of potentially useful catalytic materials with a range of gel compositions, under realistic synthesis conditions. Information gained from such data will allow syntheses of these materials to be optimised both for phase purity and selected catalytic properties.

In the next chapter these in situ synthetic studies are extended to a range of other MeAPOs, many of which have potentially novel catalytic properties. Additionally, these MeAPOs, including the CoAIPOs dealt with in this chapter, are studied with the EXAFS technique in order to ascertain the nature of the heteroatoms within the aluminophosphate framework environment.

3.7) References


33) Collaborative Computational Project 14 – CCLRC Daresbury Laboratory.


A Structural Study of the Effects of Substituting a Range of Heteroatoms Into a Microporous Aluminophosphate System Using The In Situ EDXRD and EXAFS Techniques

4.1) Chapter Overview

In chapter 3 the effects of substituting small quantities of cobalt for aluminium in a microporous aluminophosphate system were described. The cobalt was found to interact with a range of template molecules, resulting both in alterations of the crystallisation kinetics and the formation of a range of crystalline phases.

In the present chapter this work is extended to study the effects of substituting a range of heteroatoms into the same templated aluminophosphate systems. These heteroatoms include several first row transition metals in addition to magnesium and silicon, the incorporation of each of which within the aluminophosphate framework has previously been reported\textsuperscript{1-2}.

The incorporation of such heteroatoms discussed in this chapter into aluminophosphate frameworks has been shown to produce materials with a wide range of properties giving rise to many potential uses in industrial applications, which include highly selective acid\textsuperscript{3-10}, oxidation\textsuperscript{11-12} and bi-functional catalysts\textsuperscript{13-15} for the production of fine chemicals. Some of these materials are currently being commercially exploited, including SAPO-34 in the methanol to olefin (MTO) process\textsuperscript{16-17}. In addition, other promising catalytic materials include the highly active
acid catalyst MgAPO-36 (MAPO-36) for the catalytic cracking of alkanes\textsuperscript{18-19} and also both CrAPO-5 and CrAPO-11 for the oxidation of benzylic and cyclic alcohols\textsuperscript{20}.

The aim of this study was to carry out a systematic investigation of the effects of these heteroatoms on a synthesis gel under otherwise standard reaction conditions rather than to alter the synthesis conditions for each material in order to gain a pure heteroatom substituted product. In particular we aimed to discover the role of the heteroatom on the synthetic process and investigate how addition of the heteroatom not only affects the properties of the final product but also influences the nature of this product.

It was found that alteration of the heteroatom type had a profound effect on both the kinetics of crystallisation and the nature of the final products. These heteroatom effects were once again found to be strongly influenced by the nature of the template molecule. EXAFS data were subsequently recorded for many of the products in order to ascertain the location of the heteroatoms within the resulting framework structures. In many cases, for example, cobalt, manganese and iron, the heteroatom was found to have successfully incorporated into the framework while for chromium and nickel, the heteroatoms were found to occur as extra-framework, octahedral species, such as the hydroxide. The links between the nature of the heteroatom species and the crystallisation kinetics were subsequently considered.

Results are also described for an \textit{in situ} calcination and reduction study that was implemented for one of the iron substituted aluminophosphate samples, using an environmental cell developed at the Davy-Faraday Research Laboratory and shown in figure 4.1\textsuperscript{21}. EXAFS data from these experiments was then compared with similar studies of cobalt substituted aluminophosphate systems carried out previously\textsuperscript{21-22}. From this work, the potential for using FeAPO-5 as a stable, shape selective catalyst
was investigated. This study was prompted by a consideration of the Redox chemistry of iron, which indicated that pure FeAPO-5 (FAPO-5) had potential to exhibit novel catalytic properties. Based on the initial findings described in this chapter, further investigations of iron substituted aluminophosphates are in progress at the DFRL.

4.2) Experimental

4.2.1) Sample Preparation Procedure for a Range of MeAPOs (Me/P=0.04) at 443K using a Range of Organic Template Molecules

1) A series of MeAPOs were produced using the standard method for a CoAlPO-5 gel with TEA, TEAOH, TPA and TPAOH templates as described in chapter 3 (section 3.2.1.2). The 0.20g of cobalt (II) acetate required for a cobalt concentration of 0.04 was replaced by an appropriate quantity of each of the heteroatoms in a water soluble form as listed in table 4.1.

2) Each gel was then treated hydrothermally at 443K with in situ EDXRD data being recorded. Upon completion of crystallisation, each sample was thoroughly washed with distilled water and then dried for later analysis with EXAFS.

3) Dried samples for EXAFS analysis were ground to a uniform consistency with a pestle and mortar and then pressed into pellets, these typically being 20mm in diameter and containing 80mg of sample.

4) Sample disks not undergoing post synthetic treatment were mounted on a sample holder and then positioned in the synchrotron beam, in this case for transmission mode EXAFS data collection.
Table 4.1 – The quantity of each heteroatom source material required for the synthesis of MeAPOs where Me/P=0.04.

<table>
<thead>
<tr>
<th>Gel Type</th>
<th>Soluble Form</th>
<th>Quantity Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO₄</td>
<td>N/A</td>
<td>0.00g</td>
</tr>
<tr>
<td>CoAlPO₄</td>
<td>Co(II) Acetate</td>
<td>0.20g</td>
</tr>
<tr>
<td>Co(III)APO₄</td>
<td>Co(III) Acetylacetate</td>
<td>0.29g</td>
</tr>
<tr>
<td>ZnAPO₄</td>
<td>Zn(II) Acetate</td>
<td>0.18g</td>
</tr>
<tr>
<td>MAPO₄</td>
<td>Mg(II) Acetate</td>
<td>0.18g</td>
</tr>
<tr>
<td>Mn(II)APO₄</td>
<td>Mn(II) Acetate</td>
<td>0.20g</td>
</tr>
<tr>
<td>Mn(III)APO₄</td>
<td>Mn(III) Acetylacetate</td>
<td>0.21g</td>
</tr>
<tr>
<td>Fe(II)APO₄</td>
<td>Fe(II) Acetate</td>
<td>0.14g</td>
</tr>
<tr>
<td>Fe(III)APO₄</td>
<td>Fe(III) Acetylacetate</td>
<td>0.28g</td>
</tr>
<tr>
<td>CuAPO₄</td>
<td>Cu(II) Acetate</td>
<td>0.16g</td>
</tr>
<tr>
<td>NiAPO₄</td>
<td>Ni(II) Chloride</td>
<td>0.16g</td>
</tr>
<tr>
<td>CrAPO₄</td>
<td>Cr(III) Acetylacetate</td>
<td>0.28g</td>
</tr>
<tr>
<td>SAPO₄</td>
<td>Cab-O-Sil</td>
<td>0.05g</td>
</tr>
</tbody>
</table>

5) Samples requiring post synthetic treatment were placed in a sample holder and then inserted into the airtight environmental cell shown schematically in figure 4.1 and treated as follows:-

a) Calcination – Samples were placed within the furnace under a constant oxygen flow and the temperature slowly ramped (10 Kmin⁻¹) to 823K where they were heated for three hours and then slowly cooled. Once cooled the cell was sealed to preserve the oxygen atmosphere and the sample disk was moved from the furnace to the Kapton window for EXAFS analysis.
b) Reduction – After calcination and EXAFS analysis, the sample was moved back into the furnace and placed under a constant gas flow consisting of 4% hydrogen in nitrogen. The sample was slowly ramped (10 K min⁻¹) to 673 K and kept at this temperature for one hour before cooling to room temperature for EXAFS measurement in a sealed environment.

Figure 4.1 – A schematic of an in situ cell used for the heat treatment of MeAPO samples under controlled atmospheric conditions with constant gas flow. The gas inlet and outlet tubes are additionally equipped with quartz taps to seal the desired atmosphere within the cell when collecting XAS data for the cooled sample. Quartz runners within the main body of the cell allow the sample to be easily moved between the furnace and the Kapton window after cooling. (The cell has also been designed to be compatible with conventional vacuum line fittings and can sustain a typical vacuum of 10⁻⁴ Torr). The cell was developed at the DFRL by Sankar et al21-22.
4.2.2) Data Collection

EDXRD data were recorded on station 16.4 at the Daresbury SRS using a hydrothermal cell\textsuperscript{23} in a similar way to that discussed in previous chapters. These data were collected using a 3-element detector array\textsuperscript{24-25} with each detector element being separated by ca. 2.8° 20. For the main series of experiments described, the detector array was set with the bottom detector at a fixed angle of 1.29° 20 resulting in the middle detector being set at 4.08° 20. Later, supplementary experiments were carried out at similar angles, the values of which are detailed with the corresponding data. Scans were recorded every 60 seconds over a period typically of 60 minutes.

EXAFS data were collected on station 7.1 at the Daresbury SRS using a transmission geometry. Technical details of the stations and experimental geometries have been described in chapter 1. Data were collected using both conventional EXAFS and the quick EXAFS (QuEXAFS) mode available on this station. Within time constraints, the maximum number of data sets possible were recorded for each sample in order later to sum these data for improved statistics during analysis.

Where required for confirmation of crystal phase identities, conventional X-ray diffraction patterns of the final products were recorded on a Siemens D500 diffractometer with a pre-sample monochromator set for Cu-K\(\alpha_1\) radiation. Scans were collected over an angular range 5-50°20 and typically recorded over 10-12 hours.
4.2.3) Data Analysis

Using a similar methodology to that described in chapters 2 and 3, the Dlconvert and Xfit packages provided by the CCP14 resource at Daresbury\textsuperscript{26} were used first to convert the EDXRD data into an appropriate format and then to fit the areas under each reflection to a Gaussian function. The resulting data were then analysed using the Microsoft Excel package in order to compare the synthesis curves for each crystalline phase as a function of time. Scans were recorded every 60 seconds and the peak intensity, corrected for beam decay, was used as a gauge of the changing crystallinity of each crystal phase.

Analysis of the EXAFS data was carried out using the EXCALIB, EXBROOK, and EXCURV98\textsuperscript{27} suite of programs described in chapter 1. Due to the nature of data collection in QuEXAFS mode, interpolation and summing of data sets collected in this mode was carried out using the Motplot program also available on XRSSERV1. As a guide to local heteroatom environments during analysis, EXAFS data for model compounds eg Fe(II) acetate were collected and, where required, the Inorganic Crystal Structure Database (ICSD) on CDS was accessed for structural information on a range of appropriate compounds. These data were visualised using the GUI Ortep3\textsuperscript{28} program also available from the CCP14 resource at the Daresbury Laboratory\textsuperscript{26}. EXAFS data and the associated Fourier transforms were plotted with the Microcal Origin 5.0 package.

Where conventional laboratory X-ray diffraction data were recorded, the data sets were compared with standards from both the JCPDS crystal structure database and the Collection of Simulated XRD Powder Patterns for Zeolites\textsuperscript{29}. A direct
comparison between these data and the EDXRD data was enabled using the Dragon\textsuperscript{30} program available on XRDSV1 at the CCLRC Daresbury Laboratory.

4.3) Results and Discussion

Here are reported the results of the analysis of data collected by EDXRD and EXAFS for each of the different heteroatoms studied. We begin with a brief recap of the results for both pure aluminophosphate and cobalt aluminophosphate gels discussed in detail in the last chapter. The effects of substituting each of the additional heteroatoms are then reported, describing both the differences in kinetics and the crystal phases formed. The qualitative features of the crystallisation kinetics have been used as the basis for the order in which the subsequent MeAPOs are discussed, with those exhibiting properties most similar to those of the CoAlPOs being considered first. EXAFS data for the heteroatom substituted samples, with the exceptions of magnesium and silicon (these being outside the energy range of station 7.1) were considered in relation to the kinetic findings. The aim of this was to discover any relation between the crystallisation kinetics and the nature of the heteroatom within the substituted aluminophosphate system. Additionally, the results of an in situ oxidation-reduction study of the FeAPO-5 sample produced with TEAOH template are reported.

Due to restricted beam time, these investigations concentrated on only a single heteroatom concentration (Me/P=0.04) for many of the heteroatoms. However, further studies were carried out over several Me/P concentrations for certain heteroatoms that exhibited either unusual phenomena during synthesis as in the case of zinc or
possessed potentially novel catalytic properties as in the case of iron and manganese. A comparison of the crystallisation kinetics when using both soluble metal (II) and metal (III) sources was carried out in situ for cobalt and manganese while an iron (III) source was later studied in conventional laboratory synthesis experiments.

4.3.1) Aluminophosphate

Figure 4.2 above, originally discussed in chapter 3, summarises the effects of altering the organic template molecule in an aluminophosphate gel of otherwise standard composition. A general trend was observed whereby increasing the size of the template molecule TEA<TEAOH<TPA<TPAOH resulted in a slowing of the crystallisation kinetics, although the gradients of the growth curves for TEA and TEAOH are relatively similar. A decrease in the stability of the resulting product with
increasing size was also noted with the TEA and TEAOH templates producing stable AFI phases while TPA and TPAOH templates produced increasingly unstable products. The AlPO-5 (AFI) phase was found to be the only product formed within the period of the experiment except in the case of the TEAOH template where a small quantity of a secondary phase, believed to be AlPO-18 (AEI), was produced. Possible reasons for these observations were proposed in chapter 3 based on both the differing size and basicities of the template molecules.

4.3.2) Co(II) and Co(III) Substituted Aluminophosphate Gels

The effects of substituting cobalt for aluminium in the precursor gel using cobalt (II) acetate as the soluble cobalt salt were also discussed in detail in chapter 3, using different template molecules and a range of cobalt concentrations. Briefly recapping these results, it was found that for the TEA template, increasing the proportion of cobalt above Co/P=0.03 resulted in a slowly increasing proportion of the secondary CoAlPO-34 (CHA) phase being formed. However, high levels of cobalt had to be substituted (Co/P≥0.10) in addition to increasing the TEA content of the pre-cursor gel to produce a pure chabazitic phase. For TEAOH, low levels of cobalt substitution up to Co/P=0.04 were found to slowly increase the proportion of the AEI phase observed in the pure aluminophosphate phase. However, at higher levels of cobalt substitution, CHA was preferred as the secondary phase and was found to become dominant over AFI.

For TPA, low levels of cobalt substitution where Co/P<0.02 were found to produce an unstable AFI phase while further increasing the cobalt concentration
resulted in the formation of an increasing proportion of the stable secondary phase, CoAlPO-36 (ATS). Finally, for TPAOH, at a cobalt concentration Co/P=0.04, the AFI phase, which had been observed rapidly to collapse in the pure aluminophosphate form, appeared to stabilise after a partial framework collapse and remained stable after a period of 80 minutes when scanning was stopped.

In direct comparison with figure 4.2 above, figure 4.3 shows the crystallisation curves for the formation of the AFI phase at 443K where Co/P=0.04 for each of the organic template molecules under study. Considering the sample made with TEA template, it can be seen that the crystallinity of the final AFI product is similar to that for the aluminophosphate gel. However, a comparison of the AFI phases produced with the TEAOH template shows a dramatic drop in the crystallinity of the AFI phase indicating a reduction in the total quantity of AFI formed.

![Figure 4.3 - Comparative crystallisation curves for the synthesis of AFI carried out at 443K for a cobalt substituted gel where Co/P=0.04. Syntheses were undertaken with a range of organic template molecules and illustrate the differences in kinetic behaviour and stability of the resulting AFI. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.](image-url)
These differences can be explained by considering the differing behaviour of TEA and TEAOH with regards to the relative proportions of AFI and secondary phase in the competitive formation as described above and illustrated in figures 4.4a and 4.4b. The increase in the proportion of secondary phase is much greater for the TEAOH synthesis, where the AFI and AEI synthesis curves cross repeatedly as both phases compete for the available crystallisation resources.

Figure 4.4c illustrates the competitive formation of AFI and ATS with TPA template and shows that the AFI phase slowly collapses over time while ATS remains stable. It does appear however that the presence of cobalt in the gel acts to slow down this collapse. A comparison of figure 4.2 and figure 4.3 once again shows that less AFI phase crystallises from the cobalt-substituted gel due to the competitive formation of ATS.
Figure 4.4 – Comparative crystallisation curves for syntheses carried out at 443K for a cobalt substituted gel where Co/P=0.04 and the organic template is a) TEA, b) TEAOH and c) TPA. Plots illustrate the competitive formation behaviour with each of the templates. Data were plotted from the AFI (100), CHA (100), AEI (110) and ATS (110) reflections and have been corrected for beam decay and intensity.
As mentioned previously, it was observed in each case that the product samples were blue in colour, indicative of tetrahedral co-ordination as compared to the pink colour observed in the cobalt (II) acetate source in which cobalt is known to be octahedrally coordinated. The case for tetrahedral co-ordination was supported by EXAFS data recorded for the samples described above, confirming in each case that the cobalt was in a tetrahedral coordinated state, which in turn strongly suggested incorporation into the aluminophosphate framework structure. Furthermore, the Co-O bond distances for these samples as described in table 4.2 below were close to the accepted values (ca. 1.94Å) for a tetrahedrally coordinated, framework substituted sample as described by others.\(^{22}\) Figures 4.5a and 4.5b respectively show comparisons between the experimental and theoretical EXAFS data and the corresponding experimental and theoretical Fourier transforms for the in situ synthesised sample with TEA template where Co/P=0.04. The data were fitted to a single co-ordination shell, thus considering only the environment of the oxygen atoms immediately surrounding the central cobalt atom.

