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**Novel low temperature preparation methods for mixed complex oxide catalysts and their characterisation using *in situ* SR techniques**

Thesis submitted for the degree of Doctor of Philosophy

by

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2003
Abstract

The crystallisation of complex mixed oxide and metal phosphate oxidation catalysts prepared using a number of synthetic methods have been studied using in situ synchrotron radiation techniques. Some of these synthesis procedures have previously been employed to produce catalysts whilst others were new methods, making use of hydrothermal technology and zeolite precursors. For the iron phosphates catalysts studied it was observed that all of the synthetic methods employed produced a catalyst precursor having the chemical composition FePO₄·2H₂O. During calcination this phase transformed into the tridymite and quartz forms of FePO₄ although, the material produced by hydrothermal methods was found to be the most phase pure and possess a higher surface area. A comparative study of the three catalytically active forms of bismuth molybdate revealed similar findings with two of the three phases observed (by EDXRD) to form directly from a precursor gel with an Avrami-Erofe’ev kinetic analysis of the crystallisation process suggesting that the mechanisms of formation were different for each phase. Hydrothermal methods were also used to prepare cobalt and manganese substituted aluminophosphate structures AFI and AEI, which were found to be efficient catalysts for the methanol to olefin reaction. However, it was also observed that during calcination to remove the structure-directing agent, that some of the cobalt and manganese in the tetrahedral framework sites underwent oxidation from 2+ to 3+ although the extent of this was found to be dependent upon both structure type and metal ion. Finally an investigation was carried out into the use of ion-exchanged zeolites as precursors for the low temperature crystallisation of the spinel structure CoAl₂O₄. The results from this study suggested that very small spinel particles formed within the XRD amorphous collapsed zeolites although both zeolite structure type and cobalt salt were thought to have an effect on phase formation.
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Acknowledgements

During the course of my PhD and the subsequent writing of this thesis I have been fortunate enough to have received assistance, support and advice from many people all of whom made it such an enjoyable three years and have made it possible for me to get at least this far. To this end I would like to thank my supervisor Dr G. Sankar for his guidance, endless enthusiasm for the project and a countless number of Fosters and from whom I learnt a lot. Furthermore I would also like to thank my other supervisors Profs. Catlow and Price for both their insights and support. I am also grateful for the help and assistance I received from the other members of the DFRL including Dave Gleeson, for his EXAFS tutorials, Christianna Zenonos for some pointers on synthesis, Ilona Franklin for her assistance throughout and Matt Johnson, Craig Bull and Adrian Smith without whose help some experiments might not have been carried out. Other DFRL people to whom I would also like to thank include Mike Sheehy, Ian Watts, and Dave Madill for technical support and Rich, Tom, Howard, Tim, Naseem, Martin, Katie, Donna, Florian and Gavin for some helpful pints, hints and tips during this time and to everyone else whom I have had the pleasure to meet and work with since coming to the RI.

Finally I would like to thank all of my family and friends, especially Claudette, Mum, Dad, Simon, Rachel, Simon, Rachael and Matt for their love and support without which none of this would be possible.
Chapter 1

Introduction

1.1) Catalysis today

The life we live today could not be possible without the contributions made by the chemical industry. The effect it has had on the preservation (ie. the development of synthetic drugs such as β-blockers for heart conditions and Penicillins or Tetracyclines to fight against infection and disease) and improvement of lives (through the manufacture of various fertilizers, fabrics and advanced materials) is immeasurable but it is safe to say that the increase in the average life span of a human being over the last one hundred years, has gone hand-in-hand with the advances it has made. Central to the production of these ‘advanced chemicals’ are catalysts, which are used in one form or another in almost 90% of industrial manufacturing processes\(^1\) and consequently the development and understanding of this scientific subject is of great importance.

Catalysts are essentially the ‘added ingredient’ which reduce the energy required (activation energy) in order for a chemical reaction to reach equilibrium (figure 1.1) although they remain both physically and chemically unaltered in the process.\(^2\) The term ‘catalysis’ (meaning ‘loosening down’ in Greek) was first coined by Berzelius in 1835 but the phenomena was already being exploited commercially before this date with the invention of a tinderbox in the early 1820s which worked by the reaction of hydrogen and oxygen over platinum.\(^1\) Since this time the field of catalysis has grown in both breadth and prominence in order to meet the demands that an increasingly more populated and advancing world requires. However the drawbacks of such increased economies of scale is the amount of harmful waste produced since many of the industrial catalytic processes use environmentally unfriendly chemicals and are rarely 100% efficient. This has led to global problems with pollution in the environment threatening our very existence and has prompted action from world governments forcing chemical industries (mainly by the imposition of Green taxes) to make manufacturing processes more efficient and eco-friendly. Since the costs of such environmentally positive policies have been passed on to the
chemical industries so they have been forced to rethink their business strategies and try and minimise production costs in order to maintain profits. With respect to catalysts and catalytic processes there are essentially two ways in which their development can help to bring about such changes. The first and seemingly more straightforward of such means involves developing existing technologies in order to make them more economically viable. This can be achieved though the improvement of either an existing catalytic process and/or catalyst in order to enhance its performance, particularly its selectivity, to a particular reaction. Such a process was for a long time empirically driven, but since more effort has been afforded to the identification of key catalytic concepts so the approach has become more rational in its basis. Alternatively entirely new manufacturing processes can be developed (particularly when current processes become less economically viable) and such an approach is normally centred upon the capability of a particular catalyst to deliver outstanding performance. In either case, catalysis research and development is being driven in the direction where both yields and selectivities are maximised and waste and by-product generation is minimised.

Figure 1.1 Energy profile diagram demonstrating the effect a catalyst has on a reaction as it proceeds. The catalysed reaction (E cat) has a lower energy barrier to overcome than the uncatalysed reaction (E uncat) since the reaction proceeds via a different path involving intermediate species (Int.) and transition states (TS1 and TS2 - hypothetical descriptions of the atoms at the point of highest energy in the reaction pathway) and therefore approaches equilibrium more quickly.
1.2) Catalytic properties and processes

For a catalytic process to be economically viable the catalyst must possess certain physical properties. These include high activity and long-term stability although nowadays with the drive for by-product minimisation perhaps the most important criteria is selectivity or the ability for a catalyst to convert the reactants to a specific product. The ultimate aim for all industrialised catalytic processes is the production of a specific product (near 100% specific) continuously and as quickly as possible at a temperature close to ambient. In reality many industrial processes are not even remotely close to achieving such levels of performance. However in contrast nature, and in particular enzymes, have been achieving such feats for many millions of years.

The amazing selectivity of enzymes (they are able to distinguish between geometric and even optical isomers selectively converting them into corresponding stereospecific products (typically 100% specific) at very high turnover frequencies (which are often in the order of $10^3$ molecules per enzyme per second) all of which is achieved under ambient conditions)\(^1\) has been attributed to their containing very particularly shaped active sites that only allow specific reactants to interact with it in a way which has often been described as analogous to a lock-and-key type interaction.\(^4\) If man then is to emulate enzymatic catalytic performance he needs to be able to design catalysts that possess well-dispersed and defined active sites and also to engineer a catalytic process where reactants can quickly diffuse towards the catalyst and selectively react before diffusing away. This then is the ultimate challenge, which drives the design and development of new homogenous and heterogeneous catalytic systems forward.

1.2.1) Homogenous catalysis

Homogenous catalysis is the form of catalysis in which both reactant and catalyst are in the same physical state. Normally it is carried out in the liquid phase and involves the use of either soluble metal complexes or acids/bases at temperatures below 250°C. Two of the most industrially well-known processes are the production of acetic acid via the Monsanto or Cativa\(^5\) process (using a mixture of rhodium and
HI) with an annual production of ca 7.0 million tonnes per year and alkene oligimerisation via the Shell Higher Olefin process (SHOP) (ca 1.0 mte y\(^{-1}\)) using a nickel chelate catalyst.\(^6\) In general homogenous processes are characterised by both high activity and more importantly high selectivity but are often plagued with problems such as catalyst instability and recyclability, problems that are often exacerbated by the fact that the best catalysts often contain precious metals. However it is normally much easier to investigate the reaction mechanism and structure of the active site than for heterogeneous systems therefore allowing for the potential rational design and development of new catalysts.\(^2\)

1.2.2) Heterogeneous catalysis

Despite the obvious advantages of using homogenous catalysts the majority of industrial processes make use of heterogeneous systems since they are generally cheaper and much easier to recover after use. Furthermore since most heterogenous reactions are carried out in the gas phase over a solid catalyst and over a range of temperatures normally in excess of 250°C, there is a greater scope for the circumvention of both kinetic and thermodynamic barriers that often limit the reactions taking place and for empirical tailoring of the catalyst to give a wider range of products from one feedstock.\(^1,2\) These solid catalytic materials can be divided into two main categories.

1) Bulk catalytic materials – consisting of a uniform material.
2) Supported catalysts – where the active catalytic material is finely dispersed over the surface of another higher surface area material.

Bulk catalytic materials are often used in high temperature applications particularly where the catalyst requires a good mechanical strength and are often made up of more than one component, which are commonly referred to as major (the essential ingredient for reaction) and minor parts. The minor components are added normally to improve on activity, selectivity or thermal stability. An example of such a system is the multicomponent molybdate (MCM) \(K_xNi_yCo_zFe_2BiMoO_x\) used for acrolein production where \(\alpha-Bi_2Mo_3O_{12}\) phase is thought to be the major active part
but small amounts of the additional minor components are necessary to bring about enhanced activity.\textsuperscript{7}

For high activity at modest temperatures, forms that present a high surface area to the reactants are desirable. To this end the use of supports allows for the active component to be dispersed over a much larger area than is normally possible from the production of finely divided or porous bulk catalytic materials. However the support can also confer enhanced mechanical strength and can also bring about structural and electronic modifications to the catalyst, which can aide the reaction process.\textsuperscript{2}

Whilst heterogeneous systems are typically less selective than their homogenous counterparts they are often more active being able to provide a greater amount of product in a shorter time scale. As such it is estimated that these catalytic processes are responsible for the production of 85\% of all bulk, intermediate and fine chemicals\textsuperscript{8} and some of the most important commercial reactions carried out today are listed below in Table 1.1.\textsuperscript{1,2,7,9-12}

\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
Process & Catalyst \\
\hline
Fluid Catalytic cracking & Silica-alumina/Zeolite Y \\
Hydrodesulphurisation & Cobalt Molybdenum oxides \\
Benzene alkylation & Zeolite Y/ZSM-5 \\
Ethylene polymerisation & Chromium oxide on silica \\
Syn Gas production & Magnetite & Copper-Zinc oxide \\
Alkane isomerisation & Platinum on acidified Alumina. \\
Propylene oxidation & Bismuth Molybdates \\
\hline
\end{tabular}
\caption{A list of important industrialised heterogeneous catalytic reactions.}
\end{table}

However since there is now a need to produce more selective catalysts in order to minimise the production of waste, efforts are now being made to try and combine the advantages of the homogenous system (high selectivity) with the low cost, stability and ease of recovery of the heterogenous catalyst or in other words to ‘heterogenise’ the homogenous catalysts by either the physical or chemical attachment of the original homogenous catalyst to a support material\textsuperscript{13-15} Already this approach has yielded a catalyst (a zeolite with the internal surface coated with phosphoric acid), which is now the basis for all synthetic ethanol production through the hydration of ethylene.\textsuperscript{2}
1.3) Selective oxidation catalysis

The last example in Table 1.1 represents a type of one of the most important industrialised catalytic processes that is responsible for one quarter of the value of the chemicals produced by all catalytic processes worldwide.\textsuperscript{16} This type of catalysis is known as selective oxidation. The majority of these reactions are heterogenous and involve the conversion of organic feeds in the vapour phase, over a solid catalyst, to useful products containing the same number of carbon atoms. A list of some of the important commercialised reactions is given in Table 1.2.\textsuperscript{8,16-20}

Table 1.2 A list of important industrialised catalytic oxidation reactions.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactant</th>
<th>Product</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allylic (Amm)Oxidation</td>
<td>Propylene</td>
<td>Acrolein/Acrylonitrile</td>
<td>MCM/FeSb oxide</td>
</tr>
<tr>
<td>Paraffinic Oxidation</td>
<td>n-butane</td>
<td>Maleic Anhydride</td>
<td>VPO\textsuperscript*</td>
</tr>
<tr>
<td>Oxidative dehydrogenation</td>
<td>Methanol</td>
<td>Formaldehyde</td>
<td>Iron Molybdate</td>
</tr>
<tr>
<td>Oxidative dehydrogenation</td>
<td>Propane</td>
<td>Propene</td>
<td>Supported Pt or Chromia-alumina</td>
</tr>
<tr>
<td>Aromatic Oxidation</td>
<td>(\alpha)-Xylene</td>
<td>Phthalic Anhydride</td>
<td>(\text{VO}_x) on TiO\textsubscript{2}</td>
</tr>
<tr>
<td>Three-way auto exhaust</td>
<td>(\text{CO})\textsubscript{a}H\textsubscript{b}n\textsubscript{c}\textsubscript{d}\textsubscript{e}\textsubscript{f}</td>
<td>(\text{CO}_2)\textsubscript{g} + (\text{H}_2\text{O})\textsubscript{h}\textsubscript{i} + (\text{N}_2)\textsubscript{j} + (\text{CO}_2)\textsubscript{k}</td>
<td>Pt/Pd/Rh on Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
</tbody>
</table>

\* MCM = Multicomponent Molybdates
\* VPO = Vanadium Phosphate

In the light of the need to develop cheaper and more environmentally friendly processes so potentially new oxidation processes have emerged which make use of readily available reactants and produce less harmful waste and some of these are listed in Table 1.3.\textsuperscript{16,21,22} Included in this list is the zeolytic material TS-1 which is already used for the production of catechol and hydroquinone from phenol\textsuperscript{21} on an industrial scale but has been chosen to illustrate the potential of such materials as possible partial oxidation catalysts since they possess a much larger area for reaction (their voluminous internal area being their ‘effective’ surface area). Other successful and
noteworthy applications of microporous structures have been for the conversion of alkanes to alcohols, ketones and diacids using either atmospheric oxygen or \( \text{H}_2\text{O}_2 \).\textsuperscript{23}

**Table 1.3** A list of potentially important catalytic oxidation reactions.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactant</th>
<th>Product</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxidation</td>
<td>Ethylene</td>
<td>Ethylene Oxide</td>
<td>TS-1\textsuperscript{a}</td>
</tr>
<tr>
<td>Paraffin</td>
<td>Propane</td>
<td>Acrylonitrile</td>
<td>VTeNbMo oxide on SiO(_2)</td>
</tr>
<tr>
<td>Ammonoxidation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraffinic</td>
<td>Iso-butane</td>
<td>Methacrylic Acid</td>
<td>Heteropoly acids (Phosphomolybdates)</td>
</tr>
<tr>
<td>Oxidation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOFC\textsuperscript{f}</td>
<td>Methane</td>
<td>( \text{CO}_2 + \text{H}_2\text{O} )</td>
<td>Yttria stabilised ZrO(_2)</td>
</tr>
</tbody>
</table>

\( ^{a} \) TS-1 = Titanosilicate-1.

\( ^{f} \) SOFC = Solid oxide fuel cell.

### 1.3.1) Properties of a selective oxidation catalyst.

Since selective heterogeneous oxidation catalysis was first put into practise at an industrial level over sixty years ago, many spectroscopic, catalytic, formulaic and more recently computational studies have been undertaken in order to try to rationalise and determine which properties of the catalyst affect the orientation of a reaction towards a particular product.\textsuperscript{24,25} During this time many concepts and ideas have been put forward in order to explain some of the phenomena observed during catalytic reaction and in particular to explain why hydrocarbons do not undergo total oxidation to the most thermodynamically stable carbon oxides. More recently it has been proposed that there are seven main principles ("seven pillars") that underpin selective heterogeneous oxidation catalysis (listed in Table 1.4).\textsuperscript{26} However, whilst these concepts are well illustrated with respect to many known examples it appears as though there are aspects and phenomena which have been observed in such catalytic reactions whose roles are not so clear including:

a) The function and relevance of both point and extended defects in the creation of active sites,\textsuperscript{24,27}

b) The role of water and in particular the effect of surface hydroxylation on oxidation reaction mechanism\textsuperscript{24,28} and

c) The effects of the addition of promoters on reaction mechanism.\textsuperscript{24,28-30}
Table 1.4 The Seven Pillars of Oxidation catalysis.