*Table 4.2 — EXAFS parameters for CoAPOs produced with a range of templates.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Co/P</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2(\sigma^2))</th>
<th>(E_f) (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEA</td>
<td>0.04</td>
<td>4.0</td>
<td>1.930</td>
<td>0.012</td>
<td>-6.26</td>
<td>27.99</td>
</tr>
<tr>
<td>2</td>
<td>TEAOH</td>
<td>0.04</td>
<td>3.9</td>
<td>1.943</td>
<td>0.013</td>
<td>0.57</td>
<td>24.69</td>
</tr>
<tr>
<td>3</td>
<td>TPA</td>
<td>0.04</td>
<td>3.9</td>
<td>1.954</td>
<td>0.016</td>
<td>1.22</td>
<td>26.28</td>
</tr>
<tr>
<td>4</td>
<td>TPAOH</td>
<td>0.04</td>
<td>4.0</td>
<td>1.953</td>
<td>0.018</td>
<td>1.41</td>
<td>24.86</td>
</tr>
</tbody>
</table>

\(N=\) shell occupancy, \(R=\) radial distance (Å), \(A=\) Debye-Waller factor (2\(\sigma^2\)), \(E_f=\) Edge position relative to the calculated vacuum zero (eV).
Figure 4.5 – a) Co K-edge EXAFS data and b) the associated Fourier transform for the synthesis of CoAlPO-5 with Co(II) acetate where Co/P=0.04 with the TEA template at 443K. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.2 (Sample 1).
In addition to using cobalt (II) acetate as a soluble cobalt source for substitution into aluminophosphate gels, cobalt (III) acetylacetate was also considered for syntheses at 443K with both the TEA and TEAOH templates. Figures 4.6a and 4.6b compare the AFI crystallisation curves for the two cobalt sources with TEA and TEAOH templates respectively. The kinetic behaviour in each case does not appear greatly affected by the cobalt source, with differences in the TEAOH profiles for AFI being caused by differing fluctuations during the competitive formation with AEI. The synthesis with TEA template was once again observed to produce a small quantity of CHA but this reflection was too weak to plot an accurate crystallisation curve. The competitive crystallisation of AFI and AEI for the cobalt (III) acetylacetate source with TEAOH is shown in figure 4.6c.
Figure 4.6 - Comparative crystallisation curves for AFI in syntheses carried out at 443K for cobalt (II) acetate and cobalt (III) acetylacetate substituted gels where Co/P=0.04 using a) TEA and b) TEAOH templates. Plot c) illustrates the competitive formation of AFI and AEI with the Co(III)acetylacetate source. Data were plotted from the AFI (100) and AEI (110) reflections and have been corrected for beam decay and intensity.
As mentioned previously, Cobalt (II) acetate is pink while, in comparison, the cobalt (III) acetylacetate source is dark green. However, in both cases the resulting cobalt aluminophosphates are deep blue for a pure AFI phase and a dark grey-blue when significant quantities of either AEI or CHA are present. This colour change is indicative of cobalt in a tetrahedral environment as would be expected for cobalt species substituted into the aluminophosphate framework. In addition, it can be seen from table 4.3 and figure 4.7 below that the EXAFS parameters are very similar for both sources and are once again indicative of tetrahedrally coordinated, framework incorporated cobalt. Considering this evidence together with the similar kinetic behaviour of syntheses carried out with each source, it would therefore appear that either of these two cobalt sources can be used with equal effect to synthesise microporous cobalt aluminophosphates.

Table 4.3 – EXAFS parameters for CoAlPOs with Co(II) and Co(III) sources.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Co/P</th>
<th>Co Source</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ²)</th>
<th>E_f  (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEA</td>
<td>0.04</td>
<td>CoAc₂</td>
<td>4.0</td>
<td>1.930</td>
<td>0.012</td>
<td>-6.26</td>
<td>27.99</td>
</tr>
<tr>
<td>2</td>
<td>TEAOH</td>
<td>0.04</td>
<td>CoAc₂</td>
<td>3.9</td>
<td>1.943</td>
<td>0.013</td>
<td>0.57</td>
<td>24.69</td>
</tr>
<tr>
<td>5</td>
<td>TEA</td>
<td>0.04</td>
<td>CoAc₃</td>
<td>3.9</td>
<td>1.944</td>
<td>0.013</td>
<td>-0.41</td>
<td>26.78</td>
</tr>
<tr>
<td>6</td>
<td>TEAOH</td>
<td>0.04</td>
<td>CoAc₃</td>
<td>4.0</td>
<td>1.953</td>
<td>0.019</td>
<td>1.97</td>
<td>41.25*</td>
</tr>
</tbody>
</table>

* Noisy data.
Figure 4.7 – a) Co K-edge EXAFS data and b) the associated Fourier transform for the synthesis of CoAlPO-5 with Co(III) acetylacetate where Co/P=0.04 with the TEA template at 443K. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.3 (Sample 5).
4.3.3) Zinc Substituted Aluminophosphate Gels

Zinc, like cobalt, has been successfully incorporated into a wide range of microporous aluminophosphate materials, including the AFI, AEI, CHA and ATS structures. Several of these ZnAPOs have proved to be active acid catalysts for the conversion of methanol to hydrocarbons. However, unlike cobalt, the framework-substituted zinc does not exhibit variable oxidation states when exposed to regimes of calcination and reduction, so zinc substituted materials cannot be used in oxidation or bi-functional catalytic applications. ZnAPOs are therefore suitable for shape selective catalytic applications where the effects of changing oxidation state may have an adverse effect. Furthermore, the ZnAPO structures have been reported to have slightly lower maximum catalytic activities in similar reactions than equivalent cobalt structures, but slightly higher activities than equivalent manganese and iron substituted structures. Such variations in catalytic activity and structure allow the possibility of MeAPOs being tailored for specific catalytic applications, where the activity can affect the selectivity of the catalyst.

Zinc was initially substituted at a constant concentration Zn/P=0.04 into precursor gels containing TEA, TEAOH, TPA and TPAOH templates and syntheses were carried out at 443K. The competitive formation of AFI and chabazitic phases was subsequently investigated over a range of zinc concentrations with the TEAOH template. These later experiments were carried out at a fixed angle broadly similar to that for the initial experiments of 1.29°20; this angle was later calibrated as 0.91°20. Additionally, reflections indicative of the possible formation of a highly unstable intermediate were observed to form with the TPAOH template and this phenomenon was subsequently investigated.
4.3.3.1) The Effect of Varying the Template Type for Gels where Zn/P=0.04 at 443K

Substituting zinc, where Zn/P=0.04 into the aluminophosphate system at 443K can promote the formation of secondary crystalline phases and thus has a complicating effect on the observed kinetics of crystallisation of AFI formation, shown in figure 4.8a below. In this case, the TPA template produced AFI in the fastest time and in a highly crystalline form. However, as described below, both the TEAOH and TPA templated synthesis resulted in the competitive formation of secondary phases, with a pure AFI phase crystallising only in the TEA templated synthesis.

The secondary phases formed with the TEAOH and TPA templates have been confirmed as identical to those formed for cobalt, these being AEI and ATS respectively. The kinetic data for these competitive crystallisations are shown in figures 4.8b and 4.8c.
Figure 4.8 – a) Comparative crystallisation curves for syntheses carried out at 443K for a zinc substituted gel where Zn/P=0.04 and the organic template is TEA, TEAOH and TPA. Plots (b) and (c) illustrate the competitive formation behaviour with TEAOH and TPA respectively. Data were plotted from the AFI (100), AEI (110) and ATS (110) reflections and have been corrected for beam decay and intensity.
With gels containing TPAOH template, an interesting observation was repeatedly recorded whereby shortly before and during the early stages of AFI crystallisation, an extra reflection appeared at the lower energy (larger d-spacing) end of the pattern as shown in figure 4.9. It is possible that this reflection is due to the formation of a highly unstable layered phase just prior to the formation of the stable AFI phase. Similar phases have previously been reported in other in situ EDXRD experiments, including that reported by Francis et al.\textsuperscript{35-36} during in situ investigations of the synthesis of the microporous oxy-fluorinated gallophosphate ULM-5, using the same experimental set-up as ourselves\textsuperscript{23}.

![Figure 4.9 - Time resolved EDXRD data sets for the synthesis carried out at 443K with a zinc substituted gel where Zn/P=0.04 and the organic template is TPAOH. The formation of a possible unstable transitory intermediate phase can be seen as an extra reflection at ca. 37keV appearing just before those for AFI and ATS.](image-url)
Data from the middle detector was in this case not able to assist in the identification of the intermediate phase due both to its low crystallinity and the simultaneous crystallisation of the AFI and ATS phases. Subsequent attempts to isolate this unstable intermediate phase for detailed structural analysis have to date proved unsuccessful. Its unstable nature is highlighted in figure 4.10, which also shows the formation of the AFI phase and a secondary ATS phase. Zinc was the only heteroatom that, when substituted into the pre-cursor gel, was observed to form the ATS structure with the TPAOH template.

A consideration of the nature of the heteroatom within the microporous aluminophosphate system can often be aided by clues from the colour of the products, as in the case of cobalt. However, with zinc each of the products was white, in common with the vast majority of zinc compounds. The collection of Zn K-edge
EXAFS data, however, indicated a tetrahedrally coordinated zinc environment for samples synthesised with each of the four template molecules as shown in table 4.4. Typical fits to both the EXAFS data and the corresponding Fourier transform, in this case for the sample produced with the TEA template are shown in figures 4.11a and b.

The radii of the fitted co-ordination shells (Zn-O) for each sample shown in table 4.4 were found to be similar to those values reported by Sankar et al. of 1.92Å\textsuperscript{22} for both the ZnAPO-18 and -36 structures and Tušar et al.(1.94Å)\textsuperscript{34} for the ZnAPO-47 (CHA) structure and attributed in both cases to tetrahedrally coordinated, framework substituted zinc. In comparison, the wurtzite form of zinc oxide, while being tetrahedral, has a larger Zn-O radial distance of 1.98Å\textsuperscript{34}, while the zinc hydroxide structure has a highly distorted tetrahedral co-ordination, with bond lengths ranging from 1.875-2.063Å.\textsuperscript{74}

**Table 4.4 – EXAFS parameters for ZnAPOs synthesised with a range of templates.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Zn/P</th>
<th>Zn Source</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ(^2))</th>
<th>Ef (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>TEA</td>
<td>0.04</td>
<td>ZnAc(_2)</td>
<td>4.1</td>
<td>1.920</td>
<td>0.012</td>
<td>-1.74</td>
<td>29.33</td>
</tr>
<tr>
<td>8</td>
<td>TEAOH</td>
<td>0.04</td>
<td>ZnAc(_2)</td>
<td>4.0</td>
<td>1.926</td>
<td>0.013</td>
<td>-1.71</td>
<td>46.52</td>
</tr>
<tr>
<td>9</td>
<td>TPA</td>
<td>0.04</td>
<td>ZnAc(_2)</td>
<td>4.1</td>
<td>1.920</td>
<td>0.013</td>
<td>-2.09</td>
<td>32.76</td>
</tr>
<tr>
<td>10</td>
<td>TPAOH</td>
<td>0.04</td>
<td>ZnAc(_2)</td>
<td>4.0</td>
<td>1.936</td>
<td>0.014</td>
<td>-2.87</td>
<td>26.72</td>
</tr>
</tbody>
</table>
Figure 4.11 – a) Zn K-edge EXAFS data and b) the associated Fourier transform for the synthesis of ZnAlPO-5 with Zn(II) acetate where Zn/P=0.04 with the TEA template at 443K. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.4 (Sample 7).
4.3.3.2) The Effect of Varying the Level of Zn Substitution with the TEAOH Template at 443K

Increasing the level of zinc substitution resulted in the formation of AFI with steadily decreasing crystallinity but in this case with no significant decrease in reaction rate as shown in figure 4.12a. In contrast, figure 4.12b shows that the secondary chabazitic phase begins to crystallise increasingly earlier as the level of zinc increases. However, the quantity of secondary phase remains small within the time-scale of the experiment, probably due to the low crystallisation rate of this phase even when the zinc loading has increased to levels where no AFI crystallises. It is likely though, that in a similar way to cobalt, the nature of the secondary phase at low heteroatom concentrations is different to that at higher cobalt concentrations. ZnAPO-18 has been reported to form only at low levels of zinc substitution, typically 2-6%.9 22 In comparison, Tušar et al.34 have reported the formation of ZnAPO-47 (CHA) with ca.20% of the framework aluminium being substituted by zinc while González et al.33 have reported the synthesis of the ZnAPO-34 (CHA) with a chemical composition indicating ca. 10% framework zinc substitution.
Figure 4.12 – Comparative crystallisation curves for a) AFI and b) CHA in syntheses carried out at 443K for a range of zinc concentrations using the TEAOH template. Data were plotted from the AFI (100) and CHA(100) reflections and have been corrected for beam decay and intensity.
4.3.4) Magnesium Substituted Aluminophosphate Gels

Magnesium and zinc are generally considered to have similar chemical behaviour in the divalent state with respect to the types of compound formed. Similar behaviour may therefore be expected when substituting these materials into aluminophosphate pre-cursor gels. Indeed, Zn and Mg substituted gels are frequently reported to form similar microporous aluminophosphate phases under the same synthesis conditions. Many different microporous MgAPO structures (normally classified as MAPOs) have been synthesised, in addition to those discussed here including previously known structures such as MAPO-39, MAPO-11 and MAPO-20 as well as several novel frameworks such as DAF-1, STA-1 and STA-2.

A great deal of interest has been shown in the synthesis of MAPOs because these structures are among the most catalytically active materials of their kind. In an early paper describing metal substitution in microporous aluminophosphates, Wilson et al. reported that magnesium substituted structures were more catalytically active than equivalent structures with either cobalt, manganese or iron. In fact, the MAPO-36 structure rivals the protonated form of faujasite (zeolite H-Y) in its activity as a superacid for the catalytic cracking of alkanes. Furthermore, Akolekar et al., upon investigating the catalytic activities of ATS structures containing multiple heteroatoms in combination on the n-aliphatic and aromatic hydrocarbon conversion reactions, consistently found the best performance with combinations including magnesium. In fact, the pure MAPO-36 was found to be the most active of all apart from the magnesium silicon form (MAPSO-36). They found, by temperature programmed desorption of pyridine that this effect was due to magnesium having the strongest acid sites. However, there are disadvantages in such strong acidity which
may provoke rapid coking and thus deactivation of the catalyst and can also simply result in the catalytic selectivity favouring the formation of unwanted products.

In this study we have discovered that, as shown in figure 4.13, magnesium substituted aluminophosphates do indeed produce secondary phases with TEAOH and TPA, with the crystallisation behaviour of magnesium substituted gels being in many ways similar to that of both the cobalt and zinc substituted aluminophosphates. A pure AFI phase crystallises with TEA as for zinc, while AEI forms competitively with AFI in the TEAOH experiment (figure 4.13b) and as with cobalt, ATS is the dominant phase formed in the TPA synthesis along with a small quantity of AFI (figure 4.13c). A comparison of the crystallisation curves for AFI formation with each of these templates (figure 4.13a) shows that, once again, the TEA and TEAOH templated systems exhibit very similar kinetic behaviour in terms of the crystallisation rates while TPA forms a less crystalline AFI product more slowly.
Figure 4.13 – a) Comparative crystallisation curves for the synthesis of an AFI phase with a magnesium substituted pre-cursor gel at 443K where Mg/P=0.04 using TEA, TEAOH and TPA templates. Plots (b) and (c) illustrate the competitive formation with TEAOH and TPA templates respectively. Data were plotted from the AFI (100), AEI (110) and ATS(110) reflections and have been corrected for beam decay and intensity.
Unfortunately, it was not possible to carry out Mg K-edge EXAFS experiments on station 7.1 as magnesium is outside the energy range of this experimental apparatus. Likewise, no clue as to the situation of the magnesium within the aluminophosphate system can be gained from the colour of the samples. We may however postulate due to the close similarities in the kinetic behaviour of the MAPO gels with the CoAlPO and ZnAPO gels and the evidence of framework substitution from other sources under similar experimental conditions, that Mg is likely to have entered the framework. Confirmation of this could be gained from soft EXAFS experiments, which could also be carried out at the Daresbury synchrotron radiation source on experimental station 3.4. In addition, FT-IR analysis of the calcined sample would reveal the presence of any acid sites in the framework produced by magnesium incorporation.

4.3.5) Mn (II) and Mn (III) Substituted Aluminophosphate Gels

Manganese is similar to cobalt in having multiple oxidation states of which Mn (II) is the most stable. This Mn(II) state is however, readily oxidised to Mn (III), allowing manganese substituted aluminophosphates to have applications as redox catalysts in addition to the acidic character brought about by the framework charge. As with the other MeAPOs described so far, many aluminophosphate structures have been reported into which manganese has been successfully framework incorporated. These include MnAPO-5, an effective and highly selective catalyst for the dehydrogenation of ethane to ethene\textsuperscript{42}, MnAPO-18\textsuperscript{43} MnAPO-20\textsuperscript{44,45}, MnAPO-34\textsuperscript{46}, MnAPO-44\textsuperscript{46-47}, MnAPO-36\textsuperscript{48}. In addition, many of these structures have been
synthesised with the additional substitution of silicon, giving rise to enhanced catalytic activity. Vieira et al.⁴⁹ also reported enhanced activity in the transformation of n-butane to isobutene and isobutane when MnAPO-11 was used as a support for platinum.