1) Oxygen from the crystal lattice is the oxygen source for oxygen insertion reactions.
2) Low metal-oxygen bond strength for ease of oxygen removal.
3) Ease of incorporation of dopants into the host structure.
4) Redox behaviour including the presence of redox pairs ($\text{Fe}^{2+/3+}$ and $\text{V}^{3+/5+}$ in iron phosphate and vanadium phosphate) which often involves catalysis via a Mars and van Krevelen mechanism (figure 1.2).
5) Site isolation or the spatial separation of active sites.
6) Multifunctionality of active sites.
7) Phase cooperation in multiphasic mixed metal catalysts.

Figure 1.2 Schematic of a Mars and van Krevelen mechanism adapted from Vedrine et al.\textsuperscript{28}

But it is perhaps interesting to note that many studies have shown that the catalytic properties of a solid very much depend on the way in which it is prepared. In other words it is one thing to design a catalyst with the desired chemical composition and physical properties but it is another thing to actually make it.
1.4) Catalyst preparation

In principle there are a large number of synthesis procedures that have been used for the preparation of selective oxidation catalysts but in practice certain synthesis procedures have proved more popular than others. Conventionally most catalysts are prepared via precipitation/gelation (and variations along these lines as detailed in figure 1.3)\textsuperscript{31} from solutions or solvents containing metal salts (organic and inorganic) or organometallics since this allows for mixing of ingredients at the atomic scale therefore enabling the synthesis to occur stoichiometrically, quickly and homogenously. Such methods are normally preferred over mechanical milling and high temperature mixing or decomposition of solids in the absence of a melt, as these methods are normally very slow since it takes time for the reactants to diffuse together and react.\textsuperscript{32} However both approaches are often beset with problems, including the crystallisation of unwanted (inactive) phases, sample inhomogeneity and sintering during heat treatment, all of which are detrimental to catalyst performance and for the elucidation of active catalytic phases. Furthermore the use of organics in some preparation procedures is often expensive and can be dangerous since organic vapours are often given off during reaction.\textsuperscript{33,34} These problems are well illustrated in the case of the preparation of a number of different catalyst systems including the iron phosphate, bismuth molybdate and spinel catalysts studied in this thesis.

Despite this list of well-documented problems it is somewhat surprising that the development of new catalyst preparation routes has so far met with relatively little success. There have been some noteworthy attempts to devise novel preparation procedures including the use of supercritical CO\textsubscript{2} to develop a superior vanadium phosphate catalyst\textsuperscript{35} whilst polymerisation complexes, microemulsions, chemical vapour deposition techniques and the use of precursor ion exchanged zeolites have also been utilised to produce various metal oxide materials with enhanced surface areas.\textsuperscript{33,36,37} However, the main disadvantages with using such techniques seems to be their lack of universal application, the use of expensive reagents that cannot be recovered after use or problems with the scaling up to produce the catalyst on the tonne scale. As a result there still exists an opportunity for the development of new synthetic approaches in order to avoid some of these problems and to produce catalysts either more cheaply or via a more environmentally friendly route. One technique however that does seem applicable for the preparation of a large number of
different types of solid, and shows the potential for being able to make use of readily available and cheap reagents and is already used on an industrial scale are hydrothermal methods.\textsuperscript{38}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{flowchart}
\caption{Flowchart summarising the various solution techniques and the juncture at which hydrothermal methods have been employed to prepare mixed metal oxide catalysts.\textsuperscript{39}}
\end{figure}

1.4.1) Hydrothermal methods for the production of condensed phases.

The term hydrothermal refers to the use of water as a reaction medium which is heated above 100°C in a sealed container under mild pressure (\textit{ca} 20 atmospheres) and under such conditions the solvent properties are slightly different from those at ambient. Initially the technique was developed in order to recreate the natural synthesis conditions existing under the earth's crust in order to prepare naturally occurring compounds in the laboratory.\textsuperscript{38} As a result one of the earliest reported uses of hydrothermal methods as a synthetic approach was for the production of quartz (SiO$_2$) crystals from silicic acid in 1845.\textsuperscript{38} From a commercial viewpoint the technology was first exploited for the preparation of pure aluminium hydroxide from bauxite ore 1892 and it has been the standard method used to prepare both synthetic aluminosilicates and metal phosphates since Barrer (in 1948) used such methods to prepare the first zeolite with no natural counterpart.\textsuperscript{39,40} However a real interest in the application of mild hydrothermal methods for the preparation of metal oxides can be traced to 1992 when the Mobil group produced a report detailing the hydrothermal
synthesis of large mesoporous MCM-41 molecular sieves.\textsuperscript{41} This discovery initiated further investigation into whether similar transition metal oxides could be synthesised and resulted in the production of hexagonal and layered Tungsten, Molybdenum and Vanadium oxides.\textsuperscript{42,43} Since then this soft chemical approach has been successfully used for the preparation of a number of different layered, microporous and condensed metal oxide, metal phosphate, metals sulfides etc. phases in not only water but also in some cases organic solvent (solvothermal) and some examples are detailed in Table 1.5 below.\textsuperscript{44,45}

**Table 1.5** detailing the successful synthesis conditions and potential applications of hydrothermally mixed metal oxides and phosphates.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Synthesis Conditions</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO₄</td>
<td>FeSO₄ + H₃PO₄ + LiOH in H₂O at 120°C for 5 hours.</td>
<td>Battery cathode</td>
<td>46</td>
</tr>
<tr>
<td>Mesoporous SnO₂</td>
<td>Treatment of a mixture of tin isopropoxide, 1-tetradecylamine in propan-2-ol at 80°C for 24 hours</td>
<td>Solid-state gas sensor</td>
<td>47</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>TiO₂ + Ba(OH)₂.8H₂O in H₂O at 125°C for 12 hours.</td>
<td>Capacitors and electro-optic devices</td>
<td>48</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>Mn₃O₄ + LiOH in H₂O at 170°C for 4 days.</td>
<td>Battery cathode or ion-exchangers</td>
<td>42</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>ZrCl₄ + NH₄OH in H₂O pressurised at 100MPa at 300°C for 24 hours</td>
<td>Ceramic and catalyst support</td>
<td>49</td>
</tr>
</tbody>
</table>

The advantages of using such a synthetic approach appears to be that it is easily reproducible, good for obtaining a homogenous mix and allows for easy addition of other dopants. The materials often possess enhanced physical properties and, furthermore, because uniform crystals of the active phases are often formed directly at relatively low temperatures there is often no need for further heat treatment which is often detrimental to both the material’s stability and surface area and since heterogenous catalytic processes occur at the surface the amount of active area is crucial to its performance.\textsuperscript{19,50} A particular advantage of the use of hydrothermal over precipitation methods is that, because the operating temperatures are generally below 200°C, compounds that may decompose at elevated temperatures can now be utilised.

However hydrothermal technology has been extended beyond straightforward synthesis to include the following list of applications as listed in Table 1.6 which also
includes a summary of the advantages in using hydrothermal techniques for the preparation of powders.\textsuperscript{51}

Table 1.6 List of various hydrothermal reactions and the advantages of using such technology for the preparation of metal oxide powders.

<table>
<thead>
<tr>
<th>Hydrothermal Reaction</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Growth</td>
<td>1) Phase pure powders are formed directly from solution not needing further treatment by either milling or calcination.</td>
</tr>
<tr>
<td>Treatment</td>
<td></td>
</tr>
<tr>
<td>Dehydration</td>
<td>2) Possible to control degree of crystallinity by reaction temperature and time.</td>
</tr>
<tr>
<td>Extraction</td>
<td></td>
</tr>
<tr>
<td>Ion-exchange</td>
<td>3) Can control particle size (therefore surface area) and shape by varying both temperature and time.</td>
</tr>
<tr>
<td>Sintering</td>
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<td>Oxidation</td>
<td>4) Low temperature preparation route allowing for the synthesis of new metastable phases.</td>
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<td>Crystallisation</td>
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<td>Decomposition</td>
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<td>Hydrolysis</td>
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More recently the technique has been extended to synthesis using microwaves with the apparent advantage being that the kinetics of the crystallisation process is faster by one or two orders of magnitude as compared to conventional hydrothermal processing.\textsuperscript{52}