During our kinetic studies of the MnAPO system, both Mn(II) and Mn(III) sources were investigated at a fixed manganese concentration (Mn/P=0.04). The Mn(III) source was only considered with the TEA template due to a limited supply of this source. Subsequent studies were also carried out over a range of Mn(II) concentrations using the TEAOH template allowing us to compare the behaviour of manganese with that of cobalt in terms of competitive crystallisation.

4.3.5.1) The Effect of Varying the Template Type for Gels where Mn/P=0.04 at 443K

Figure 4.14 below shows the observed crystallisation kinetics of the AFI phase for a series of manganese substituted gels where Mn/P=0.04 at 443K for the TEA, TEAOH and TPA templates. On this occasion, the TEAOH templated gel was the first to exhibit crystallisation with AFI reflections being first observed after 16 minutes compared to 21 minutes for the TEA gel. However, the growth rates for TEA and TEAOH were very similar as previously observed, for the pure aluminophosphate gel while both templates produced equally crystalline material.

Use of the TPA template was once again found both to slow the rate of synthesis and to produce a less crystalline product. The Mn²⁺ was observed to act in a similar way to Co²⁺, Zn²⁺ and Mg²⁺ by appearing to have somewhat of a stabilising
effect on the AFI phase, preventing the rapid structural collapse observed in the pure aluminophosphate sample.

Figure 4.14 - Comparative crystallisation curves for AFI in syntheses carried out at 443K for manganese substituted gels where Mn/P=0.04 using TEA, TEAOH and TPA templates. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.

Syntheses carried out with both Mn(II) and Mn(III) sources exhibited virtually identical crystallisation curves and in each case produced comparable, well crystalline pure AFI phases as can be seen in figure 4.15. The white Mn(II) acetate and the brown Mn(III) acetylacetate sources both produced white MnAPO-5 products, indicative of the manganese having successfully substituted into the framework in a tetrahedral co-ordination, a result subsequently confirmed by EXAFS as discussed below.

The more noisy appearance of the Mn(II) crystallisation curve was simply due the synchrotron beam current being considerably lower when this scan was recorded. This result, as with that for cobalt appears to indicate that the Mn(II) and Mn(III)
sources are essentially interchangeable for the production of MnAPO-5 and probably other microporous MnAPOs.

![Figure 4.15 - Comparative crystallisation curves for AFI in syntheses carried out at 443K for manganese (II) acetate and manganese (III) acetylacetate substituted gels where Mn/P=0.04 using the TEA template. Data were plotted from the AFI (100) reflection and has been corrected for beam decay and intensity.](image)

The Mn K-edge EXAFS data and associated Fourier transform for the sample produced with Mn(II) acetate and TEAOH are shown in figure 4.16 overleaf while the parameters from fitted EXAFS data of the other samples are listed in table 4.5 below. The large R-factors for samples 13 and 14 were due to the presence of an electronic glitch in the data but this did not significantly affect the fit to a single co-ordination shell.

Analysis of this EXAFS data indicates that samples produced from the Mn(II) acetate source with each of the different templates exhibit tetrahedral co-ordination as would be expected if framework substitution had occurred. The radial Mn-O distances gained from the single shell fits are indicative of framework incorporated manganese and are significantly shorter than those expected for octahedrally co-ordinated
Mn(OH)₂ and hydrated manganese complexes such as Mn(H₂O)₆²⁺. For such compounds, the Mn-O lengths are typically in the range 2.1-2.2 Å.⁷⁵-⁷⁶

Comparison of those samples produced using the Mn (II) and Mn(III) acetate sources show similar results as was also the case with cobalt, discussed previously. Once again, it may be suggested that either Mn(II) or Mn(III) acetate can be used to equal effect in the synthesis of MnAPOs.

### Table 4.5 – EXAFS parameters for MnAPOs synthesised with a range of templates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Mn/P</th>
<th>Mn Source</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ²)</th>
<th>Eᵣ (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>TEA</td>
<td>0.04</td>
<td>MnAc₂</td>
<td>3.8</td>
<td>2.012</td>
<td>0.014</td>
<td>-1.32</td>
<td>26.49</td>
</tr>
<tr>
<td>12</td>
<td>TEAOH</td>
<td>0.04</td>
<td>MnAc₂</td>
<td>3.8</td>
<td>2.012</td>
<td>0.013</td>
<td>-1.01</td>
<td>26.09</td>
</tr>
<tr>
<td>13</td>
<td>TPA</td>
<td>0.04</td>
<td>MnAc₂</td>
<td>3.9</td>
<td>2.032</td>
<td>0.017</td>
<td>-0.23</td>
<td>35.81*</td>
</tr>
<tr>
<td>14</td>
<td>TEA</td>
<td>0.04</td>
<td>MnAcAc₃</td>
<td>4.1</td>
<td>2.001</td>
<td>0.014</td>
<td>-0.30</td>
<td>35.44*</td>
</tr>
</tbody>
</table>

*Glitched data.
Figure 4.16 - a) Mn K-edge EXAFS data and b) the associated Fourier transform for the synthesis of MnAPO-5 with Mn(II) acetate where Mn/P=0.04 with the TEAOH template at 443K. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.5 (Sample 12).
4.3.5.2) The Effect of Varying the Level of Mn Substitution with the TEAOH Template at 443K

Several different concentrations of manganese were substituted into pre-cursor gels in order to compare the effect of changing manganese concentration with that for the cobalt substituted gels discussed in chapter 3. Unlike for the CoAPO₄ gels, no secondary phase formation was observed until the manganese concentration was increased to Mn/P=0.14. Clarification of the exact nature of the secondary phase was not possible due to competitive AFI formation and the low crystallinity of this phase, but considering the high manganese concentration it is likely to be CHA as opposed to AEI. Furthermore, increasing the concentration above Mn/P=0.18 resulted once again in only AFI being formed. Figures 4.17a and 4.17b show the crystallisation curves for AFI and CHA over these concentrations and it can be seen that in both cases, increasing the manganese concentration generally acts to both slow the crystallisation and reduce the crystallinity of the product phases. Variations in the data quality are mainly an artefact of varying synchrotron beam intensity at the time of data collection.

The effect of altering the manganese concentration produces a significantly different result to that observed for cobalt where increasing the cobalt concentration tended to promote the formation of an increasingly more crystalline AEI or CHA phase. This result suggests that the secondary chabazitic phase is unstable in comparison to the AFI phase even at high manganese concentrations. Furthermore, if we consider that the AFI framework can only accept low levels of heteroatom substitution, we must therefore consider the nature of the excess manganese. At these higher manganese concentrations, the samples increasingly take on a pale pink colour,
indicating the likely presence of octahedrally co-ordinated, extra-framework hydrated
Mn$^{2+}$ manganese species such as Mn(H$_2$O)$_6^{2+}$, which is pale pink.\textsuperscript{37}

a) AFI

![Graph](image)

b) CHA

![Graph](image)

\textbf{Figure 4.17 – Comparative crystallisation curves for a) AFI and b) CHA in syntheses carried out at 443K for a range of manganese concentrations using the TEAOH template. Data were plotted from the AFI (100) and CHA(100) reflections and have been corrected for beam decay and intensity.}
As additional evidence for the presence of extra-framework manganese at high manganese concentrations, EXAFS analysis of these samples shows a trend whereby the Mn-O bond length tends to increase with increasing Mn/P as summarised in table 4.6. This trend can be more clearly observed in figure 4.18, where the error bars represent the standard deviation of ±0.02Å generally accepted for bond lengths calculated from EXAFS data. This increase in the Mn-O distance ties in well with the idea that an increasing proportion of the manganese is present as extra-framework Mn(H₂O)₆²⁺ which has Mn-O bonds in the range 2.117-2.210Å. While an increase in co-ordination number can be observed at high Mn/P levels for samples 17 and 18, this cannot really be considered significant as coordination number measurement with EXAFS is generally only considered accurate to within ±10%. In figure 4.19 can be seen plots of the EXAFS data and the associated Fourier transform for the sample with the highest loading of manganese (Mn/P=0.26).
Table 4.6 – EXAFS parameters for MnAPOs synthesised with TEAOH over a range of manganese concentrations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Mn/P</th>
<th>Mn Source</th>
<th>N</th>
<th>R</th>
<th>A</th>
<th>E_0</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>TEAOH</td>
<td>0.04</td>
<td>MnAc_2</td>
<td>3.8</td>
<td>2.012</td>
<td>0.013</td>
<td>-1.01</td>
<td>26.11</td>
</tr>
<tr>
<td>15</td>
<td>TEAOH</td>
<td>0.10</td>
<td>MnAc_2</td>
<td>3.7</td>
<td>2.059</td>
<td>0.024</td>
<td>-1.74</td>
<td>30.61</td>
</tr>
<tr>
<td>16</td>
<td>TEAOH</td>
<td>0.18</td>
<td>MnAc_2</td>
<td>3.8</td>
<td>2.078</td>
<td>0.026</td>
<td>-0.05</td>
<td>31.88</td>
</tr>
<tr>
<td>17</td>
<td>TEAOH</td>
<td>0.22</td>
<td>MnAc_2</td>
<td>4.2</td>
<td>2.128</td>
<td>0.026</td>
<td>-0.11</td>
<td>34.40</td>
</tr>
<tr>
<td>18</td>
<td>TEAOH</td>
<td>0.26</td>
<td>MnAc_2</td>
<td>4.3</td>
<td>2.151</td>
<td>0.029</td>
<td>-0.77</td>
<td>31.65</td>
</tr>
</tbody>
</table>

Figure 4.18 – Graph showing the trend in increasing Mn-O distance with increasing levels of manganese substitution into a precursor gel synthesised at 443K with TEAOH template. Error bars represent the standard deviation generally accepted for bond lengths calculated with the EXAFS technique (±0.02Å)
Figure 4.19 – a) Mn K-edge EXAFS data and b) the associated Fourier transform for the synthesis of MnAPO-5 with Mn(II) acetate where Mn/P=0.26 with the TEAOH template at 443K. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.6 (Sample 18).
4.3.6) Fe(II) and Fe(III) Substituted Aluminophosphate Gels

During the period immediately following the initial discovery of microporous aluminophosphates\textsuperscript{51}, there was a great deal of interest in the substitution of a wide range of heteroatoms, including iron into these structures\textsuperscript{2}. Union Carbide were the first to claim the synthesis of iron substituted aluminophosphates and classified these materials as FAPOs.\textsuperscript{52} Initial studies on these FAPOs, carried out using techniques such as Mössbauer spectroscopy appeared to suggest that the iron directly substituted for Al(III) as Fe(III) with the result that the framework remained neutral and would thus exhibit no acid catalytic activity.\textsuperscript{53}

Later studies using EPR spectroscopy\textsuperscript{54-55} reported the nature of the iron species within the aluminophosphate system to be considerably more complicated, with Fe(II) and Fe(III) species being present in the framework in a variety of both tetrahedral and octahedral environments. However, there has been much debate regarding the interpretation of the EPR data, with the use of early model systems such as FePO\textsubscript{4}\textsuperscript{54} being later discredited due to the effect of strong magnetic exchange interactions in such pure iron compounds.\textsuperscript{56} Catana et al.\textsuperscript{54} later interpreted EPR signals to represent Fe(III) in defect sites in addition to identifying isomorphously substituted tetrahedral Fe(II) and Fe(III) in oxidic iron clusters.

In a recent study Brückner et al.\textsuperscript{56} used Mössbauer and EPR spectroscopies to investigate the nature of Fe(II) and Fe(III) species in FAPO-5 produced via both microwave and conventional synthesis. They again concluded that both Fe(II) and Fe(III) species are present in the framework and also claimed that in as-synthesised, hydrated FAPOs all of the iron ions are in an octahedral environment, while upon calcination, tetrahedral Fe(III) centres were formed. As described below, our EXAFS
studies regarding the coordination environments of iron in FAPO-5 disagree significantly with the findings of others discussed above.

It is likely that many of the uncertainties that have arisen during these studies of the FAPO-5 system are simply due to the use of different synthesis methods which can have profound effects on the nature of the iron within the aluminophosphate system. This problem has resulted in comparisons of data between samples that are obviously different, even to the extent of being different colours\textsuperscript{55-56}.

During the course of our investigations on the FAPO-5 system, a series of \textit{in situ} experiments were carried out with a constant concentration of the Fe (II) acetate source, where Fe/P=0.04 using TEA, TEAOH and TPA templates and also using TEAOH over a range of Fe(II) acetate concentrations (Fe/P=0.04-0.20). Subsequent laboratory experiments were performed with an Fe(III) source to compare the nature of the crystalline phases produced. Finally, \textit{in situ} EXAFS studies were carried out for a pure FAPO-5 sample synthesised using TEAOH where Fe/P=0.04, within a specially designed environmental cell. During this investigation, the sample was calcined in oxygen and subsequently reduced under a H\textsubscript{2}/N\textsubscript{2} atmosphere with EXAFS data being recorded of the changes in the iron coordination environment after each step.
4.3.6.1) The Effect of Varying the Template Type for Gels where Fe/P=0.04 at 443K

*Figure 4.20* shows the effect of substituting a fixed concentration of iron(II) acetate where Fe/P=0.04 into pre-cursor gels containing TEA, TEAOH and TPA templates and subsequently undergoing hydrothermal treatment at 443K. While each of the gels were found to begin crystallisation just after 20 minutes within a period of *ca.* 3 minutes TPA begin to crystallise first followed by TEAOH and TEA. However, the rates of crystallisation as obtained from the gradients of the curves are very similar. Using TEAOH resulted in the formation of a stable, well crystalline pure AFI phase, while that produced with TEA was found to be less crystalline and comparatively unstable as indicated by a steady drop in reflection intensity after completion of crystal growth. TPA was even less crystalline and stable, beginning to collapse rapidly after completion of crystallisation.

![Comparative crystallisation curves for AFI in syntheses carried out at 443K for iron substituted gels where Fe/P=0.04 using TEA, TEAOH and TPA templates. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.](image)
These observations were compared with the appearance of the washed and dried FAPO products where we found that TEAOH produced a white product, TEA produced a very pale green product and TPA produced a mixture consisting of a mainly white product with dark green flecks. Laboratory syntheses with each of these templates confirmed these results, with the TEAOH repeatedly producing a white sample with Fe(II) acetate. Substituting this iron source with Fe(III) acetylacetate was found to produce light green products with all of the templates. The green colouration observed in these situations may be indicative of the presence of an extra-framework Iron (II) species such as Fe(H$_2$O)$_6^{2+}$ within the microporous structure, which has been reported as being sea green in colour$^{37}$. For this reason, the TEAOH synthesis was used in the subsequent experiments described later.

Park and Chon$^{55}$ reported that samples produced using pseudoboehmite, 85% H$_3$PO$_4$, FeCl$_2$ and TEAOH template were also found to be white. Upon calcination in nitrogen then air at 780K for 5 hours each, these samples were reported to become off-white in colour. This also agrees with our findings from the FeAPO-5 calcination experiment discussed below (section 4.3.1.6.3). In contrast, Brückner et al.$^{56}$ used aluminium isopropoxide, H$_3$PO$_4$, Fe(II)/Fe(III) sulphate and cyclohexylamine template. Their samples were light green with the Fe(II) source and light brown with the Fe(III) source, strongly suggesting the presence of extra-framework Fe(II) and Fe(III) species such as Fe(H$_2$O)$_6^{2+}$ and FeO(OH) respectively. As mentioned above, direct comparison of the findings from characterisation of such samples is not really justifiable, especially when using techniques such as Mössbauer and EPR spectroscopies to study the nature of the iron in the system.

Subsequent Fe K-edge EXAFS analysis of the samples synthesised with the TEA and TEAOH templates indicated that the iron is tetrahedrally coordinated with
bond lengths shown in table 4.7. While these bond lengths are similar to those exhibited by Fe(H2O)62+, (1.97-1.99Å)77 the data cannot be fitted to an octahedrally coordinated model. Figures 4.21a and 4.21b show respectively the EXAFS data and the corresponding Fourier transform with the best fit for a single co-ordination shell model in each case. This result contrasts directly with those recently reported in the Mössbauer and EPR spectroscopic investigation carried out by Brückner et al.56, who claimed that all iron ions in as-synthesised samples were octahedrally co-ordinated. The calcined samples were reported to contain tetrahedrally co-ordinated Fe(III) species.

The octahedral coordination reported for the as-synthesised samples could be due to the tetrahedrally co-ordinated framework iron species additionally being coordinated to two extra-framework species such as hydroxyl groups or organic ions derived from the template. Another possibility, considering the green and brown colours reported respectively for the Fe(II) and Fe(III) samples, is that the iron species were indeed octahedral but occurred as hydrated extra-framework species.

Table 4.7 – EXAFS parameters for FAPOs synthesised with TEA and TEAOH template molecules.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Fe/P</th>
<th>Fe Source</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ²)</th>
<th>E_f (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>TEA</td>
<td>0.04</td>
<td>FeAc₂</td>
<td>4.1</td>
<td>1.957</td>
<td>0.015</td>
<td>-0.01</td>
<td>24.85</td>
</tr>
<tr>
<td>20</td>
<td>TEAOH</td>
<td>0.04</td>
<td>FeAc₂</td>
<td>4.4</td>
<td>1.974</td>
<td>0.017</td>
<td>0.17</td>
<td>27.40</td>
</tr>
</tbody>
</table>
Figure 4.21 – a) Fe K-edge EXAFS data and b) the associated Fourier transform for the synthesis of FeAPO-5 with Fe(II) acetate where Fe/P=0.04 with the TEA template at 443K. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.7 (sample 19).
In contrast, the AFI phase observed to crystallise during synthesis with the TPA template had collapsed completely back to an amorphous state. Subsequent Fe k-edge EXAFS analysis indicated that this collapse had also brought about a change in the local environment of the iron as can be seen in table 4.8. In this case, the best fit to the data appears to be closer to that of an iron oxide structure, having significantly larger values for Fe-O that are similar to those found in γ-Fe₂O₃ (2x1.980Å and 2x2.106 Å). The EXAFS data and corresponding Fourier transforms for this data are shown in figures 4.22a and 4.22b.

Table 4.8 – EXAFS parameters for the FAPO synthesis with TPA template.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Fe/P</th>
<th>Fe Source</th>
<th>Atom Type</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ²)</th>
<th>E_r (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>TPA</td>
<td>0.04</td>
<td>FeAc₂</td>
<td>O</td>
<td>2.3</td>
<td>1.921</td>
<td>0.018</td>
<td>-2.59</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>O</td>
<td>2.7</td>
<td>2.094</td>
<td>0.020</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe</td>
<td>2.3</td>
<td>3.021</td>
<td>0.025</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe</td>
<td>2.3</td>
<td>3.224</td>
<td>0.022</td>
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</tbody>
</table>
Figure 4.22 – a) Fe K-edge EXAFS data and b) the associated Fourier transform for the collapsed FeAPO-5 phase synthesised with Fe(II) acetate where Fe/P=0.04 with the TPA template at 443K. The black line represents the experimental data while the red line represents the best fit using four coordination shells as detailed in table 4.8 (sample 21).
4.3.6.2) The Effect of Varying the Level of Fe Substitution with the TEAOH Template at 443K

The effects of altering the iron concentration with the TEAOH template are shown in figure 4.23 below where it can, once again, be seen that, as for both cobalt and manganese, increasing the quantity of iron reduces both the crystallisation rate and the crystallinity of the AFI. It is interesting to note that even at high levels of iron substitution no secondary crystalline phases are observed. The samples appeared white even at high levels of iron substitution, suggesting that the bulk of the iron has been successfully incorporated into the framework even at high Fe/P.

![Figure 4.23 - Comparative crystallisation curves for AFI in syntheses carried out at 443K for a range of iron concentrations using the TEAOH template. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.](image)

EXAFS studies of samples containing these large concentrations of iron found that increasing the levels of iron substitution up to Fe/P=0.20 did not produce a significant change in the Fe-O radial distance, as shown in table 4.9. A result which is in marked contrast to the increasing Mn-O distance observed previously. This
provides further evidence for the iron being successfully incorporated into the aluminophosphate framework even at these higher iron concentrations.

Table 4.9 – EXAFS parameters for FAPOs synthesised with TEAOH and a range of iron concentrations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Fe/P</th>
<th>Fe Source</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ²)</th>
<th>E_r (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>TEAOH</td>
<td>0.04</td>
<td>FeAc₂</td>
<td>3.8</td>
<td>1.974</td>
<td>0.017</td>
<td>0.17</td>
<td>27.40</td>
</tr>
<tr>
<td>23</td>
<td>TEAOH</td>
<td>0.10</td>
<td>FeAc₂</td>
<td>4.1</td>
<td>1.965</td>
<td>0.014</td>
<td>0.84</td>
<td>24.52</td>
</tr>
<tr>
<td>24</td>
<td>TEAOH</td>
<td>0.14</td>
<td>FeAc₂</td>
<td>4.0</td>
<td>1.966</td>
<td>0.015</td>
<td>-0.48</td>
<td>20.69</td>
</tr>
<tr>
<td>25</td>
<td>TEAOH</td>
<td>0.20</td>
<td>FeAc₂</td>
<td>4.0</td>
<td>1.974</td>
<td>0.016</td>
<td>-0.31</td>
<td>22.24</td>
</tr>
</tbody>
</table>

4.3.6.3) An EXAFS Study of the Redox Characteristics of FeAPO-5

In order to investigate the redox properties of FAPO-5, a 20mm disk was pressed from 130mg of the white sample synthesised with TEAOH where Fe/P=0.04. The disk was then placed in a sample holder which in turn was placed within an environmental cell specially designed for such experiments and previously described in figure 4.12. EXAFS data were subsequently collected for the as prepared sample then after calcination under flowing O₂ for 3 hours at 823K and finally after exposure to reducing conditions under a flow mixture of 4%H₂ in N₂ for 1 hour at 673K.

Upon calcination under O₂, a slight colour change was noted, with the previously white sample disk becoming an off-white creamy colour, a change previously reported by Park and Chon. This colour change coincided with a
significant reduction in the coordination radius for Fe-O as shown in *table 4.10*. The EXAFS spectra and associated Fourier transforms for the sample in its as-prepared and calcined states are shown in *figures 4.24* and 4.25 respectively, while *figure 4.26* highlights the shift in the coordination radii shown as a shift in the position of the main peak of the Fourier transformed data. No change in the coordination number was found to have occurred during calcination, indicating that the bulk of the iron is likely to have remained as framework substituted species, in agreement once again with the findings of Park and Chon\textsuperscript{55}. Subsequent exposure of the calcined sample to reducing conditions appeared to have no significant affect on either the colour of the sample or the EXAFS spectrum.

*Table 4.10 – EXAFS parameters for FAPO5 undergoing a cycle of thermal treatments whereby the sample is exposed to oxidising then reducing conditions.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Fe/P</th>
<th>Treatment</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ²)</th>
<th>E_f (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>TEAOH</td>
<td>0.04</td>
<td>As prep’d</td>
<td>4.4</td>
<td>1.957</td>
<td>0.015</td>
<td>-1.03</td>
<td>20.19</td>
</tr>
<tr>
<td>27</td>
<td>TEAOH</td>
<td>0.04</td>
<td>Calcined</td>
<td>4.2</td>
<td>1.855</td>
<td>0.011</td>
<td>-2.41</td>
<td>26.26</td>
</tr>
<tr>
<td>28</td>
<td>TEAOH</td>
<td>0.04</td>
<td>Reduced</td>
<td>4.0</td>
<td>1.850</td>
<td>0.010</td>
<td>-2.03</td>
<td>26.30</td>
</tr>
</tbody>
</table>

A consideration of the observed changes in the FAPO-5 sample during exposure to oxidising and then reducing conditions leads to more than one possible explanation for the change in Fe-O radial distance. The Fe-O radial distance of *ca.* 1.97Å for the as prepared sample can be attributed to either Fe\textsuperscript{2+} in a tetrahedral coordination or Fe\textsuperscript{3+} in an octahedral coordination. When the sample is exposed to an
oxidising environment, the subsequent reduction in the radial distance to 1.86 Å can be explained by either:

\[ \text{Fe}^{2+}(\text{Tet.}) \rightarrow \text{Fe}^{3+}(\text{Tet.}) \quad (4.1) \]

or

\[ \text{Fe}^{3+}(\text{Oct.}) \rightarrow \text{Fe}^{3+}(\text{Tet.}) \quad (4.2) \]

In this case, the EXAFS data appears to favour the change of oxidation state explanation, as the data was best fit with a coordination number of \textit{ca.} 4. However, recent follow up work carried out at the DFRL\textsuperscript{54} for several further FAPO samples suggests that a change of coordination state may also occur in some samples during calcination. Further work is in progress in order to elucidate this situation. Such a change in coordination state could be explained by the Fe in the framework being coordinated to 4 framework oxygens and two extra-framework water molecules. Upon heating, the water would be driven out of the system, resulting in a change to tetrahedral coordination.

If however, we consider that the Fe(II) species is oxidised to Fe(III) we find that the Fe(III) species are not reduced back to Fe(II) under the experimental conditions of this investigation. While others have reported the oxidation of Fe(II) to Fe(III) in FAPO-5 by calcination in oxygen or air, only Cubeiro et al.\textsuperscript{58} report on the effects of subjecting the calcined sample to reducing conditions. They exposed the sample to pure H\textsubscript{2} at 723K for 16 hours and subsequently reported the reduction of the Fe(III) species in FAPO-5 to Fe(II) as observed by Mössbauer spectroscopy. However, a consideration of the redox chemistry of Fe(II) and Fe(III) reveals that these materials should be readily interconverted by the use of only mild oxidizing and reducing agents and so the conditions used in our experiment were expected to be
sufficiently reducing to promote this conversion. It is probable that with the iron substituted into the aluminophosphate framework, stronger reducing conditions than those provided in our experiment are required to cause an Fe(III) $\rightarrow$ Fe(II) conversion. Unfortunately, due to limited beamtime we could not immediately repeat the thermal treatment, and opportunity had not arisen by the time of writing for it to be repeated in a later beamtime allocation.
Figure 4.24 – Fe K-edge EXAFS data for FeAPO-5 samples synthesised with Fe(II) acetate where Fe/P=0.04 using the TEAOH template at 443K. These figures represent a) the as prepared sample after washing and drying and b) the same sample after calcination at 823K for 3 hours under flowing O₂. The black line represents the experimental data while the red line represents the best fit to a single co-ordination shell as detailed in table 4.10 (Samples 26 and 27).
Figure 4.25 — Fourier transforms of the Fe K-edge EXAFS data for FeAPO-5 samples synthesised with Fe(II) acetate where Fe/P=0.04 using the TEAOH template at 443K. These figures represent a) the as prepared sample after washing and drying and b) the same sample after calcination at 823K for 3 hours under flowing O₂. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.10 (Samples 26 and 27).
Figure 4.26—A comparison of the fourier transforms of the Fe K-edge EXAFS data for the as prepared and calcined FeAPO-5 samples highlighting the reduction in distance for the first co-ordination shell upon calcination. The green line represents the as prepared sample while the blue line represents the calcined sample.

Similar investigations have been carried out by Sankar and Barrett\textsuperscript{21-22} on the Redox characteristics of a range of cobalt substituted aluminophosphate frameworks using a similar experimental apparatus with almost identical experimental conditions. They observed a similar drop in the Co-O co-ordination radius upon calcination under O\textsubscript{2}, which was accompanied by a colour change in the sample from blue to green. Such a change is indicative of a transition from Co(II)\textsubscript{(tet.)} to Co(III)\textsubscript{(tet.)}. However, cobalt was observed to easily reduce back to the Co(II)\textsubscript{(tet.)} state when using the same experimental conditions that had been unsuccessful with iron, which may be explained by a comparison of the stabilities of the Me(II)\textsubscript{(tet.)} and Me(III)\textsubscript{(tet.)} oxidation states for cobalt and iron. While for both metals the Me(II) state is most stable, the
Fe(III) state is significantly more stable than the Co(III) state in comparison to their respective Me(II) states. Such a difference may mean that Fe(III) is less inclined to reduce to Fe(II) under mild reducing conditions than Co(III) is to reduce to Co(II).

In conclusion, while the state of the framework iron species in the as prepared sample is currently uncertain, there is definite evidence for the formation upon calcination of Fe(III) in a tetrahedral coordination.

4.3.7) Copper Substituted Aluminophosphate Gels

In contrast to many of the first row transition metals, there has been a relatively low level of interest in copper framework substituted aluminophosphate structures although there have been several publications dealing with the ion exchange of copper cations into aluminophosphate structures. This lack of publications may be due to early claims made by workers such as Rajic et al.\textsuperscript{59} that aluminophosphates are not formed in the presence of Cu (II). Duke et al.\textsuperscript{44} have since claimed the synthesis of AIPO-20, possibly containing small quantities of framework substituted copper as indicated by a small change in the lattice parameters gained from XRD patterns.

During the EDXRD crystallisation studies of a copper substituted aluminophosphate gel, we found many similarities to the behaviour observed with iron. Figure 4.27 shows that in a copper substituted aluminophosphate gel, TEAOH produces the most stable and crystalline AFI phase with the fastest growth rate while the TPA sample collapses rapidly after completion of crystallisation and the TEA sample behaves in an intermediate way, decreasing slowly in crystallinity. Once
again, no secondary crystal phases were observed for any of the templates. The resulting washed and dried AFI products were observed to have a pale green colour.

![Figure 4.27 - Comparative crystallisation curves for AFI in syntheses carried out at 443K for copper substituted gels where Cu/P=0.04 using TEA, TEAOH and TPA templates. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.](image)

Cu K-edge EXAFS indicates the copper to be in a tetrahedrally coordinated environment. Furthermore, the Cu-O co-ordination radius was found to be very similar to that for the Co-O coordination radius discussed previously as can be seen in table 4.11, overleaf. This is consistent with the consideration that the ionic radii for Co$^{2+}$ and Cu$^{2+}$ are almost identical.

A consideration of these data would appear to suggest that a small quantity of copper has indeed been successfully substituted into the microporous aluminophosphate framework. However, there is other contradictory evidence to be considered in that Cu(OH)$_2$ has a distorted tetrahedral co-ordination with 2x1.929Å and 2x1.943Å bonds. Therefore, using EXAFS alone we cannot with certainty confirm the nature of the copper within the aluminophosphate framework.
Table 4.11 – Comparison of EXAFS parameters for copper and cobalt substituted MeAPOs synthesised with a range of template molecules.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Me/P</th>
<th>Metal Source</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ²)</th>
<th>E_f (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>TEA</td>
<td>0.04</td>
<td>CuAc₂</td>
<td>3.8</td>
<td>1.933</td>
<td>0.012</td>
<td>0.96</td>
<td>30.49</td>
</tr>
<tr>
<td>26</td>
<td>TEAOH</td>
<td>0.04</td>
<td>CuAc₂</td>
<td>3.7</td>
<td>1.939</td>
<td>0.011</td>
<td>-0.32</td>
<td>24.93</td>
</tr>
<tr>
<td>27</td>
<td>TPA</td>
<td>0.04</td>
<td>CuAc₂</td>
<td>3.7</td>
<td>1.949</td>
<td>0.016</td>
<td>-0.80</td>
<td>47.05</td>
</tr>
<tr>
<td>1</td>
<td>TEA</td>
<td>0.04</td>
<td>CoAc₂</td>
<td>4.0</td>
<td>1.930</td>
<td>0.012</td>
<td>-6.26</td>
<td>27.99</td>
</tr>
<tr>
<td>2</td>
<td>TEAOH</td>
<td>0.04</td>
<td>CoAc₂</td>
<td>3.9</td>
<td>1.943</td>
<td>0.013</td>
<td>0.57</td>
<td>24.69</td>
</tr>
<tr>
<td>3</td>
<td>TPA</td>
<td>0.04</td>
<td>CoAc₂</td>
<td>3.9</td>
<td>1.954</td>
<td>0.016</td>
<td>1.22</td>
<td>26.28</td>
</tr>
</tbody>
</table>
Figure 4.28 – a) Cu K-edge EXAFS data and b) the associated Fourier transform for the synthesis of FeAPO-5 with Cu(II) acetate where Cu/P=0.04 with the TEAOH template at 443K. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.11 (sample 26).
4.3.8) Nickel Substituted Aluminophosphate Gels

Relatively few framework substituted NiAPO structures have been successfully synthesised. Those reported to date include NiAPO-5 and NiAPO-11. These catalysts have been reported to be effective in the selective isomerisation of camphene to produce tricyclene over 2-bornene. In addition, according to Xu et al., NiAPSO-34 has proved to be a highly selective catalyst for the conversion of methanol to ethene and is much more thermally stable than CoAPSO-34.

It can be seen in *figure 4.29* below, that the kinetic behaviour of nickel substituted aluminophosphate gels with TEA, TEAOH and TPA templates appears to follow the general trend previously seen for iron and copper. TEAOH produced the most stable product and the TPA templated product underwent a rapid collapse after completion of crystallisation. In this case the TPA containing gel begins to crystallise later and has a slower crystallisation rate than either TEAOH or TEA, which have similar growth rates.

*Figure 4.29 – Comparative crystallisation curves for AFI in syntheses carried out at 443K for nickel substituted gels where Ni/P=0.04 using TEA, TEAOH and TPA templates. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.*
Considering the samples produced with all three templates, the light green precursor gel produced with green nickel (II) chloride was found to produce pure AFI products with a pale yellow-green colour. This coloration is usually attributed to octahedrally coordinated nickel, as opposed to nickel in a tetrahedral environment, which tends to produce intensely blue complexes. Unfortunately, many of the publications concerning nickel substituted microporous aluminophosphate materials have failed to mention the colour of the final product, an exception to which was Duke et al., who reported an unsuccessful attempt to synthesise NiAPO-20. The pale-green product with an ALPO-20 structure was believed to contain occluded octahedral nickel species.