One drawback of hydrothermal methods is that it doesn’t lend itself to a rational approach for the synthesis of desired solid materials. In particular the synthesis of new materials is still something of a black art in which many experimental parameters (including temperature, time, reagent choice, fill of the hydrothermal vessel, etc.) can be varied using a process of trial and error. However, in the light of recent developments of time resolved \textit{in situ} methods\textsuperscript{53-55} for the study of phase crystallisation (particularly by Energy Dispersive X-ray diffraction (EDXRD)) it has been possible to obtain a real insight into hydrothermal crystallisation processes and as such it is then possible to control and optimise the conditions necessary to prepare a particular phase.
1.5) *In situ* methods

In order to improve upon a particular synthetic process it is important to know how it works. To do this it is necessary to monitor the synthesis reaction so that any important intermediates, phase transformations, changes in coordination and oxidation state can be observed. Such *in situ* monitoring is important since a simple comparison between the synthesis mix before reaction and the final phase formed after it or even by the quenching of reactions at elevated temperatures for post mortem analysis, does not provide sufficient insight into how a catalyst forms. However in order to take such measurements on catalysts under conditions of formation and reaction it is necessary to develop special reaction cells and this has been achieved through the intelligent design of a number of *in situ* cells\(^8\) so that it is now possible to monitor reactions as they occur and obtain information both on the conditions under which certain phases form and for catalytic purposes, on catalytic reaction mechanisms. Such *in situ* measurements have been successfully carried out using a whole range of spectroscopic and diffraction instruments including UV-Vis, IR, NMR, MS, EPR, XAS, XRD and EDXRD and more recently even more powerful techniques have resulted from the successful combination of more than one instrument yielding complimentary information and include the use of combined EPR and UV-Vis and XRD/XAS.\(^{8,53,56-58}\)

The application of such techniques during catalyst formation/activation has made it possible to obtain a real insight into crystallisation processes particularly when using EDXRD where a time resolution in the order of 1-2 minutes is achievable. This then makes it possible to determine the kinetics of reaction, which is often the first stage involved in elucidating a reaction mechanism, and also provides information on how to control and optimise the conditions necessary to prepare a particular phase.\(^{59,60}\)
1.6) Project overview

During the course of the thesis in situ time resolved SR techniques (mainly EDXRD and combined XRD/XAS) have been applied in order to follow the crystallisation and phase transformations processes occurring when the important industrial catalysts iron phosphates and bismuth molybdates have been prepared using both conventional co-precipitation procedures and a new approach using hydrothermal techniques. In both cases the use of the hydrothermal technique to prepare these catalysts results in a more phase pure product with a larger surface area and such findings could well have important implications for future catalytic application. Continuing along the lines of new preparative routes the use of ion exchanged zeolites as precursors for the low temperature crystallisation of condensed mixed oxide phases has also been investigated for the preparation of the spinel structure CoAl₂O₄ using XAS and XRD with results from this study suggesting that very small spinel particles form within the XRD amorphous collapsed zeolites.

Finally the redox capability of cobalt and manganese substituted aluminophosphates structures –5 and –18 were investigated using a combination of XAS, EPR and the catalytic conversion of methanol to olefin (MTO). Results suggest that although both systems are oxidised from the as prepared 2+ oxidation state to 3+ on calcination the extent of oxidation is both dependent upon the metal ion and structure type.
1.7) References


Chapter 2

Experimental Methods

2.1) Chapter overview

The reason for using the various experimental techniques for characterising the materials studied in this thesis is discussed along with some of the basic theory behind the interpretation of the data obtained.

2.2) X-ray Diffraction

X-ray diffraction (XRD) is a technique that is routinely applied to study the long range ordering in solids. Although a large amount of information relating to the atomic arrangement in these structures can be gleaned from using this technique it has been used in this thesis mainly to identify and compare the crystallinity and purity of the materials prepared, since the work has primarily concentrated on the production of crystallographically well-known phases by new preparative methods. Diffraction patterns have been collected on powdered, pelleted and amorphous samples using a conventional laboratory based diffractometer and at the Synchrotron Radiation Source (SRS) in both angular and energy dispersive modes.

Powder X-ray patterns were recorded in the conventional angular dispersive mode using Bragg-Brentano geometry. Two diffractometers were used to record the diffraction patterns (Siemens D500 and a FR571 Enraf Nonius diffractometer) both of which were equipped with an X-ray tube source and copper target. A schematic of the set-up is shown in figure 2.1.
2.2.1) Theory of diffraction

Unlike visible light the wavelength of X-rays are similar to the atomic spacing between the constituent atoms in solids (both in the order of a few angstroms) and are therefore susceptible to diffraction. The degree to which the x-rays are diffracted is both a function of the interplanar lattice spacings and element constitution and in this respect is unique for every solid.\(^1\),\(^2\)

Laue first discovered the diffraction of X-rays by crystals in 1912, but it was S. L. Bragg whom later proposed a simple mathematical formula to explain the phenomena as a function of incident x-ray angle and separation between the lattice planes (equation 2.1). It was proposed by Laue that diffraction is the interference phenomena caused by an object in the path of the X-ray waves.\(^3\) The X-ray waves that are reflected from the lattice planes but remain in phase, interfere constructively and give rise to strong signals or ‘peaks’ in a diffraction pattern. By the same token X-rays that are reflected out of phase will result in weak or non-existent signals as a result of destructive interference.\(^4\)

\[ n\lambda = 2d \sin\theta \]  \hspace{1cm} (2.1)
From equation 2.1 it is possible (for a fixed X-ray wavelength (\(\lambda\))) to
determine both the lattice plane identity and separation (d) from the position of the
diffraction peak (2\(\theta\)). For a simple cubic crystal

\[
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]  

(2.2)

The quantity \(a\) is equal to the length of the unit cell which is the fundamental sub unit
of a lattice plane and from which the entire crystal can be constructed by periodic
repetition. The terms \(h\), \(k\) and \(l\) are known as Miller Indices and describe a particular
lattice plane in the structure. The near integer experimental values for these terms can
be calculated when \(\sin^2\theta\) (equation 2.3) is multiplied by a constant as follows:

\[
\sin^2\theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)
\]  

(2.3)

This process is known as indexing. Some types of unit cell give characteristic and
easily recognizable patterns of lines. For example the first seven reflections from a
primitive cubic lattice correspond to the (100), (110), (111), (200), (210), (211) and
(220) lattice planes which are derived from the values calculated from the sum of \(h^2\)
+ \(k^2\) + \(l^2\) (equation 2.3) equal to 1-6 and 8. The value \(h^2 + k^2 + l^2 = 7\) is missing
since the sum of the squares of three integers cannot equal 7. This omission, which
is characteristic of the primitive cubic lattice, is known as a systematic absence.
Another example of this is the body centred cube where a reflection is present for a
specific Miller plane if \(h + k + l = 2n\), where \(n\) is an integer and therefore the (100)
reflection is absent.\(^4\)

2.2.2) Using synchrotron radiation for collecting powder X-ray data.

Normally data recorded on laboratory based X-ray equipment is sufficient for
carrying out phase identification and the determination of phase purity but is not so
suitable for \textit{ab initio} structure solution or refinement. This is because the peak shapes
are often difficult to model mathematically and there are often problems with peak
resolution and overlapping reflections at high angles. To some extent these problems can be overcome by using long data collection times to improve the signal to noise ratio and by using more powerful computers to carry out refinements using the latest software. However most of the problems associated with collecting good powder X-ray diffraction data from laboratory sources is avoided when using Synchrotron Radiation (SR) and High Resolution Powder Diffraction (HRPD). This technique benefits from there being a more intense tunable X-ray source allowing for quicker data collection times at any wavelength with a better peak resolution and easy to model peak shapes.\textsuperscript{5}
2.3) Use and application of synchrotron radiation for materials characterisation

Synchrotron radiation (SR) has been used extensively to characterise the materials studied in this thesis. In particular three important techniques have been used which include X-ray absorption spectroscopy (XAS), XRD and Energy-dispersive x-ray diffraction (EDXRD). SR is the intense polychromatic electromagnetic radiation that is emitted when electrons, accelerated in magnetic fields, are deflected from their course.\textsuperscript{5,6} This phenomenon was originally observed as an undesirable energy loss in the first particle accelerators used for high-energy physics studies, but it was soon realised that such a spread of energies of high brilliance could be utilised for scientific benefit and the first dedicated synchrotron storage rings for the exploitation of SR were conceived.\textsuperscript{6} A basic storage ring is shown in figure 2.2 and consists of an array of several bending magnets, which constrain the electron orbit under vacuum. Initially electrons are fired from a linear accelerator (LINAC) before they are accelerated to near relativistic speeds in a booster ring and injected into a storage ring. On reaching a bending magnet in the storage ring the electrons are accelerated radially but emit SR tangentially which is then siphoned off. This energy loss needs to be continuously replaced with the appropriate electromagnetic radiation to ensure lifetimes in the timescale of hours as opposed to minutes if the radiation were not to be replenished. At least every 24 hours a new batch of electrons is injected into the storage ring from the LINAC since the SR intensity declines over time as a result of collisions with residual gas molecules in the imperfect vacuum.\textsuperscript{6}