The data subsequently collected during Ni K-edge EXAFS analysis of our samples was able to confirm the nature of the nickel within the sample as shown in figures 4.30a and 4.30b. The Ni-O bond distances obtained from our data and listed in table 4.12 were more characteristic of those for the nickel (II) hydroxide Ni(OH)$_2$ where Ni-O = 2.073Å than those described by Xu et al. for samples where nickel has been successfully incorporated into the framework structure. Consideration of the evidence suggests that in this case the nickel has not been incorporated into the framework and instead exists as an octahedrally coordinated extra-framework species, most likely as the nickel (II) hydroxide.
Figure 4.30 - a) Ni K-edge EXAFS data and b) the associated Fourier transform for the NiAPO-5 phase synthesised with Ni(II) chloride where Ni/P=0.04 with the TEAOH template at 443K. The black line represents the experimental data while the red line represents the best fit to two coordination shells as detailed in table 4.12 (sample 22).
Table 4.12 – EXAFS parameters for NiAPOs synthesised with a range of templates.

<table>
<thead>
<tr>
<th>Smpl. No.</th>
<th>Template</th>
<th>Ni/P Type</th>
<th>Ni Source</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ²)</th>
<th>Eᵣ (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>TEA</td>
<td>0.04 O</td>
<td>NiCl₂</td>
<td>5.8</td>
<td>2.075</td>
<td>0.020</td>
<td>0.59</td>
<td>37.70*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni</td>
<td></td>
<td>6.1</td>
<td>3.054</td>
<td>0.029</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>TEAOH</td>
<td>0.04 O</td>
<td>NiCl₂</td>
<td>5.8</td>
<td>2.118</td>
<td>0.033</td>
<td>-1.55</td>
<td>28.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni</td>
<td></td>
<td>6.2</td>
<td>3.079</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>TPA</td>
<td>0.04 O</td>
<td>NiCl₂</td>
<td>6.1</td>
<td>2.055</td>
<td>0.018</td>
<td>2.14</td>
<td>27.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni</td>
<td></td>
<td>5.9</td>
<td>3.058</td>
<td>0.033</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Glitch at ca. 8.3Å⁻¹

4.3.9) Chromium Substituted Aluminophosphate Gels

There has been much interest in microporous CrAPO structures as potential catalysts for the oxidation of benzylic and cyclic alcohols⁶³-⁶⁶, however there is some question as to whether the chromium actually substitutes into the framework or instead forms an occluded octahedral species such as the hydroxide within the pores. Both CrAPO-5 and CrAPO-11 structures have been reported⁶⁵ but no evidence of framework substitution has been provided.

As isomorphous substitution requires tetrahedral coordination of Cr(III) which is very rare in inorganic complexes, tetrahedral coordination of Cr(III) should be difficult to achieve. This is because the crystal field stabilisation energy of octahedral Cr(III) is much greater than for the tetrahedral Cr(III) species.¹
Substituting chromium into the aluminophosphate pre-cursor gel in the form of Chromium (III) acetylacetate was found to alter the kinetics of crystallisation in a different way to the other metals discussed previously as shown in figure 4.31. Chromium substituted gels were found to begin forming later and to crystallise significantly more slowly than for either pure aluminophosphate gels or the other MeAPOs. In each case, within the timescale of the experiment, the only phase to crystallise was AFI. The nature of the template did not appear to significantly affect the induction period prior to crystallisation but did appear to alter the rate at which crystallisation occurred. In each case, the product was intensely green in colour, suggesting the formation of an extra-framework Chromium (III) compound such as the hydroxide.

Figure 4.31 – Comparative crystallisation curves for the synthesis of AFI from a chromium substituted aluminophosphate gel where Cr/P=0.04. Data were plotted from the AFI (100) reflection and have been corrected for beam decay and intensity.
EXAFS analysis of these chromium compounds, shown in figures 4.32a and 4.32b, the parameters of which are listed in table 4.13 indicated that the chromium was in an octahedrally coordinated state. This supports the hypothesis that the chromium had formed an extra-framework octahedral complex within the pores of the aluminophosphate framework. Furthermore, the pH of the reaction gel will tend to coincide with the pH range 6.5-10.5 within which Cr(OH)$_3$ is likely to precipitate$^{63}$. This crystallisation may act to inhibit the growth of the aluminophosphate framework causing the observed slowdown in crystallisation rate.

The diameter of the Cr-O co-ordination sphere agrees most closely with those values for Cr(H$_2$O)$_6^{3+}$ complexes such as [(Cr(H$_2$O)$_6$)]$^{3+}$(NO$_3$)$_3$(H$_2$O)$_3$, which has 2x1.961 Å, 2x1.948 Å and 2x1.957ÅCr-O bonds. In comparison, the hydroxide CrO(OH) is normally reported having longer Cr-O bonds in the region 1.99-2.10Å.$^{82}$

Table 4.13 – EXAFS parameters for CrAPOs synthesised with a range of templates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Template</th>
<th>Cr/P</th>
<th>Cr Source</th>
<th>N</th>
<th>R (Å)</th>
<th>A (2σ$^2$)</th>
<th>E$_f$ (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>TEA</td>
<td>0.04</td>
<td>CrAcAc$_3$</td>
<td>6.0</td>
<td>1.956</td>
<td>0.014</td>
<td>3.51</td>
<td>28.57</td>
</tr>
<tr>
<td>26</td>
<td>TEAOH</td>
<td>0.04</td>
<td>CrAcAc$_3$</td>
<td>6.3</td>
<td>1.965</td>
<td>0.015</td>
<td>3.23</td>
<td>24.88</td>
</tr>
<tr>
<td>27</td>
<td>TPA</td>
<td>0.04</td>
<td>CrAcAc$_3$</td>
<td>6.3</td>
<td>1.961</td>
<td>0.014</td>
<td>2.77</td>
<td>26.64</td>
</tr>
<tr>
<td>28</td>
<td>TPAOH</td>
<td>0.04</td>
<td>CrAcAc$_3$</td>
<td>6.2</td>
<td>1.954</td>
<td>0.014</td>
<td>4.18</td>
<td>32.84</td>
</tr>
</tbody>
</table>
Figure 4.32 – a) Cr K-edge EXAFS data and b) the associated Fourier transform for the synthesis of CrAPO-5 with Cr(III) acetylacetate where Cr/P=0.04 with the TEAOH template at 443K. The black line represents the experimental data while the red line represents the best fit to a single coordination shell as detailed in table 4.13. (Sample 26)
4.3.10) Silicon Substituted Aluminophosphate Gels

Silicon substituted aluminophosphates (SAPOs) have been the subject of a great deal of interest as acid catalysts for a variety of applications as they have proven to be good shape selective catalysts for the conversion of methanol to light hydrocarbons\(^4\). SAPO-34 has furthermore found commercial use in the methanol to olefin (MTO) process\(^9\). The SAPO analogues of many of the known microporous aluminophosphate structures have been successfully synthesised, including AFI\(^6\), AEI\(^9\), CHA (as both SAPO-34 and SAPO-44)\(^68-69\), AFO\(^70\) etc , while further structures have been produced from combined metal and silicon analogues such as MeAPSO-36\(^48\).

In these studies, silicon was substituted into the aluminophosphate gel in the form of the commercially available, highly reactive fumed silica, Cab-O-Sil M5. Each of the metals discussed above is generally accepted to substitute directly for aluminium in the framework structure (if substitution occurs). However, there has been much debate concerning the means of silicon substitution into aluminophosphate frameworks, with mechanisms being suggested both for isolated substitution with phosphorous and via a mechanism known as silicon island formation, whereby both aluminium and phosphorous atoms are replaced by clumps of silicon atoms within the framework.\(^71-72\) The substitution of Si with Al, forming a positively charged framework has, however not been reported\(^73\). Sastre et al.\(^73\) carried out a series of calculations in order to clarify this picture and found that “there is a significant driving force for aggregation of Si substituted into SAPOs” and also that “there is an appreciable energy penalty for the formation of Si-O-P bridges.” They reported on the basis of the above findings that 2Si and 4Si islands were unstable compared to 5Si and
8Si islands. Such a substitution mechanism has been put forward to explain the slowdown in crystallisation often reported in laboratory syntheses for SAPOs as compared to AlPOs.

Weyda and Lechert made a detailed study of the factors influencing the formation of SAPO-5 over a range of synthesis conditions and found that pure SAPO-5 samples could be produced with a range of templates, including TEA, TPA, DEA (diethyl-ethanolamine) and TPAOH. In general agreement with our observations throughout this study they reported that “the main difference of the different substances (templates) seems to be given by molecular size and geometry”, with the gels containing tetrapropylammonium salts crystallising after a longer induction period than those gels containing trialkylamine salts. They also reported that the induction period before crystallisation was first observed increased linearly with increasing silica content. Additionally, increasing the silica content caused the final crystallinity of the product to drop. Both of these observations agree with the trends we observed previously for the ZnAPO, MnAPO and FAPO systems.

In this current investigation, the comparative kinetics of crystallisation indicate a trend very similar to that for the AlPO and several of the MeAPOs, as shown in figure 4.33, whereby TEA and TEAOH have very similar curves and begin to crystallise the AFI phase more quickly than with TPA. In each case, pure AFI phase was produced. The fact that a significant slowdown in the crystallisation kinetics in comparison to the AlPO is not seen is not unreasonable considering the low level of silicon substitution into the aluminophosphate gels (Si/Al=0.04). In fact, Weyda and Lechert observed only a small increase in crystallisation time for a gel containing much higher quantities of silica (Si/Al=0.20). This result may reasonably be explained by the level of silicon substitution being too low for the formation of
silicon islands i.e. not enough to form clusters of at least 5Si atoms throughout the framework. The silicon would instead simply disperse throughout the framework by Si→P substitution in a similar way to Me→Al substitution for the MeAPOs and thus not incur any slowdown in crystallisation kinetics such as may occur if Silicon islands were to form. Such an occurrence would be consistent with the findings of Sastre et al. However, it may also simply be the case that in this instance the silica has not been incorporated into the aluminophosphate framework. Unfortunately, as with magnesium, Si K-edge EXAFS data could not be collected as the edge occurs outside the operational range of station 7.1. Therefore, it was not possible to confirm the nature of the silicon within the aluminophosphate system in this case.

From the findings made in this investigation, it would appear worthwhile carrying out further in situ investigations into the crystallisation kinetics of SAPOs over a wide range of Si/Al ratios in order better to compare the data with the
incorporation models proposed by Sastre\textsuperscript{73} and others. Additionally, positive confirmation of the nature of the silicon within the system could be made with either soft EXAFS or FT-IR spectroscopy, the latter allowing us to observe the formation of any acid sites that would form if Silicon had indeed been successfully incorporated into the framework.

4.4) Summary and Conclusions

From a consideration of both the EDXRD data and the EXAFS data subsequently recorded for the metal substituted aluminophosphates, several general observations can be made. Firstly, the nature of the substituted metal does indeed often appear to have a profound effect on both the kinetics of crystallisation and the nature of the resulting secondary phases. For cobalt, manganese, iron, zinc, and possibly copper, framework substitution appears to occur, while for chromium and nickel the metal appears to form octahedral extra-framework complexes within the pores of the aluminophosphate frameworks. In the cases of magnesium and silicon it was not possible to confirm the nature of the heteroatom within the aluminophosphate system, but it is likely from a comparison of the kinetic data that magnesium does indeed substitute into the framework while silicon in this particular instance does not.

It was further noted that the metals involved in successful framework substitution could be separated into subgroups, whereby cobalt, zinc and magnesium behaved in a similar way, with competitive crystallisation of secondary phases taking place. Iron and copper on the other hand did not produce secondary phases while manganese was found to produce small quantities of a secondary chabazitic phase.
over a small range of manganese concentrations with TEAOH template. Even when
the heteroatom did not substitute into the framework, differences were noted in the
kinetic behaviour of the gels. While the kinetics of the nickel substituted gel were
similar to those for the iron and copper gels, the chromium substituted gel formed
much more slowly, probably due to the rapid precipitation of a hydrated chromium
complex such as Cr(\(\text{H}_2\text{O}\))\(\text{Cr}^{3+}\), which may have inhibited the growth of the
aluminophosphate framework.

Interestingly, where the effect of using different valence states was
investigated i.e. for cobalt and manganese, there appeared to be no difference in either
the final product or the crystallisation kinetics. Considerable variation was noted in
the effects of using different template molecules, but there did appear to be a general
trend whereby TEA produced almost pure MeAPO phases while TEAOH and TPA
promoted the formation of significant quantities of chabazitic phases and ATS
respectively.

For zinc, manganese and iron, it was found that increasing the quantity of the
heteroatom resulted both in a drop in crystallisation rate and a reduction in the
crystallinity of the resulting products. EXAFS data collected for iron and manganese
over these concentration ranges indicated that large quantities of iron could be
substituted into the framework while still producing a pure AFI phase. On the other
hand, increasing the manganese concentration of the gel resulted in the formation of
an increasing proportion of extra-framework manganese species.

This investigation shows that EDXRD used in conjunction with an element
specific technique such as EXAFS can give important insights into the interaction of
templates and heteroatoms within the aluminophosphate system. In situ EDXRD
allows us to study the long range ordering and crystallisation kinetics of the system in
real time while EXAFS allows us to gain further insights into the interactions of the heteroatom within the system. Combining this information allows us to consider the overall picture as to how the heteroatom acts to influence the final state of the microporous products. Using a similar combined approach, in addition to other complementary techniques such as FT-IR should allow us to optimise the synthesis conditions for the production of catalytic materials with highly selective properties. Detailed knowledge of the behaviour of heteroatoms and their interactions with template molecules within such systems will prove especially useful for those attempting to optimise the synthesis of multimetal substituted AlPOs and SAPOs. The ‘tuneable’ properties of such materials will be a major step forward in the search for designer catalysts for highly specific uses in the fine chemicals industry.
4.5) References


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57) Sankar G., Private Communication (1999)


74) Zn(OH)$_2$ Structure Ref. No. 5239 Inorganic Crystal Structure Database.

75) Mn(OH)$_2$ Structure Ref. Nos. 9353, 9860 Inorganic Crystal Structure Database.

76) Mn(H$_2$O)$_6^{2+}$(F')$_2$ Structure Ref. No. 39744 Inorganic Crystal Structure Database.

77) Fe(H$_2$O)$_6$(NO$_3$)$_3$(H$_2$O)$_3$ Structure Ref. No. 39744 Inorganic Crystal Structure Database.

78) γ-Fe$_2$O$_3$ Structure Ref. No. 17880 Inorganic Crystal Structure Database.

79) Cu(OH)$_2$ Structure Ref. No. 5676 Inorganic Crystal Structure Database.

80) Ni(OH)$_2$ Structure Ref. No. 24986 Inorganic Crystal Structure Database.

81) [(Cr(H$_2$O)$_6$)]$^{3+}$(NO$_3$)$_3$(H$_2$O)$_3$ Structure Ref. No. 33752 Inorganic Crystal Structure Database.
Chapter 5

A Study of the Synthesis, Structure and Stability of the Microporous Titanosilicate ETS-10 and Related Materials

5.1) Introduction

5.1.1) Overview

This chapter describes an investigation of a recently discovered microporous titanosilicate structure known as ETS-10 (Engelhard Titanosilicate 10), which has a range of interesting properties, making it a potentially important material for a wide range of industrial applications. Such applications include use as a desiccant in CFC free air conditioners, the base catalysis of important reforming reactions such as the dehydrocyclisation of n-hexane to benzene and applications in the optoelectronics industry. In addition, as described in detail below, the disordered ETS-10 structure is composed of a mixture of ordered polymorphs, of which polymorph A exhibits a chiral structure similar to that reported for one of the polymorphs of zeolite beta. Isolation of this polymorph, possibly by the use of a chiral template could produce a chiral catalyst.

The work described in this chapter was carried out using both laboratory powder X-ray diffraction and a range of synchrotron radiation characterisation techniques including EDXRD, EXAFS and high temperature in situ XRD studies of ETS-10 thermal stability.
In situ EDXRD was used to follow the crystallisation of ETS-10, while the effects of altering the pre-cursor gel composition were investigated both in the laboratory and in situ. Small changes to the gel composition were found to alter the crystallisation kinetics and affect the nature of the products. Formation of ETS-4, a second, smaller pore, microporous titanosilicate was observed from a sodium enriched gel. An EXAFS investigation into the local environment around the framework titanium ions was also performed for the synthesised ETS-10 sample and compared with published data.

Finally we report an in situ study of the thermal stability of the titanosilicate framework and its breakdown at elevated temperatures to form a crystalline ceramic phase related to that of the natural mineral narsarsukite, as well as an unidentified secondary phase. This study was carried out on the as prepared ETS-10 as well as a sample of sodium cation exchanged ETS-10 using fast angular dispersive x-ray diffraction on station 9.3 at the Daresbury SRS. These in situ experiments were performed under nitrogen. However, we also report a set of conventional thermal studies carried out in air, where noticeable differences in the stability of the ETS-10 samples were observed.

The work was performed with the aim of better understanding the synthesis conditions under which titanosilicates such as ETS-10 crystallise. A better understanding of the factors involved in producing these potentially important materials may allow us to tailor make a range of new microporous titanosilicate structures with industrially important applications. Thermal studies were performed in order to observe whether post synthetic ion-exchange treatment altered the thermal stability of the structure or could be used as a means of changing the structure of the resulting crystalline breakdown products.
5.1.2) The structure and Properties of ETS-10

5.1.2.1) Structure

ETS-10 is a microporous titanosilicate with the formula (Na_{1.5} K_{0.5})TiSi_{2}O_{13} and a novel structure containing a three-dimensional array of large (typically 4.9Å x 7.6Å), ellipsoidal 12-ring pores. It was originally discovered by the Engelhard corporation in 1990¹. It has a large pore framework similar in size to zeolite Y (FAU) and zeolite beta (BEA). Unlike other microporous titanosilicates such as TS-1, where the titanium is tetrahedrally coordinated, the titanium has octahedral co-ordination.

In a similar way to zeolite beta, the ETS-10 structure is highly disordered, being a mixture of several ordered polymorphs. The extreme faulting present in the ETS-10 structure coupled with the inability to produce crystals large enough for single crystal diffraction analysis initially made the solution of this structure extremely difficult. Such a solution was finally achieved by Anderson et al in 1994⁵-⁶ using a multiple technique approach including high resolution electron microscopy (HREM), electron and X-ray diffraction, solid state NMR and chemical analysis. The fundamental elements of this model are widely accepted and have been used as the basis for the majority of later studies of ETS-10.

While the description given here of the ETS-10 structure is based largely on that of Anderson et al.⁵, additional information from a variety of sources has also been taken into account. Sankar et al.⁷ considered in detail the nature of the -Ti-O-Ti-O-Ti- chains using EXAFS spectroscopy and found the Ti-O bonds to be alternatively long and short. Additionally, a recent communication by Wang et al.⁸ describes the first crystal structure refinement of the ETS-10 structure achieved from single crystal X-
ray diffraction data. This description was carried out on a pure sodium sample and indicated a framework model broadly consistent with that of Anderson et al. but additionally included a detailed experimental determination of the extra-framework cation sites.

The ETS-10 structure is comprised of corner sharing $\text{SiO}_4^{4-}$ tetrahedra and $\text{TiO}_6^{8-}$ octahedra linked through bridging oxygen atoms. The structure is arranged in such a way that all of the pores are lined with silicate units, with the titanate units being recessed. The structure can be envisaged as being constructed of a series of rods consisting of two chains of silicate 5-rings connected by octahedral titanate units, where each titanium atom is linked via oxygen to 4 silicon atoms in two 3-rings and also via oxygen to other titanium atoms. These $-\text{O-Ti-O-Ti-O-}$ linkages form long straight chains running through the structure as illustrated in figures 5.2 and 5.3. All silicon atoms except those at the apex of each 5-ring are connected to 3 silicon atoms and one titanium atom via oxygen [Si(3Si,1Ti)], while the apical silicon in each 5-ring is an Si(4Si,0Ti) unit. These rods are joined together in an orthogonal fashion, sharing the apical silicon in each 5-ring.

As noted above, the ETS-10 structure exhibits a high degree of disorder, being composed of a combination of ordered polymorphs, the end members of which are described as polymorph A and polymorph B. These polymorphs can be constructed from different stacking sequences of the common basic unit $\text{Si}_{40}\text{Ti}_{18}\text{O}_{104}^{16-}$, produced by repeating this unit in two dimensions with P1 symmetry and unit cell parameters $a=b=14.84\text{Å} \ c=13.54\text{Å} \ \alpha=\beta=\gamma=90^\circ$. The sheets run parallel to the main orthogonal channels ($a$-$b$ plane) and contain two orthogonal sets of $-\text{O-Ti-O-Ti-O-}$ chains with associated silicate units. The disorder is manifested as a displacement of adjacent sheets in the $a$-$b$ plane, which is always $\frac{1}{4}$ unit cell in the $a$-direction and $\frac{1}{4}$ unit cell
in the \( b \)-direction. All possible ordered and disordered polytypes as well as reported line defects can be produced from different stacking sequences of the eight possible sheets, which in the actual ETS-10 structure are assumed to stack randomly, producing the observed disorder.

Figure 5.1 – A graphical representation of the ETS-10 Polytype A structure, illustrating views along the \( x \), \( y \) and \( z \)-axes respectively. Titanium atoms are pink, silicon atoms are yellow while oxygen atoms are red. The continuous -O-Ti-O-Ti-O- chains can be clearly seen in each view.
Polymorph A has the main straight channels running along the [100] and [010] directions, arranged in a zigzag pattern as shown in figures 5.1a and 5.1b. Chiral symmetry is manifested as either a left- or right-handed spiral 12-ring channel along the [001] direction with a pitch of 27.08Å as shown in figure 5.2. The symmetry is reported as either P4₁ or P4₃ where a=b=14.84Å c=27.08Å and α=β=γ=90°.

![Figure 5.2 - A graphical representation of the spiral channel of ETS-10 Polytype A with the surrounding framework removed for clarity. Titanium atoms are pink, silicon atoms are yellow while oxygen atoms are red. The continuous -O-Ti-O-Ti-O- chains can be clearly seen in each view.](image)

In comparison, polymorph B, shown in figure 5.3 overleaf, has C2/c symmetry with unit cell parameters a=b=21.00Å, c=14.51Å, α=γ=90° and β=111.12°. In this case, the main straight 12-ring channels are along [110] and [1-10] and are arranged in a diagonal manner as shown in figure 5.3d. A third 12-ring straight channel runs along the [001] direction.
Figure 5.3 – A graphical representation of the ETS-10 Polytype B structure illustrating views down a) the x-axis, b) the y axis c) the z axis and d) the xy direction, along which the main 12-ring channel system can be observed. Titanium atoms are pink, silicon atoms are yellow and oxygen atoms are red. The continuous -O-Ti-O-Ti-O- chains can clearly be seen in each view.
As previously reported, Sankar et al.\textsuperscript{7} have made a detailed study of the local structure around the titanium atoms with coordination shells including the six oxygen atoms arranged in a disordered octahedral coordination to titanium and extending further to the two titanium and 4 silicon atoms as illustrated in figure 5.4 below. They discovered that the -O-Ti-O-Ti-O- chains were, contrary to the findings from X-ray diffraction studies, composed of alternately long and short Ti-O bonds of length 1.71Å and 2.11Å. These bond lengths average out to produce a value in good agreement with the bond length of 1.87Å reported by Wang et al.\textsuperscript{8} The four Ti-O-Si linkages were found to have a Ti-O bond length of 2.02Å by EXAFS\textsuperscript{7} as compared to the 1.99Å from X-ray diffraction.\textsuperscript{8} A similar EXAFS investigation is described later which confirms the earlier findings of Sankar et al.\textsuperscript{7}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5_4.png}
\caption{The local environment of a titanium atom in ETS-10 as reported by Sankar et al.\textsuperscript{6} from Ti K-edge EXAFS.}
\end{figure}
In addition to structural dis ordering, a number of different defects have been reported from HREM studies. The most prominent are the large micropores produced by the coalescence of two or more 12-ring pores, which are formed due to insufficient formal linkages in certain sheet stacking combinations. Such defects provide access for large molecules and may affect the catalytic properties of this material.

Extra-framework cations are required to charge balance the double negative framework charge associated with each Ti^{4+} octahedron. These cations are generally sodium and potassium with a typical distribution in the as prepared material of 75% Na^+ and 25% K^+. There have recently been several reports of ETS-10 produced in forms containing solely Na^+ ions as well as organically templated forms where at least a proportion of the framework charge is balanced by an organic cation.

Wang et al., as mentioned above, have recently described the siting of the extra-framework cations in the pure sodium form of ETS-10 from single crystal X-ray diffraction studies and have found the sodium ions to be present in two non-equivalent positions. Na(1) is located near the Si(1)O_4 tetrahedra and is coordinated to eight oxygen atoms at distances 2.50-2.99Å while the occupancy of Na(2) is split into two equivalent positions 1.67Å apart, each of which has five coordinating oxygen atoms at 2.57-2.62Å, all located on one side of the position. The nearest oxygen atom positions on the opposite side are greater than 3.6Å away. The apparently one-sided co-ordination that results implies that there are disordered space-filling species such as H_2O molecules which complete the co-ordination sphere of Na(2). Wang et al. could not confirm the location of such species due to overlap of the electron densities with those of atoms in the titanosilicate framework columns. Prior to this single crystal study, cation location and distribution was primarily investigated using computational modelling techniques including that carried out by Grillo et al. in 1996, using Monte
Carlo modelling to calculate the $K^+$ and $Na^+$ arrangements within the minimum energy structures. They reported minimum energy framework structures that showed only small deviations from the model by Anderson et al.\textsuperscript{5} but these results found 4 different cation sites. Sankar et al.\textsuperscript{7} also used lattice energy minimisation calculations in addition to EXAFS mentioned earlier in order to predict the distribution of extraframework cations within the framework.

### 5.1.2.2) Related Structures

Recent work on ETS-10 synthesis has concentrated in two main areas, the first of these being towards the formation of isostructural materials in which silicon or titanium atoms are substituted by other atoms. One of the earliest of these modifications was the substitution of a proportion of the silicon by aluminium and gallium to produce ETAS-10\textsuperscript{13} and ETGS-10\textsuperscript{13}. Rocha et al.\textsuperscript{14} later reported the formation of a phase designated AM-6, the vanadium analogue of ETS-10, whereby framework titanium was completely replaced by vanadium. More recent work by the same workers has been reported in which boron has been substituted in place of some of the silicon to form ETBS-10\textsuperscript{15} while niobium has replaced some of the titanium to form ETNbS-10\textsuperscript{16}. Recent studies indicate the possibility of novel base catalytic properties with such modified materials \textsuperscript{16-17}. 
5.1.2.3) Optimisation

A second area of investigation has centred around attempts to produce crystals of ETS-10 large enough for accurate characterisation by methods such as single crystal X-ray diffraction as described by Wang et al.\textsuperscript{8} This problem arises because ETS-10 typically forms crystallites with a size range of 1-5μm, causing problems during material processing and characterisation. The inability to produce crystals of a desired size may also prejudice the usefulness of ETS-10 for a range of potential applications. Wang et al.\textsuperscript{8} produced crystals with sizes up to 45μm using a procedure involving synthesis at considerably higher temperatures and pressures than normally used. However, such syntheses tend to produce a low yield of ETS-10 typically \textit{ca.} 20% together with a mixture of impurity phases including quartz and silicalite. Other methods used in an attempt to improve product crystal size include seeding the mixture\textsuperscript{5} and adding organic molecules to the synthesis gel\textsuperscript{10}.

5.1.2.4) Properties of ETS-10

\textit{a) Adsorption and Ion-exchange Capability}

The Na\textsuperscript{+} and/or K\textsuperscript{+} cations within ETS-10 can be easily exchanged with a variety of other cations including protons\textsuperscript{18} and metals such as caesium\textsuperscript{9} 19 and platinum\textsuperscript{3}, which allow the possibility of producing highly dispersed catalytic centres for base catalysis. Furthermore, the high concentration of exchangeable cation sites makes ETS-10 a highly hydrophilic molecular sieve with a large sorption capacity for polar molecules, making it very suitable as an adsorbent.\textsuperscript{10} There are also applications
for ETS-10 in the removal of heavy metals from contaminated liquids. For example it is highly selective to the uptake Pb$^{2+}$ ions, a use for which it has been patented.$^{20}$

ETS-10 is being actively considered as a desiccant for use in a new generation of CFC free air conditioning systems because water does not bond to the framework as strongly as in conventional aluminosilicate zeolites, resulting in more facile removal of adsorbed water at lower temperatures.$^{18}$

This behaviour follows from the structure, in which the TiO$_6^{2-}$ octahedra are only exposed to the 7-ring channels and so concentrate the point charges in these channels. The result of this charge concentration is that water molecules in the main 12-ring channels are somewhat removed from these charges, resulting in weaker water-framework interactions.$^{18}$

b) Catalysis

The acidity of H-ETS10 is rather modest and so is its acid catalytic activity.$^{21}$ Additionally, the recessed nature of the titanium in the framework precludes any activity as an epoxidation catalyst as observed in other titanosilicate materials such as TS-1 and purely siliceous Ti-zeolite-$\beta$. However, the material has been found to exhibit excellent basic catalytic properties for use in reforming reactions. In fact, the basicity of ETS-10 materials is found to be considerably stronger than that of the zeolite X type catalysts, which form one of the most basic systems in the zeolite family.$^9$. It has also been reported that basicity of ETS-10 may be further increased by ion-exchange with Cs cations and impregnation with Cs$_2$O$^9$. ETS-10 catalysed reactions reported to date include the conversion of isopropanol with a high selectivity towards acetone$^9$, the dehydrocylisation of n-hexane to benzene$^3$ and the dehydration of $t$-butanol with a high selectivity for isobutene$^{17}$. 
Further catalytic uses of ETS-10 may be possible upon isolation of polymorph A, possibly by use of a chiral template as is currently being attempted for the similarly disordered aluminosilicate, zeolite beta. A chiral framework may well allow for the selective production, at much reduced cost, of a single chiral form of a chemical. Such a process could prove invaluable for manufacturing the precursor chemicals used in drug production where it is often the case that only one chiral form is medicinally beneficial. The unwanted isomer can even be positively detrimental as was found in the case of Thalidomide.

c) Optoelectronic Properties

The long, straight -O-Ti-O-Ti-O- chains found in ETS-10 have provoked considerable interest as they behave like quantum wires of uniform and well defined geometry. These can be used as model systems for the study of quantum size effects and may in the future lead to a range of applications in the optoelectronics industry.

Having surveyed the current literature for ETS-10 with respect to the structure and properties of this interesting material, the following sections go on to describe a series of conventional and in situ investigations into the structure, synthesis and stability of ETS-10. We also describe the major crystalline phases other than ETS-10 that were produced as a result of these experiments.
5.2) Experimental Procedures and Results

For reasons of clarity, the section relating to experimental methodology, results and discussion for chapter 5 have been combined. The findings are subsequently compiled and evaluated in a later conclusion.

5.2.1) Synthesis of ETS-10

A pure sample of ETS-10 was synthesised using a method based on that of Liu and Thomas\textsuperscript{24}, using commercial titanium dioxide and silica sources. These were respectively P25, produced by Degussa and having the oxide composition 76% anatase and 24% rutile and the colloidal silica source, Ludox HS-40. The pre-cursor gel was synthesised as described below and the crystallisation of the product was carried out under hydrothermal conditions in a similar way to that for the aluminosilicate and aluminophosphate materials described in previous chapters. An organic template was not required for this synthesis.

5.2.1.1) Conventional Laboratory Synthesis Procedure

ETS-10 samples were prepared in the laboratory from a precursor gel of composition $\text{TiO}_2 : 5\text{SiO}_2 : 3\text{NaOH} : 0.75\text{KF} : 94.5\text{H}_2\text{O}$ as follows:-

1) 1.0g of the P25 TiO$_2$ source was dispersed by stirring into 15.63g of distilled water.
2) 1.5g of NaOH (Aldrich) and 0.54g of KF (Aldrich) were added to the TiO$_2$/water mixture.
3) The resulting mixture was then stirred for 5 minutes.

4) 7.22ml of Ludox HS-40 were then added slowly with vigorous stirring and this stirring was continued for a further 30 minutes.

5) Samples were then transferred to autoclaves, sealed and then placed in a 200°C oven for times ranging from 22 to 117 hours (See table 5.1).

6) Due to the very fine particulate nature of the product, samples could not be washed and filtered but were instead centrifuged between washings.

7) Washed samples were dried and then characterised by X-ray diffraction.

As can be seen in table 5.1 below, samples were synthesised over periods of time ranging from 22 to 117 hours. The first sample removed after 22 hours was found to contain a mixture of ETS-10 and P25, while later samples were found to contain pure ETS-10. The most crystalline sample was observed after 52 hours with longer syntheses exhibiting a noticeable drop in product crystallinity as is often observed in such metastable systems, even though no dense or secondary phase was seen to form. Changes in the pH of the samples were also noted, with the precursor gels having a pH of 13-14 and the resulting reaction mixture after synthesis having a lower pH in the range 11-12. This is likely to be a result of uptake of sodium into the framework, reducing the quantity of NaOH present in the gel.

Figure 5.5 below, shows the resulting pure ETS-10 laboratory X-ray powder diffraction pattern for the 52-hour synthesis at 473K. This pattern is in good agreement with ETS-10 diffraction patterns published elsewhere.24-25
Table 5.1 – Synthesis times for the laboratory preparation of ETS-10 and the resulting products.