On its own a simple storage ring operating at \textit{ca} 2 GeV such as in the SRS, gives a spectrum which rapidly drops off in intensity at higher energies. To extend the energy range and increase SR intensity at the upper end of the spectrum magnetic insertion devices are added.\textsuperscript{6} These include wigglers to extend the energy range, multipole wigglers that cause constructive interference from a series of successive ‘wiggles’ and undulators, which create a series of very sharp peaks in the spectrum, allowing enhancement at certain frequencies.
The advantages of using synchrotron radiation for scientific study can be summarised accordingly:\textsuperscript{5-7}

1) High incident light intensity with a flux, resolution and brilliance far greater than laboratory based equipment. This is particularly useful for measuring ultra dilute samples and for fast data collection times.

2) Highly tuneable selection of wavelength and spread of energies that can be utilised for a number of different spectroscopic measurements all under one roof. (inc. Energy Dispersive X-Ray Diffraction (EDXRD))

3) The radiation is totally plane polarised with respect to the storage ring, which has been utilised for polarisation dependent studies and on magnetic systems.

4) The beam is also highly collimated in the plane of the synchrotron and as such diffraction peaks are more narrow and better resolved with much reduced peak widths at half maximum.

**Figure 2.2** Schematic of 2\textsuperscript{nd} generation storage ring showing the tangential synchrotron radiation output from the bending magnets. Initially electrons are fired from a linear accelerator (LINAC) into a booster ring before being accelerated further and injected into the storage ring.
2.4) X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is an ideal technique used for studying the electronic and structural properties of catalysts under both in situ and ex situ conditions.\textsuperscript{8-12} As it is element specific there is no requirement for long-range order (as required by X-ray diffraction), which makes it possible to probe the local structure around atoms of interest when only a few weight percent are present. However it is still a ‘bulk’ technique (ie. sampling all of the atoms of a particular absorbing element equally) and hence the local structure information which can be ascertained is a reflection of the average bond length, co-ordination number and degree of disorder around the absorber.

In a typical experiment the energy of the X-ray photons are varied and as they pass through the sample are attenuated according to Lambert’s law (equation 2.4):\textsuperscript{8,11,13}

\[ I = I_0 e^{-\mu x} \]  

(2.4)

Where:

I & I\textsubscript{0} are the transmitted and incident radiation intensity, respectively
\mu is the linear absorption coefficient
x is the material thickness

A typical Fe K-edge XAS spectrum is shown in figure 2.3. It consists of three main regions, the pre-edge region, which is due to simple mass absorption, the X-ray Absorption Near Edge Structure (XANES) region and finally the Extended X-ray Absorption Fine Structure (EXAFS) region.
2.4.1) XANES

The XANES or X-ray absorption near edge structure part of an XAS spectrum refers to the region (approximately 50 eV below and 100 eV above as detailed in figure 2.3) around the absorption edge and is associated with the excitation processes of core electrons to bound or quasi-bound states. It contains information on the electronic state and local structure around the absorbing atom although multi excitation and multiple scattering effects often complicate the analysis of this region. Essentially the position of the edge has been shown to be sensitive to both the oxidation state and coordination number of the absorbing species whereas the presence of fine structure (pre-edge feature) is related to its coordination geometry and is governed by orbital selection rules. The pre-edge peak observed in the first row transition elements studied in this thesis are associated principally with a 1s-3d transition which is thought to be mainly a quadrupole transition but is also part dipole (particularly in the case of iron). However the dipole selection rule (also referred to as the Laporte selection rule) \( \Delta l = \pm 1 \) forbids this transition and theoretically any feature that is observed is due to the weaker quadrupole transition.
can gain in intensity when in a non-centrosymmetric coordination environment (ie. tetrahedral) a relaxation of this rule is observed which is due to the mixing of p orbitals from both the ligand and the 4p state of the cation, allowing a transition to take place.\textsuperscript{14,15} It has also been shown that the intensity of the transition is not only dependent on the coordination geometry but also with metal-oxygen distance.\textsuperscript{16,17}

The 1s-4p transition for first row transition elements also seen in the XANES region encompasses the X-ray absorption edge and is normally larger in intensity than the pre-edge peak since this is now not forbidden by the dipole selection rule.\textsuperscript{3} Unsurprisingly the white line intensity for octahedrally coordinated systems is greater than for tetrahedral ones since there is less d/p orbital mixing. However it is understood that this intensity is also enhanced by multiple scattering effects, which are normally greater in octahedral coordination since the bonds tend to be collinear to the absorber unlike in the tetrahedral system.\textsuperscript{10}

\subsection*{2.4.2) EXAFS}

With increasing X-ray photon energy (decreasing wavelength) the absorption coefficient ($\mu$) of the material continues to decrease as a result of X-ray attenuation by the material, until the photon energy matches the energy of an electron in a core state. At this point the electron is excited to a vacant or partially occupied excited state or to the continuum and $\mu$ rapidly increases corresponding to an abrupt increase in absorption intensity. This is known as an absorption edge. The ‘type’ of absorption edge is dependent upon whether the X-ray energy is able to excite an electron from the ls orbital resulting in a ‘K-edge’, for a 2s electron an L1 edge, for 2p\textsubscript{1/2} LII, and 2p\textsubscript{3/2} LIII and so forth. Above the absorption edge the ejected photoelectron possesses a kinetic energy ($E_{Ke}$) equal to:

$$E_{Ke} = h\nu - E_b$$  \hspace{1cm} (2.5)

Where:

$h\nu$ is the photon energy
$E_b$ the binding energy
The outgoing photoelectron can be represented quantum mechanically as a spherical wave with a wavelength (\( \lambda \)) defined by equation 2.6:

\[
\lambda = \frac{2\pi}{k}
\]  

(2.6)

where \( k \) represents the photoelectron with a kinetic energy defined as in equation 2.7:

\[
k = \sqrt{(2m / h^2) \cdot (E-E_0)}
\]  

(2.7)

where \( m \) is the electron mass, \( h \) is equal to \( h/2\pi \) (where \( h \) is the Planck constant) and \( E-E_0 \) the energy of the photoelectron minus the energy required to eject it from a core state.\(^8\)\(^1\)\(^1\)

The transition probability of this radiative transition is thought to be a function of the initial and final-state wave functions and is proportional to the linear absorption coefficient (\( \mu(E) \)).\(^8\)\(^1\)\(^1\)\(^1\) Such transitions are allowed when the two wave-functions differ in their charge distributions in a manner corresponding to an electric dipole.\(^1\)\(^0\) However this dipole approximation is only valid when the wavelengths of the photons are larger than the size of the absorbing atom.\(^1\)\(^1\) The final state wave-function consists of two parts corresponding to the ejected photoelectron wave and a backscattered wave. It is the combination of the constructive and destructive interference between these two wave-functions (as a function of the distance between absorber and scatter) as detailed in figure 2.4 that give rise to the oscillatory Extended X-ray Absorption Fine Structure (EXAFS) observed between 50 and 1000 eV beyond the absorption edge. This modulation of \( \mu(E) \) as a result of the interference effects is described in equation 2.8.
\[ \mu_{\text{total}} = \mu_0[1 + \chi_{\text{ex}}] \] (2.8)

The term \( \chi_{\text{ex}} \) is then a sum of all of the respective interference patterns from all neighbouring atoms. This term can be broken down further (equation 2.9) to yield a formula, which is essentially comprised of two parts: \( A_j(k) \), which describes the amplitude of the oscillations and a sine function (\( \sin \phi_j(k) \)) for the interference patterns.\(^8,^{11}\)

\[ \chi(k) = \sum A_j(k) \sin \phi_j(k) \] (2.9)

The sine function can also be broken down (equation 2.10) into two parts.\(^8,^{11}\) The first part (\( 2kR_j \)) representing the inter-atomic distance (or phase delay) between the absorbing and scattering species and a second part representing an alteration in the phase of the photoelectron wavevector (change in kinetic energy and a phase shift) as it approaches the positively charged nucleus of both the scattering species and absorber as it returns.

\[ \sin \phi(k) = \sin [2kR_j - \phi_j(k)] \] (2.10)

The amplitude part of the EXAFS equation is described in equation 2.11.
\[ A_j(k) = (N_j/kR_j^2) S_o^2 F_j(k)e^{-2k^2\sigma_j^2}e^{-2R_j/\lambda_j(k)} \] (2.11)

Equation 2.11 illustrates the contribution to the EXAFS made by \( N_j \) (the number of atoms of type j at a distance \( R_j \)) with a mean square relative displacement (\( \sigma_j \)) and the fluctuation in \( R_j \) due to structural disorder and/or thermal motion. The other terms, which make up the amplitude function include \( F_j(k) \) representing the backscattering amplitude factor as a function of \( k \) which is enhanced when the photoelectron energy equals the unique orbital energies of the backscattering species and is therefore related to the atomic number.\(^{10,11} \) The term \( S_o^2 \) is an amplitude reduction factor, which originates from intrinsic multielectron excitations (or shake-up/ shake-off processes) and is weakly dependent upon the absorbing species\(^ {10,11} \) whereas the exponential term \( 2R_j/\lambda_j(k) \) represents the mean free path of the photoelectron, which is restricted by its lifetime or losses to the overall EXAFS caused by competing physical processes.\(^ {10,11} \)

2.4.2.1) Curved-wave vs. Plane-wave approximation

Thus far the EXAFS theory described above has been for the *plane-wave approximation* in which it is assumed that atomic radii are smaller than the interatomic distances and therefore the photoelectron wave is approximated as a wave without any curvature thus simplifying the final EXAFS expression.\(^ {5-11} \) Normally however this approximation is only accurate for large values of \( k \) or \( r \) (high energy or large distances). For lower \( k \) and \( r \)-values the approximation becomes less accurate resulting in phase shift calculation errors and erroneous determinations of atomic distances particularly when light atoms are involved which scatter in the lower \( k \) regions. For such systems it is often necessary to use a more exact EXAFS theory known as *Curved-wave* theory.\(^ {18} \) However it is mathematically very complicated and is often difficult to apply in data analysis but this problem has since been circumvented by the development of a *fast curved-wave* theory, which was able to
dramatically reduce the computational time needed by simplifying the theoretical form of the exact theory.\(^{19}\)

2.4.3) Data collection

Data was collected at both the Daresbury Laboratory Synchrotron Radiation Source (SRS) on stations 3.4, 7.1, 8.1 and 9.3 (combined XRD/XAS measurements) and the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) on the Swiss-Norwegian beamline. Both synchrotrons operate with a current of between 150-250 mA however, the beam energy at ESRF is three times higher at around 6 GeV as opposed to the SRS where it is typically 2 GeV. The highly collimated, intense, tuneable radiation obtainable from a synchrotron source is ideal for the sort of materials used in this study.

For the purpose of the experiments carried out in this thesis XAS measurements were run in either transmission or fluorescence mode. For transmission experiments beam intensity measurements were collected on two ion chambers (I\(_0\) and I\(_t\)), which are filled with an appropriate mixture of gases specific to the experiment energy range in order to maximise their response. These are located either side of the sample, as shown in figure 2.5, with the difference in readings being equal to \(\mu(E)\). A double crystal monochromator (either Si (111) or (220) in all stations except the Soft X-ray EXAFS (SOXAFS) station 3.4 where an InSb (111) monochromator is used) is employed in order to produce a tuneable and highly collimated X-ray beam. The monochromator is typically detuned by ca 50\% in order to reject any higher harmonics which may cause interference. A typical experiment involves moving the monochromator angle (in concerted steps) in order to obtain a plot of sample absorbance as a function of energy. The sample step size and counting time is varied accordingly in order to obtain the necessary resolution on any pre edge features or when collecting EXAFS information several hundred eV above the edge. Before the samples are measured the position of the absorption edge is usually determined using a standard foil. This is important for accurate data recording but can also be used to check variation in edge position indicating a change in oxidation state or coordination number.
In fluorescence mode, data is normally recorded on several individual fluorescence detectors. Usually this mode is used when the concentration of absorbing species is low to give better sensitivity to the EXAFS measurements since background absorption is reduced as this is a secondary radiative process.\textsuperscript{8} As demonstrated in figure 2.6 the fluorescence detector is placed at approximately 90° to the beam in order to maximise the photon yield.
For the soft edge spectroscopy measurements the Total Electron Yield (TEY) is measured from Auger electrons produced during a secondary electron process. Since the electron yield is very low for this processes it is necessary to carry out these measurements under vacuum in order to obtain a good signal to noise ratio.

2.4.4) Combined XAS(QuEXAFS)/XRD

Normal XAS scans can take anywhere up to one hour to record. The recent development of a fast scanning mode known as Quick EXAFS (QuEXAFS), where the monochromator is moved at a constant velocity rather than in concerted steps, has reduced this to a routinely achievable 1 minute. The quality of such data is highly comparable to the normal scanning mode spectra provided the QuEXAFS set up does not contribute any significant noise (since the reduced number of photons are not thought to have any effect). When this technique is combined with XRD where the whole pattern can be collected in the order of minutes (using a curved position sensitive detector – PSD), a very powerful combined QuEXAFS/XRD in situ technique results which is sensitive to both long and short range order. As this combined technique delivers a time resolution in the order of minutes it is particularly useful when studying catalyst activation and solid-state transformation processes at elevated temperatures, which is made possible using the in situ furnace (figures 2.7 and 2.8).
Figure 2.7 Diagram of the experimental configuration on station 9.3 for collecting combined QuEXAFS/XRD data. A picture of the furnace used for these measurements is presented in figure 2.8.

Figure 2.8 In situ cell for combined QuEXAFS/XRD measurements during temperature ramping experiments.
2.4.5) EXAFS data analysis

In order to obtain detailed information on the state of the local environment of the absorbing species it is necessary to process the raw XAS data. This is done using the Daresbury Laboratory suite of analysis programmes EXCALIB, EXBROOK and EXCURVE98, although alternative codes are available at Daresbury and elsewhere to carry out similar tasks. Since the recorded data from the SRS takes the form of monochromator position vs. detector response, the first requirement in the analysis procedure is to convert the data to energy vs. absorption coefficient. This procedure is carried out using the EXCALIB programme in which it is also possible to sum a number of scans together in order to improve the signal to noise ratio and remove any glitches (which may occur as a result of sample inhomogeneity, electrical noise or spurious reflections from the monochromator) which can adversely affect the reliability of the amplitude information. The resulting data sets are then processed using EXBROOK, which carries out three main tasks.

The first part is the removal of the pre-edge slope due to mass absorption and multiple scattering effects. This is performed by fitting a polynomial function (modified Victoreen) to this region and extrapolating beyond the absorption edge.\textsuperscript{8,11} This subtraction is extrapolated to include the absorption data, yielding the absorption coefficient. Since the spectra at this point have also been normalised with respect to the edge step (normally achieved by dividing the data by the edge step at 50 eV above the edge) it is now possible to compare the XANES region (including both the pre edge and edge intensities) between samples.

The next stage in the subtraction is the determination of the edge energy (E0). Generally the edge position is taken as the first inflection point in the white line although this is not always so easy to identify. In such a case an arbitrary position at approximately half the height of the normalised edge is often used.\textsuperscript{10,11} However the value determined by these two methods may actually differ in value to the theoretical edge position and as such this value is refined during curve fitting.