<table>
<thead>
<tr>
<th>Synthesis Time (Hours)</th>
<th>Observed Crystal Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>ETS-10 + TiO₂</td>
</tr>
<tr>
<td>44</td>
<td>ETS-10</td>
</tr>
<tr>
<td>52</td>
<td>ETS-10 (most crystalline)</td>
</tr>
<tr>
<td>90</td>
<td>ETS-10</td>
</tr>
<tr>
<td>117</td>
<td>ETS-10 (lower crystallinity)</td>
</tr>
</tbody>
</table>

Figure 5.5 – A conventional laboratory powder X-ray diffraction pattern of ETS-10 synthesised at 473K for 52 hours. Data were recorded over a period of ca. 16 hours with a step size of 0.01deg using Cu-Kα, radiation.
5.2.1.2) EXAFS analysis of ETS-10

In addition to confirming the synthesis of the ETS-10 structure with powder X-ray diffraction, an EXAFS study of the same sample was performed in order to compare the local titanium environment with that reported by Sankar et al.\textsuperscript{7} and discussed earlier. In order to produce a good quality model to fit the experimental data, multiple scattering (see chapter 1 – EXAFS theory) has been taken into account using a model based on that of Sankar et al.\textsuperscript{7}. The multiple scattering effect is strongly dependent on bond angle, with the resulting enhancement of scattering amplitude being strongest at an angle of 180°. Multiple scattering pathways were created to describe the scattering along each of the Ti-O-Ti linkages and a third pathway created to describe scattering along the 4 Ti-O-Si linkages. Two separate pathways were used for the Ti-O-Ti linkages in order to account for the alternating long and short Ti-O bonds described in the original study.\textsuperscript{7}

The resulting fits to the experimental data are shown in figures 5.6a and 5.6b below, while the resulting parameters are shown in table 5.2 and are compared with the previously reported parameters of Sankar et al.\textsuperscript{7} shown in blue and in parentheses.
Figure 5.6 - a) Ti K-edge EXAFS data and b) the associated Fourier transform for a sample of ETS-10 produced using the method described above and synthesised at 473K for 52 hours. In each case the black line represents the experimental data while the red line represents the best fit using six coordination shells with the parameters shown above in Table 5.2.
Table 5.2 – EXAFS parameters used to fit experimental data for a sample of ETS-10 synthesised at 473K for 52 hours. Comparative parameters from the original model by Sankar et al. are shown in blue and in parentheses.

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>Atom Type (T)</th>
<th>Co-ordination Number (N)</th>
<th>Radial Distance (R) (Å)</th>
<th>Debye-Waller Factor (Å) (2σ²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O</td>
<td>1</td>
<td>1.72 (1.71)</td>
<td>0.008 (0.006)</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>4</td>
<td>1.98 (2.02)</td>
<td>0.011 (0.007)</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>1</td>
<td>2.05 (2.11)</td>
<td>0.010 (0.006)</td>
</tr>
<tr>
<td>4</td>
<td>Si</td>
<td>4</td>
<td>3.31 (3.31)</td>
<td>0.012 (0.009)</td>
</tr>
<tr>
<td>5</td>
<td>Ti</td>
<td>1</td>
<td>3.80 (3.76)</td>
<td>0.010 (0.010)</td>
</tr>
<tr>
<td>6</td>
<td>Ti</td>
<td>1</td>
<td>3.80 (3.76)</td>
<td>0.010 (0.010)</td>
</tr>
</tbody>
</table>

$R$-factor = 35.47

$E_f$ (Edge position relative to calculated vacuum zero) = -17.59 eV

The resulting data can be seen to compare well with those of Sankar et al. and have been used to produce the schematic representation in figure 5.7 below, showing the bond angles between each unit. Small differences in the bond angles can be seen compared to the original study reported by Sankar et al., shown previously (parameters from which are shown in blue and in parentheses). It was concluded after consideration of the small differences between this study and the original study that this model works well as a means of describing the local structure around a titanium atom in the ETS-10 framework.
5.2.1.3) An In Situ EDXRD Investigation of ETS-10 Synthesis

The synthesis of ETS-10 from a gel of identical composition to that in the laboratory preparation described above was repeated in situ on station 16.4 of the Daresbury SRS using the same specially designed hydrothermal cell described in previous chapters. The gel was heated at 473K under hydrothermal conditions and data were recorded on a 3-element solid state detector array set with the bottom detector at a fixed angle of $0.96^\circ \pm 0.2^\circ$. This setting allowed us to observe the crystallisation kinetics during the formation of ETS-10 and the corresponding
dissolution of the P25 TiO$_2$ source, as shown by the drop in intensity of the anatase reflection in figure 5.8.

Figure 5.8 – Comparative crystallisation curves for the formation of ETS-10 and the corresponding dissolution of the TiO$_2$ source at 473K. Initial growth in the TiO$_2$ reflection is attributed to initial settling out of the TiO$_2$ suspension in the unstirred system. Data were plotted for the broad ETS-10 reflection at 50KeV/6.1°20 (Cu-K$_\alpha$), which is comprised of several overlapping reflections and the anatase (101) reflection at 54KeV/25°20 (Cu-K$_\alpha$). Data have been corrected for beam decay and intensity.
Figure 5.9 – *In situ* EDXRD data sets for an ETS-10 synthesis gel produced with the composition and preparatory method previously described for a laboratory produced sample. The sample had been heated for 400 mins at 473K with data being collected on a) the bottom and b) the middle detector at fixed angles of 0.96°(2θ) and 3.67°(2θ) respectively. Reflections from the undissolved TiO$_2$ starting materials, anatase and rutile are marked A (101) and R (110) respectively. The x-axis scale in each has been converted from KeV to °(2θ) (Cu-Kα) using the DLConvert program for ease of comparison with conventional XRD patterns.
Figures 5.9a and 5.9b show the data sets collected for ETS-10 on the bottom and middle detectors respectively. These data were subsequently converted from an energy dispersive scale (KeV) to an angular dispersive (2θ) scale where λ=Cu-Kα for ease of comparison with the laboratory powder diffraction pattern (figure 5.5). We can see from the middle detector data that small quantities of the P25 starting material remain in the system after 400 minutes of synthesis at 473K, represented by the anatase (101) and rutile (110) reflections at 25°2θ (3.52Å) and 27°2θ (3.25Å) respectively. These reflections are highlighted in figure 5.10, which shows the synthesis at an early stage prior to the formation of any ETS-10.

![Graph showing EDXRD data set from an early stage in the synthesis of ETS-10](image)

**Figure 5.10** – An *in situ* EDXRD data set from an early stage in the synthesis of ETS-10 using a gel produced with the composition and method previously described for a laboratory synthesised sample. The sample had been heated for 50 mins at 473K with data shown having been collected on the middle detector at a fixed angle 3.67°2θ. No ETS-10 reflections are apparent this early in the synthesis and all visible reflections are attributed to anatase and rutile starting materials(TiO₂). The x-axis scale has in each has been converted from KeV to °2θ (Cu Kα) for ease of comparison with conventional XRD patterns.
5.2.1.4) An Investigation of the Role of Na\(^+\) and K\(^+\) Cations on ETS-10 Synthesis

In addition to precursor gels prepared with a standard ETS-10 composition, a range of modified gels were also produced using the same synthesis procedure described above. In these gels, the proportions of hydroxide and fluoride were kept constant while changing the type of hydroxide or fluoride salt used. For example, NaOH was replaced by KOH and/or NaF replaced KF in order to produce gels with four different compositions as illustrated in table 5.3 below. All quantities are expressed in mole fractions.

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>TiO(_2)</th>
<th>NaOH</th>
<th>KOH</th>
<th>NaF</th>
<th>KF</th>
<th>SiO(_2)</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>3.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.75</td>
<td>5</td>
<td>94.5</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.00</td>
<td>3.00</td>
<td>0.75</td>
<td>0.00</td>
<td>5</td>
<td>94.5</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3.00</td>
<td>0.00</td>
<td>0.75</td>
<td>0.00</td>
<td>5</td>
<td>94.5</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.00</td>
<td>3.00</td>
<td>0.00</td>
<td>0.75</td>
<td>5</td>
<td>94.5</td>
</tr>
</tbody>
</table>

In each case, samples were characterised by powder X-ray diffraction. It was noted that, while the original synthesis gel composition produced a pure ETS-10 phase, occasionally accompanied by small quantities of quartz impurity, altering the nature of the fluoride and hydroxide sources from this original gel composition produced impure mixtures of phases. An example of such a result is illustrated in figure 5.11 below for the NaF/NaOH synthesis.
This resulting mixture of phases was found to contain two main elements, these being quartz and another phase, later found to be a small pore titanosilicate species known as ETS-4. The formation of this alternative titanosilicate phase was not unexpected as Liu and Thomas\textsuperscript{24} had previously reported its formation from a pure sodium gel of similar composition to that for the ETS-10 gel. The sample of pure ETS-4 phase shown in red in figure 5.11 above was subsequently prepared using the gel composition suggested by Liu and Thomas\textsuperscript{24}. In this case, a gel with the composition \( \text{TiO}_2 : 5\text{SiO}_2 : 5\text{NaOH} : 0.48\text{NaF} : 94.5\text{H}_2\text{O} \) was synthesised following the procedure described previously for ETS-10. The gel was then sealed into several autoclaves and placed in an oven set at 473K for periods between 22 and 46 hours. It was also noted in some subsequent syntheses performed with the NaF/NaOH mixture that small quantities of ETS-10 formed in addition to ETS-4 and quartz.
The structure of ETS-4 has been investigated by several workers \(^{30-32}\) and is generally considered to be similar to that of the naturally occurring mineral, zorite \((figure\ 5.12a)\), the crystal structure of which was first reported in 1979 by Sandomorskii and Belov\(^ {29}\). They reported a disordered structure with a framework similar to that of another mineral, related to zorite, known as nenadkevichite \((figure\ 5.12b)\) but, due to the presence of diffuse reflections, they could only partially solve the structure. A recent study by Philippou et al.\(^ {30}\) using \(^{29}\)Si MASNMR and HREM in addition to powder X-ray diffraction, have suggested that although the ETS-4 structure is related to that of zorite, it is not the synthetic equivalent of this mineral. They propose that ETS-4 can be considered as an intergrowth system of a zorite-like and a nenadkevichite-like structure or alternatively that the structure is highly defective with adjacent 12 membered rings coalescing to form large pores that have been reported in HREM images\(^ {30}\).
Another recent study carried out by Cruciani et al. (1998)\textsuperscript{32} has used high resolution synchrotron X-ray powder diffraction in order to elucidate the structural relationships between ETS-4 and zorite. They report direct evidence for ETS-4 and zorite sharing the same structure but find no evidence for nenadkevichite reflections in their sample. A notable feature of the ETS-4 structure is its low thermal stability compared to ETS-10, the former decomposing at ca. 473-523K while the latter
remains stable at temperatures in excess of 823K as described in detail later in this chapter. Several researchers\textsuperscript{30, 32} have postulated that this low stability is due to water molecules forming part of the ETS-4 structure. Cruciani et al.\textsuperscript{32} suggest that hydrogen bonding between extra-framework water molecules and framework oxygen causes the instability at elevated temperatures.

The two gels produced using KOH do not appear to produce either ETS-10 or ETS-4, instead producing mainly quartz with small amounts of at least one unidentified crystalline phase. It can be seen in figure 5.13 that there are small reflections present at \textit{ca.} 6°2θ in a similar low angle position to those of ETS-10 seen in the original synthesis. However, the other reflections do not correspond with ETS-10 so the significance of this observation is uncertain but may indicate the formation of small quantities of a microporous phase. The major difference between these two syntheses can be seen in each case as a single differing reflection between the first two quartz reflections at \textit{ca.} 21°2θ and 27°2θ. Unfortunately, repeated experiments to date have failed to synthesise any of these unidentified phases with sufficient crystallinity or purity for accurate identification.
5.2.1.5) An *In Situ* EDXRD Investigation of the Role of Na\(^+\) and K\(^+\) Cations on ETS-10 Synthesis

Upon consideration of the differences observed in the laboratory when using synthesis gels containing various combinations of NaOH, KOH, NaF and KF, it was decided to carry out a similar series of experiments *in situ* in order to observe any differences in crystallisation kinetics between these systems. This was done by comparison of the changing intensities of the single reflection observed on the bottom detector for each gel between 50-55KeV (6.1-6.4°2θ Cu-K\(\alpha\)) and shown later (figure...
As can be seen in figure 5.14 below, there were indeed large kinetic differences between gels of different composition.

The original composition ETS-10 synthesis gel (KF/NaOH) was found to produce crystalline ETS-10 much more quickly than any of the other combinations, while the NaF/NaOH gel was found to crystallise most slowly and after a much longer induction period. The KF/KOH and NaF/KOH gels exhibit similar kinetic behaviour, intermediate in both rate and induction period to the KF/NaOH and NaF/NaOH gels.

Some of these differences in formation kinetics appear to be related to the nature of the crystalline phase. For example it can be seen in figure 5.15b that both of the KOH containing gels produce the same unidentified phase as well as exhibiting similar kinetic behaviour. As expected, the KF/NaOH gel produced crystalline ETS-10, but the NaF/NaOH gel, which was expected from the laboratory syntheses, to
form ETS-4, instead began to crystallise as ETS-10. Philippou et al.\textsuperscript{30} reported the ETS-4 structure to be very sensitive to a High Resolution Transmission Electron Microscope (HRTEM) beam, making the technique unsuitable for analysis of this material. Considering the low thermal stability of this material discussed previously, the energy of the synchrotron white radiation beam may be sufficient to in some way disrupt the hydrogen bonding between extra-framework water molecules and framework oxygen that, Cruciani et al.\textsuperscript{32} propose, form an integral element of the ETS-4 structure. However, even though the experimental conditions were equivalent for the laboratory and \textit{in situ} syntheses, further syntheses would need to be carried out in the \textit{in situ} cell without beam before a positive claim could be made for beam effects in this case.

The relatively slow formation of ETS-10 from the sodium rich gel appears to indicate that either the presence of potassium cations is favourable for ETS-10 formation or alternatively that too much sodium retards the formation of ETS-10.

The short time scale of this experiment in comparison to the conventional laboratory syntheses is highlighted by the presence of prominent reflections due to anatase and rutile, these being remnants of the P25 TiO\textsubscript{2} starting material. Furthermore, the short experimental period meant that the samples produced were not of sufficient crystallinity for identification of the unknown phase formed from the KOH gels, even with conventional powder X-ray diffraction. The use of KOH in these syntheses does not appear conducive to the formation of well crystalline samples and therefore at the time of writing we have yet to produce a sample of sufficient quality to confirm the nature of this unknown phase. The low angle reflections present in the products of the KOH syntheses can be seen in \textit{figure 5.15a} to be in a different position to those for ETS-10 observed in the NaOH syntheses. As with the conventional
laboratory experiments, these observations may indicate the formation of a microporous impurity phase.

Figure 5.15 – Comparative EDXRD data sets for the formation of titanosilicates at 473K using combinations of KF, NaF, KOH and NaOH. Data was collected on a) the bottom detector at 0.96°20 and b) the middle detector at 3.67°20. E=ETS-10, A=Anatase and R=Rutile. Reflections have been corrected for beam decay and intensity. The data has been converted from an energy dispersive scale (KeV) to angular dispersive (°20 λ=Cu-Kα). Data sets were recorded after ca. 400 minutes except for NaF/NaOH, recorded after 600 minutes.
5.2.2) Thermal Stability of ETS-10

Samples of ETS-10, in the as prepared and sodium ion-exchanged forms were heated in situ on station 9.3 at the Daresbury SRS under a flowing nitrogen atmosphere. Pellets of each material were placed within the specially designed high temperature cell and heated from room temperature to 1073K with a controlled temperature ramp. X-ray diffraction patterns were recorded at regular intervals in order to monitor both the thermal stability of the ETS-10 structure and to investigate any phase changes occurring during heating.

These investigations illustrated the high level of thermal stability exhibited by the ETS-10 structure, with structural collapse eventually occurring above 873K, well above the range normally required in catalytic applications. Additionally, at temperatures above 873K, the ETS-10 was observed to collapse and recrystallise as a mixture composed primarily of a ceramic phase similar to the mineral narsarsukite. This phase has been reported previously as the product of thermal collapse of the comparatively unstable ETS-4 structure but has not to our knowledge been reported to occur with ETS-10.

Subsequent work carried out in the laboratory compared the effects of heating under nitrogen with those of heating the same samples in air in a conventional furnace.
5.2.2.1) As prepared ETS-10

As can be seen in figure 5.16 below, the sample was initially heated from room temperature to 829K at a constant ramp rate of ca.5.6Kmin⁻¹, during which time XRD data sets were recorded over 5 minute periods. We can see in figure 5.17 that during this initial heating phase, the ETS-10 remained stable and was subsequently found to remain stable when the sample was held at 829K for ca.25 minutes.

![Figure 5.16 - The program of temperature ramping carried out for a sample of as prepared ETS-10 heated on station 9.3 at Daresbury under an atmosphere of flowing nitrogen.](image-url)
Figure 5.17 – *In situ* X-ray diffraction patterns recorded as a sample of as prepared ETS-10 is heated from 324K to 829K under a flowing nitrogen atmosphere. The ETS-10 structure can be seen to remain stable within this temperature range. Diffraction patterns were recorded every five minutes and $\lambda=1.4062\AA$.

Further increasing the temperature of the sample, this time at a constant ramp rate of $ca.5.4\text{Kmin}^{-1}$ resulted in the initially stable ETS-10 structure undergoing a rapid collapse as shown in *figure 5.18*. This collapse was first observed in the scan completed at 887K, which would therefore suggest that the ETS-10 structure is likely to have begun destabilising at a temperature of $ca. 870\pm10\text{K}$. The ETS-10 phase has undergone almost complete collapse by 914K, exposing several weak reflections as shown in red in *figure 5.19a*. While some of these reflections appear to be attributable to small remnant quantities of the TiO$_2$ starting materials, anatase and rutile, others appear to be due to the formation of a second, unidentified dense phase. Alternatively, these may represent a stable remnant of the ETS-10 structure as discussed in more detail below. Increasing the temperature above 1022K results in additional reflections...
being observed (figure 5.19b) which are attributed to the growth of a new crystalline structure similar to that of the rare, naturally occurring mineral, narsarsukite. At the same time, the prominent dense phase reflection attributed to anatase can be seen to have disappeared.