Since the EXAFS oscillations are represented by the sine function of the wave vector of a photoelectron ($k$), it is necessary to convert the absorption energy into the units of the photoelectron wavevector (equation 2.7).
The object of the post edge background subtraction is to extricate the contribution of the EXAFS from the rest of the absorption spectrum. This is achieved by fitting a cubic spline through the oscillations above the edge. The fitting of the spline can be improved by varying the smoothness, weighting and starting and end energies but is very much a process of trial and error. Each attempted fit can be assessed by comparing the isolated EXAFS oscillations and a Fourier Transform (FT) of $\chi(k)$. The FT gives a radial distribution function with the position of the absolute part of the transform corresponding to the distance between absorber and scatterer. The data can be weighted accordingly (ie. multiplied by a factor of $k^0$) which can be useful when distinguishing between low mass scatterers (when elements such as oxygen are present) which tend to produce a signal in the low $k$ region and high Z scatterers which produce signals at higher $k$ values.\textsuperscript{11} Essentially a successful background subtraction ensures that the intensity of the EXAFS oscillations and FT peaks are maximised and that there is no low frequency intensity in the FT $< 0.1\text{nm}$.\textsuperscript{10}

Once the background subtraction is complete it is now possible to fit a theoretical model to the isolated EXAFS data. This is done using EXCURV98, a least squares refinement programme used to calculate and evaluate a model for the local structure around the atom of interest. The models used can either be simple absorber-scatterer pairs where a known distance and coordination is used (if only a first shell analysis is required) or else a more complex model can be derived from a simulation of crystallographic data. EXCURV98 uses curved wave theory to do this since it provides more accurate phase shifts and amplitude functions providing for a better agreement with experimental results.\textsuperscript{8,11} Once a theoretical model has been determined, based upon the data inputted, it becomes possible to refine the model by varying the parameters known to contribute to the EXAFS. This variation includes the number of backscattering atoms (N), the average bond length (R), mean square relative displacement (or Debye-Waller factor) and the edge position relative to the calculated vacuum zero ($E_o$). The refinement of the data is normally undertaken in R-space since if the absorber-scatterer pair is known it is obvious when the calculated and experimental radial distribution functions do not fit. An important consideration when carrying out data refinement is the tendency for some of the refinement parameters to correlate in such a way as to produce false minima and therefore incorrect results. In particular the correlation between the coordination number and
the Debye-Waller factor is particularly strong where it is estimated that an increase in 0.01 Å can bring about a change of 0.4 in N indicating the potential for large errors.\textsuperscript{8,11} Also correlated are $E_0$ and $R$ however it is possible to produce a correlation map in order to determine the degree of correlation between such variables, which will show a series of contours displaying the minima between them and allowing the potential for false minima to be identified. Another consideration when carrying out a refinement is the number of independent data points ($N_{\text{ind}}$) which is derived from equation 2.12:\textsuperscript{11}

\[
\text{No. of independent points} = \frac{2\Delta k \Delta R}{\pi} + 2 \quad (2.12)
\]

where $\Delta k$ and $\Delta R$ are the range in both $k$- and $R$-space over which the data is fitted. A calculated value of $N_{\text{ind}}$, less than 1 would be physically meaningless since it is not possible to have more parameters than observations.\textsuperscript{11} This can also lead to a refinement producing a false minima.\textsuperscript{8}

Refinement continues until an optimum goodness of fit is achieved. The R-factor (equation 2.13)\textsuperscript{27} 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 however values of 15\% or less are difficult to obtain by fitting only a first shell. Improvements in the goodness of fit can be achieved by including higher coordination shells in the refinement. However this is only feasible if they are actually present in the sample otherwise the R-factor will decrease.

\[
R \, (\%) = \sum_{i}^{N} \frac{1}{\sigma_i} \left( \left| \chi_i^{\text{exp}}(k) - \chi_i^{\text{th}}(k) \right| \times 100 \right) \quad (2.13)
\]

It has been estimated that the parameters determined after refinement of the data are accurate to within ±0.02 Å for the EXAFS distances and within 20\% for the coordination number.\textsuperscript{11}

2.4.6) Multiple scattering

Thus far the theory used to model the EXAFS data assumes a single scattering of the photoelectron. This, however, is not sufficient to describe the EXAFS
contributions for some systems. Sometimes multiple scattering of the photoelectron needs to be considered, especially when three atoms are close together and possess an internal angle between 150-180°. In such instances the outgoing photoelectron from the absorbing atom is enhanced or strongly forward scattered by the intermediary atom, which results in an enhancement of the EXAFS amplitude before it is finally backscattered by the second neighbour. This is shown schematically in figure 2.9. However this forward scattering is greatly reduced as the bond angle approaches 150° but recently it has been shown that an improvement in the goodness of fit for a refinement can be achieved even when considering multiple scattering effects for bond angles less than 150°.\textsuperscript{27,28} For the purpose of data analysis it becomes necessary to define a model for the structure and to include this extra pathway in order to calculate the additional forward scattering effects. Hence it then becomes possible to use EXAFS to obtain more detailed structural information beyond the first few angstrom.\textsuperscript{27,28}

\textbf{Figure 2.9} An illustration of multiple scattering effects in a collinear atomic arrangement. The outgoing electron waves (solid circles) from an excited atom (purple) interact with the first scattering atom (red) and are strongly forward scattered (dashed line) before reaching the second scattering species (blue) where they are backscattered (dotted line).
2.5) EDXRD experiments

As opposed to normal angular resolved diffraction experiments the in situ EDXRD technique allows for the collection of an entire diffraction pattern over a limited d-spacing range in a period of between 1-2 minutes. This therefore enables for a much more detailed and accurate kinetic analysis than that which is obtainable by ex situ quenching methods. It is made possible because the technique relies on the polychromatic character of synchrotron radiation and as such by fixing the detector angle, diffraction intensity is measured as a function of energy. Only radiation with the correct energy (or wavelength) to satisfy Bragg’s law for diffraction from lattice planes (equation 2.14) will be reflected. This condition is detailed as follows:

\[ \lambda = \frac{hc}{E} \]  

(2.14)

Where \( h \) is Planck’s constant, \( c \) the speed of light and \( E \) the photon energy. By substituting Bragg’s law into equation 2.14 results in the following expression for d-spacing as a function of energy (equation 2.15):

\[ d = \frac{hc}{2E \sin \theta} \]

(2.15)

where \( \theta \) is the angle of the detector relative to the sample and the beam.

As mentioned previously the EDXRD technique relies on the intense polychromatic character of synchrotron radiation which is powerful enough to penetrate the walls of a Teflon lined stainless steel autoclave without loosing too much intensity so that it becomes possible to follow hydrothermal crystallisation reactions. Although an individual solid-state detector is only able to collect data over a limited d-spacing the development of the 3-element array developed by Barnes et al. enables the collection of a lot more diffraction information.\textsuperscript{29,31,32} A diagram of the EDXRD experimental set-up (station 16.4 of the SRS) is shown in figure 2.10, which also includes the output from each detector for a CoAlPO-5 structure. This particular instrument arrangement has been successfully used many times in order to study the formation of microporous materials and other systems.\textsuperscript{29,30,33-35}
2.5.1) EDXRD data analysis

The individual data files recorded for each detector (where a data set was recorded at one minute intervals for up to 2 hours) were converted into a format appropriate for use with a graphical curve-fitting package, such as Xfit available from CCP14. This programme was used in order to visualise and to extract information regarding the reflection position, area and intensity using a simple Gaussian curve fitting routine. This process was repeated for each data set in order to obtain information on the phase crystallisation processes. From the resultant plot of reflection intensity vs. time it would then be possible to model the growth process with the well-known Avrami-Erofe’ev equation,\(^{36-39}\) which is widely applied to model solid crystallisation and phase transformations to obtain information on both the rate and dimensionality of the growth process. A more detailed description of this data analysis process is given in chapter 4.

\[
(I) = \text{intensity}
\]

**Figure 2.10** A schematic representation of the 3-element detector array used on station 16.4 of the SRS for EDXRD investigations complete with detector response ((A) top detector, (B) middle detector and (C) bottom detector) on the right hand side for CoAlPO-5. Not shown in the diagram is the furnace in which the in situ hydrothermal cell is placed in order to raise the apparatus to a reaction temperature of ca 150°C. Two holes in the either side of the furnace allow unattenuated white beam intensity into the set-up to ensure that it is possible to follow the crystallisation process. The solid state detectors were inclined at fixed 2\(^\theta\) angles so that the range of photon energies available are representative of the d-spacings for the materials of interest and that they avoid reflections from both the Teflon liner and steel autoclave.
2.6) Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a powerful microscope technique which is capable of delivering topographical information at the molecular level. This information is obtained when a highly focussed electron beam is scanned across a material under vacuum producing a number of scattering and radiative emission events (figure 2.11) which, when measured, provide information on the sample shape, size and constitution.\(^{40}\)

![SEM Setup Diagram](image)

**Figure 2.11** Diagram detailing the scattering and radiative events that occur when an electron beam is scanned across a sample during observation.