Narsarsukite was previously reported by Naderi et al.\textsuperscript{34} to be the breakdown product of the thermally unstable ETS-4 structure discussed above. The powder X-ray diffraction pattern of narsarsukite from the ICSD database is shown in figure 5.20 in direct comparison to the breakdown product of ETS-10. The broad reflections observed in the angular range 35-40°20 are attributable to the presence of either an unidentified impurity phase or some structural remnant remaining after the collapse of ETS-10.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.18.png}
\caption{In situ X-ray diffraction patterns recorded as a sample of as prepared ETS-10 is heated from 833K to 1103K under a flowing nitrogen atmosphere. The ETS-10 structure can be seen to begin to destabilise from around 870K±10K, totally collapsing by 914K to form an unidentified dense phase. The later formation of extra reflections above 1049K are attributed to the narsarsukite structure. Diffraction patterns were recorded every five minutes and at A,=1.4062Å.}
\end{figure}
Figure 5.19 – Comparative in situ X-ray diffraction patterns recorded for a sample of as prepared ETS-10 heated under a flowing nitrogen atmosphere. a) Shows the ETS-10 structure at 833K and the reflections remaining at 968K after the collapse of ETS-10. The remaining reflections are attributed to impurity phases including remnant TiO₂ starting materials marked A (anatase) and R (rutile). b) Shows the recrystallisation of the collapsed phase into Narsarsukite. Diffraction patterns were recorded over a 5 minute period at λ=1.4062Å.
Figure 5.20 – Comparative in situ X-ray diffraction patterns recorded for a sample of as prepared ETS-10 heated under a flowing nitrogen atmosphere at 1173K (black), showing the resulting recrystallisation phase after the collapse of ETS-10. The plot in red shows the pattern simulated from the ICSD standard (Ref. No. 7019) for narsarsukite. The experimental diffraction pattern was recorded over a 5 minute period at $\lambda=1.40619\text{Å}$.

The structure of Narsarsukite, shown in figure 5.21 below, has been simulated from the atomic coordinates of Peacor and Buerger$^{35}$; the mineral is a tetragonal silicate composed of $\text{Si}_4\text{O}_{10}$ chains that in turn form tubes of rings of four Si tetrahedra. The tubes are then linked by chains of corner sharing titanium octahedra while the cavities between the $\text{Si}_4\text{O}_{10}$ tubes and octahedral chains contain titanium atoms. The composition of narsarsukite can therefore be written as $\text{Na}_2\text{TiOSi}_4\text{O}_{10}$ with four formula units per cell.$^{30}$
Upon removing the originally white ETS-10 sample disk, a colour change to light blue was noted, which may be attributed to the reduction of Ti$^{4+}$ to Ti$^{3+}$ caused by thermal treatment under the nitrogen atmosphere. A similar colour change was observed by Naderi et al.\textsuperscript{34} for the decomposition of ETS-4 to narsarsukite. They also described a postulated mechanism in which the ETS-4 structure re-arranges into narsarsukite, based on the observation that several reflections remained during the general collapse of ETS-4 - a similar situation to that observed for ETS-10, with several weak reflections remaining after the general structural collapse and continuing to exist after the extra reflections associated with narsarsukite have appeared. However, it may be the case that a proportion of the ETS-10 has re-arranged to form a
dense phase that remains even after the formation of narsarsukite at higher temperatures.

5.2.2.2) Sodium ion-exchanged ETS-10

As mentioned previously, ion-exchanging the charge balancing cations within microporous frameworks can profoundly alter the properties of the resulting material as both a molecular sieve and a catalyst. Such changes may conceivably have an effect on the recrystallisation products of a material having undergone thermal decomposition. The effects of exchanging the Na\(^+\) and K\(^+\) extra-framework cations with Na\(^+\) were therefore investigated in order to observe any differences in either the thermal stability or the nature of the recrystallisation products after collapse of the ETS-10 structure.

An Na\(^+\) cation-exchanged sample was chosen for thermal study in order to investigate whether the removal of K\(^+\) cations from the extra-framework sites would promote the formation of the narsarsukite thermal breakdown product in comparison to the as prepared ETS-10 sample. This was thought to be a possibility, considering that one of the essential differences in the synthetic procedures for producing ETS-10 and ETS-4, as described by Liu and Thomas\(^ {24} \) and adapted for this work, was the replacement of KF by NaF in order to form ETS-4. As discussed above, the formation of narsarsukite as a thermal breakdown product has previously been reported for this material\(^ {34} \).
In order to produce a sodium cation exchanged ETS-10 sample, the following procedure was used:

1) A 40ml batch of 0.01 molar aqueous solution of sodium chloride was made up, into which was added a 0.75g batch of the as prepared ETS-10.

2) The resulting solution was stirred at room temperature for 24 hours.

3) The sample was then filtered to remove the solution and then dried.

4) The filtered sample was then added to a further 40ml aliquot of the 0.01 molar NaCl solution and stirred for a further 24 hour period at room temperature before being filtered and thoroughly washed with distilled water, and then dried.

The ion-exchanged sample was pressed into a thin disk and then studied \textit{in situ} on station 9.3 at the Darebury SRS following the temperature program illustrated in \textit{figure 5.22}. On this occasion the ETS-10 sample was heated at a constant ramp of 5Kmin\(^{-1}\) from 313K up to 1073K where the temperature was kept constant.

The ETS-10 structure was observed to remain stable up to \textit{ca.} 813K (\textit{figure 5.23}) and then to collapse rapidly, with only reflections due to dense phase remnant TiO\(_2\) remaining by the time the temperature reaches 863K. Extra reflections were noted to form above 1013K and were attributed, like the as prepared sample, to the crystallisation of narsarsukite. Once again, the sample was noted to have undergone a colour change to light blue.
Ramp Rate=5Kmin$^{-1}$

Figure 5.22 – The program of temperature ramping carried out for a sample of Na ion-exchanged ETS-10 heated on station 9.3 at Daresbury under an atmosphere of flowing nitrogen.

Figure 5.23 – In situ X-ray diffraction patterns recorded as a sample of Na ion-exchanged ETS-10 is heated from 273K to 1073K, as detailed in figure 5.23, under a flowing nitrogen atmosphere. The ETS-10 structure can be seen to begin to destabilise from ca.813K±10K leaving only TiO$_2$. Narsarsukite reflections are observed above 1013K. Diffraction patterns were recorded every five minutes at $\lambda=1.40619\text{Å}$.
Figure 5.24 – Comparative *in situ* X-ray diffraction patterns recorded for a sample of Na ion-exchanged ETS-10 heated under a flowing nitrogen atmosphere, showing the recrystallisation of the collapsed phase into narsarsukite. Diffraction patterns were recorded over 5 minutes at $\lambda=1.40619\text{Å}$.
5.2.2.3) Comparison of the dense phases formed after thermal decomposition of ETS-10 and its Na\textsuperscript+ ion-exchanged derivative

We can see in figure 5.25 below that the recrystallisation products from both the as prepared and Na\textsuperscript+ ion-exchanged samples under flowing nitrogen are basically identical. They consist mainly of the narsarsukite phase along with small quantities of a secondary impurity phase. In addition, the temperatures at which both samples collapse and subsequently re-crystallise are also very similar.

![Figure 5.25](image)

**Figure 5.25** – Comparative *in situ* X-ray diffraction patterns recorded for samples of as prepared and Na\textsuperscript+ ion-exchanged samples of ETS-10 heated to 1073K under a flowing nitrogen atmosphere. The recrystallisation products formed after ETS-10 collapse can be seen to be identical. Diffraction patterns were recorded over 5 minutes at $\lambda=1.40619\text{Å}$.

This result appears to indicate that the Na\textsuperscript+ and K\textsuperscript+ cations that play such an important role in influencing the nature of the crystalline titanosilicate phases during
hydrothermal synthesis do not appear to have a significant influence on the nature of the thermal breakdown products of these phases when heated under flowing nitrogen. Furthermore, the ion-exchanged sample appears to be equally thermally stable when compared to the as prepared sample in this environment. However, as will be seen in the next section, there do appear to be differences when the samples are heated in air.

5.2.3) Thermal Stability in air

A similar thermal treatment was carried out for as prepared and sodium exchanged ETS-10 in air by heating samples of each material in open ceramic boats within a block furnace. Laboratory powder diffraction patterns were produced with Cu-Kα1 radiation and are shown in figures 5.26a and 5.26b below. Differences were immediately noted in the appearance of the samples treated at 973K and 1173K compared to the samples treated under nitrogen with the air treated samples being white to slightly yellowish in colour while the nitrogen treated samples were found to be blue. The blue colouration is therefore likely to be due to a change of oxidation state from Ti⁴⁺ to Ti³⁺.

Another observed difference was the increased stability of the ETS-10 structure in air over the equivalent materials under nitrogen. In both cases, the samples heated in air were observed to contain crystalline ETS-10 at 973K, ca.100K above the temperature of collapse for ETS-10 observed under nitrogen. We also see, as highlighted in 5.27, that the as prepared ETS-10 sample produced only a poorly crystalline sample of Narsarsukite in air while the Na⁺ exchanged sample produced a much more crystalline sample. This is contrary to the findings from the flowing
nitrogen experiments where the resulting products were of very similar crystallinity. Furthermore, a small quantity of the same impurity phase noted in the *in situ* experiments was found to be present with the narsarsukite product. It appears increasingly likely that this is either a highly thermally stable impurity, present in the as prepared ETS-10 sample or is a similarly stable remnant of the collapsed ETS-10 structure.
Figure 5.26 – Comparative laboratory powder X-ray diffraction patterns recorded for samples of a) as prepared and b) Na ion-exchanged ETS-10 heated in air to illustrate the collapse of the ETS-10 structure and the subsequent recrystallisation to narsarsukite. Diffraction patterns were recorded using Cu Kα₁ radiation.
Figure 5.27 - Comparative laboratory powder X-ray diffraction patterns recorded for samples of as prepared (red) and Na ion-exchanged (green) samples of ETS-10 heated in air at 1173K illustrate the differences in crystallinity of the narsarsukite phase. These samples are compared with the narsarsukite standard pattern simulated from ICSD data. Extra reflections not visible in this pattern are due to an unidentified dense impurity phase. Diffraction patterns were recorded using Cu Kα₁ radiation.
5.3) Summary and Conclusions

Samples of ETS-10 have been produced both in the laboratory and in situ on station 16.4 at the Daresbury SRS. These samples have been successfully characterised by both X-ray diffraction and EXAFS. In situ EDXRD experiments allowed us to follow the formation of the ETS-10 phase while simultaneously observing the breakdown of the anatase and rutile starting materials.

The synthesis of ETS-10 appears governed by a complex combination of factors, with small changes in these factors producing a family of alternative and impurity phases, for example, excluding potassium ions from the system appears to promote the formation of ETS-4, while replacing NaOH with KOH appears to inhibit the formation of either phase and instead produces a third and as yet unidentified phase with possible microporous character. Furthermore, alterations of the gel composition were observed in situ to have a profound effect on the crystallisation kinetics of the resulting crystal phases.

Finally, while ETS-10 appears thermally stable in both flowing nitrogen and air, the material appears to be more stable in air. In both cases, the sample eventually collapses above 823K and eventually recrystallises to form a mixture of narsarsukite and a stable impurity phase. From this work it can therefore be concluded that the complexities of these titanosilicate systems are definitely worthy of further study. Such investigations could well promote the isolation and identification of a range of new microporous titanosilicate structures with potentially useful properties and applications arising from novel arrangements of tetrahedrally coordinated silicon and octahedrally coordinated titanium species.
5.4) References


Appendix 1

**Preparation of the Mesoporous Silica MCM-41**

Samples of MCM-41 were prepared in 5g batches using the following procedure:-

1) 28.8ml of de-ionised water was stirred thoroughly in a 250ml beaker with 7.9ml of 25% TMAOH in aqueous solution (Aldrich).

2) 21.3g of cetyl trimethyl ammonium bromide (CTMAB) was then added slowly to this solution and allowed to mix thoroughly.

3) 5.0g of Aerosil 200 fumed silica were then added over about an hour, with the mixture being stirred thoroughly between additions.

4) Once all the silica had been added, the mixture was allowed to stir for a further hour, covering with a watch glass to avoid moisture loss.

5) The sample was then transferred to a polypropylene bottle, which was sealed and placed in an oven at 363K for *ca.* 15 hours.

6) The solid lump of sample was then broken up and washed thoroughly and repeatedly over several hours in order to remove the bulk of the ‘soapy’ CTMAB.

7) The washed sample was then allowed to dry before being calcined at 823K for at least 1 hour under flowing nitrogen before switching gas flow to oxygen for at least 6 hours at the same temperature.

8) The sample thus obtained was then characterised using laboratory powder X-ray diffraction as shown in *figure A1* below.
Figure A1 – A Cu-Kα1 powder X-ray diffraction pattern of MCM-41 produced using the synthesis procedure described above.
Appendix 2

Comparative Synthesis of Zeolite Beta with Cab-O-Sil M5 and MCM-41 Silica

Sources

Syntheses of aluminium rich zeolite beta were performed using the methodology described below, which was adapted from a synthesis published by Borade et al\(^1\). The Cab-O-Sil M5 fumed silica used in the original methodology was replaced by an equivalent molar quantity of silica in the form of mesoporous MCM-41, which was in turn synthesised as described in appendix 1. The two samples were then subjected to the same hydrothermal synthesis conditions for the same period and the resulting powder X-ray diffraction patterns compared as discussed below.

Sample Preparation

Pre-cursor gels with the following composition:

\[ 1.25 \text{Na}_2\text{O} : 1.0 \text{Al}_2\text{O}_3 : 10.0 \text{SiO}_2 : 1.6 \text{TEAOH} : 55 \text{H}_2\text{O} \]

were prepared as described below, using both Cab-O-Sil M5 and MCM-41.

1) 0.315g of sodium aluminate (Riedel-de Haën) containing 54\% Al\(_2\)O\(_3\) and 41\% Na\(_2\)O was added to 1.122g of 40\% TEAOH in aqueous solution (Aldrich). This mixture was then stirred for 15 minutes.

2) 0.907g of de-ionised water was then added to this mixture with constant stirring which continued until a clear solution was obtained.

3) 1g of either Cab-O-Sil fumed silica or MCM-41 were then added to this mixture and the resulting gels blended thoroughly with a spatula for a further 15-20
minutes. While the Cab-O-Sil gel formed as a rather dry and sticky paste, the MCM-41 appeared to dissolve quickly, forming a more liquid gel.

4) Each gel was then transferred to an autoclave and placed in an oven at 423K, initially for 22 hours, with the synthesis subsequently being repeated over a period of 47 hours.

5) The samples were then removed from the autoclaves, washed thoroughly and dried before being characterised by powder X-ray diffraction.

Characterisation

![Figure A2 - Comparative Cu-Kα₁ powder X-ray diffraction patterns for zeolite beta produced using the synthesis procedure described above with MCM-41 (top) and Cab-O-Sil M5 fumed silica (bottom). Hydrothermal syntheses were performed at 423K over 47 hours.](image-url)
In the case of the 22 hour syntheses, the Cab-O-Sil preparation was observed to produce a moderately well-crystalline sample of zeolite beta, while the MCM-41 preparation showed only early indications of zeolite beta reflections. However, after 47 hours, while the Cab-O-Sil preparation exhibited a small increase in crystallinity over the 22-hour sample, the MCM-41 sample as can be seen in figure A2, had formed a very crystalline zeolite beta phase. The MCM-41 product exhibits sharp reflections of much higher intensity throughout the diffraction pattern while having a slightly less intense wide, low-angle reflection than Cab-O-Sil. This reflection is associated with structural faulting in the sample, which, in a similar way to ETS-10 discussed in chapter 5, results in zeolite beta being composed of a number of polymorphs.

## Appendix 3 – List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AEI</td>
<td>AIPO-18</td>
</tr>
<tr>
<td>AFI</td>
<td>AIPO-5</td>
</tr>
<tr>
<td>AlPO-n</td>
<td>Microporous aluminophosphate (AIPO₄) with structural designation n.</td>
</tr>
<tr>
<td>ATS</td>
<td>AIPO-36</td>
</tr>
<tr>
<td>CHA</td>
<td>Chabazite (AIPO-34)</td>
</tr>
<tr>
<td>DFRL</td>
<td>Davy-Faraday Research Laboratory</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse Reflectance Infra-red Fourier Transform Spectroscopy</td>
</tr>
<tr>
<td>EDE</td>
<td>Energy Dispersive EXAFS</td>
</tr>
<tr>
<td>EDXRD</td>
<td>Energy Dispersive X-ray Diffraction</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum (Peak width at half height)</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>MeAlPO-n</td>
<td>Metal substituted AlPO-n</td>
</tr>
<tr>
<td>MeAPSO-n</td>
<td>Metal and Silicon substituted AlPO-n</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>QuEXAFS</td>
<td>Quick EXAFS</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small Angle X-ray Scattering</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SRS</td>
<td>Synchrotron Radiation Source</td>
</tr>
<tr>
<td>SAPO-n</td>
<td>Silicon Substituted AlPO-n</td>
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<tr>
<td>WAXS</td>
<td>Wide Angle X-ray Scattering</td>
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<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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