Initially the electrons are produced via an electron gun, normally containing a tungsten filament, which are focussed by a number of magnetic lenses to produce a highly collimated beam in the order of a few nanometers wide. The electrons typically penetrate into the sample to a depth of *ca* 1 micron producing a contrasted image from which it is possible to obtain particle size/shape information with a resolution of between 2-5 nm.\(^{40}\) Image resolution is achieved by controlling the electron beam diameter whereas the intensity of the emitted signals is proportional to the probe current. Therefore a delicate balance exists between the need to control the number of electrons to obtain enough signal intensity but not so much that the beam diameter and therefore the resolution is affected.
Two signals are primarily used to obtain this information; secondary electrons that are predominantly produced by the interaction between the energetic beam and weakly bound valence electrons and backscattered electrons, which as the term implies are backscattered after impinging on the sample surface. Since the beam electrons are moving at relatively high speeds with respect to the sample only small amounts of kinetic energy are lost during the backscattering and secondary electron generation process but this is enough to obtain the required topographical information.

2.6.1) Electron probe microanalysis (EPMA)

As demonstrated in figure 2.11 a number of scattering and radiative emission events occur when an electron beam strikes a sample. Whereas SEM is concerned with topographical information the technique of EPMA makes use of the emitted X-ray radiation, which contains both qualitative and quantitative information regarding the constitution of the sample. It was observed by Mosely\(^\text{40}\) that the frequency of the emitted X-ray radiation was a function of the atomic number and when the intensity of this radiation is calibrated against a standard containing the same element under the same electron bombardment conditions it is possible to obtain the amount of this species present in a mix.
2.7) Differential scanning calorimetry (DSC)

DSC is a technique that is used to study what happens to materials when they are heated. The technique involves recording the energy necessary to establish a zero temperature difference between a substance and a reference material against either time or temperature as each specimen is subjected to an identical temperature program. It is particularly sensitive to determining melting points and boiling points, crystallisation temperatures, changes in heat capacity, heat of fusion, heat of solution and heat of vaporization. The heating experiment is conducted using two sampling pans: one containing the material of interest and a second for a reference (normally a blank). Each is located on a separate heater and heat is supplied to both to produce a plot of heat output vs. temperature. When the material undergoes a phase change such as when a particular phase crystallises it gives off heat (the latent energy of crystallization). This is manifested as a drop in the heat flow to the sample (exotherm in the heat flow vs. temperature plot) since its heater doesn't have to put out much heat to keep the temperature of the sample pan rising. Integration of the area under the heat flow curve yields the enthalpy change associated with the thermal event of interest.
2.8) Thermogravimetric analysis (TGA)

Is a technique that allows for the determination of the precise weight change of a solid as it is heated at a controlled rate.\textsuperscript{1,40} It can be used, for example to determine the amount of chemically attached water or the total organic content of an otherwise inorganic substance.
2.8) References

(8) Teo, B. K. *EXAFS Basic Principles and Data Analysis* 1986, Springer Verlag.


Chapter 3

An in situ study following the structural changes in iron phosphate catalysts prepared by various synthetic methods

3.1) Chapter overview

This chapter contains the results from a series of in situ combined XRD/QuEXAFS experiments performed on iron phosphate catalysts prepared by various synthetic methods. Two of the synthesis procedures have previously been employed to produce these catalysts whilst the third is a new method employing hydrothermal techniques. The combined XRD/QuEXAFS approach supported by ex situ measurements carried out using XRD, TGA and surface area measurements, showed that all three methods produced a catalyst precursor material, having the chemical composition of FePO₄·2H₂O. The in situ study clearly shows the loss of two water molecules during the initial stages of heating and a transformation to FePO₄ having tridymite type structure takes place at temperatures above ca 100°C. The crystallinity of the tridymite phase appeared to improve upon heating to ca 500°C and above which a further transformation to a quartz phase took place. Of the three catalysts, the material produced by hydrothermal methods was found to be the most phase pure and possess a higher surface area than the materials prepared by the other two methods.

3.2) Introduction

Methyl methacrylate (MMA) is an important intermediate for a large number of chemical processes. It is conventionally prepared via the acetone cyanohydrin process according to the scheme depicted below (equation (3.1)) and has a current world capacity in the order of 2.2 million tons per annum.¹
Acetone + HCN → acetone cyanohydrin → methacrylamide → MMA  \hspace{1cm} (3.1)

However this process uses a large amount of sulfuric acid resulting in the production of ammonium sulfate as a by-product, which is difficult to recycle. As the degree of legislation brought in for the protection of the environment has increased so the costs incurred for the appropriate handling and storage of these environmentally benign chemicals has risen, forcing chemical industries to consider other possible routes for its production. One of the more viable alternative processes involves a three-step synthesis from readily available materials. The first of these steps is via propene carbonylation to produce isobutyric acid (IBA) and this is then followed by an oxidative dehydrogenation stage to produce methacrylic acid (MAA), which can then easily be esterified to yield MMA.\textsuperscript{2} It is for this second reaction (IBA to MAA) that iron-phosphate-based catalysts have been found to be very efficient.\textsuperscript{2} However it is not just for MAA production that iron phosphates have found an application since they have also been used for the production of methacrolein from isobutyraldehyde, methacrylonitrile from isobutyronitrile, pyruvic acid from lactic acid and glyoxylic acid from glycolic acid.\textsuperscript{3-9} A list of the reactants, products and the product uses are given in Table 3.1.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Product use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyric Acid</td>
<td>Methacrylic acid</td>
<td>Pre-cursor for methyl methacrylate</td>
</tr>
<tr>
<td>Isobutyraldehyde</td>
<td>Methacrolein</td>
<td>Pre-cursor for methyl methacrylate</td>
</tr>
<tr>
<td>Isobutynitrile</td>
<td>Methacrylonitrile</td>
<td>Pre-cursor for methyl methacrylate</td>
</tr>
<tr>
<td>Lactic Acid</td>
<td>Pyruvic Acid</td>
<td>Use in skin care products.</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>Glyoxylic acid</td>
<td>Use in skin care products.</td>
</tr>
</tbody>
</table>

One commonality of the successful application of iron phosphates to particular catalytic reactions is the presence of a carbon atom in the α-position to a tertiary electron-withdrawing group such as –CO\textsubscript{2}H, –CHO and –CN (equation (3.2)) in the reactant molecule.
R-CH₂-CHR'-X + 0.5 O₂ → R-CH=CHR'-X + H₂O  \hspace{1cm} (3.2)

Where:
R, R' = Alkyl groups
C = α-carbon
X = CO₂H, CHO or CN

In light of this observation the application of these catalysts has recently been extended to the production of similar organic structures such as pyruvaldehyde from hydroxyacetone and glyoxal from ethylene glycol.¹⁰,¹¹

Understandably it is thought that a unique meshing of catalyst and reactant properties is required to make these catalytic processes successful. For any catalyst used in partial oxidation reactions it is believed that the material must possess redox properties.¹² Furthermore, in the instance of iron phosphate based systems, it has been postulated that the catalyst must also possess an acidic site.¹³ Thus it has been concluded that the possession of two types of site with different properties, that is, both acidic and basic sites (the redox properties being closely related to the basic properties)¹³ are necessary for this ‘acid-formation-type partial oxidation’ to occur. Indeed these properties are inherent to many partial oxidation catalysts including both heteropolyacids and vanadium phosphates.¹³,¹⁴ However it is interesting to note that iron phosphate based catalysts appear to be poor catalysts, in comparison, for oxygen insertion type reactions, this being due to a lack of M=O species in the structure.¹³

3.2.1) Methods of preparation and catalytic performance

Since the first patent dealing with iron-phosphate-based catalysts was published in 1971¹⁵ several research articles and patents have appeared in the literature, most of which detail new preparative methods or formulations (including the addition of promoters such as cesium, silver and lead).¹⁶-¹⁸ In general, the starting iron phosphate material has been
prepared mainly by co-precipitation methods in which appropriate amounts of a ferric compound, such as ferric nitrate is dissolved in water, and to this phosphoric acid is added before the mixture is heated and dried.\textsuperscript{15} A variation on this theme is the ammonia gel method first used by Ai et al.\textsuperscript{19} Here the preparation involved the reaction of ferric nitrate solution with dilute ammonia to form an iron hydroxide gel, which was subsequently reacted with phosphoric acid before the mixture was heated and dried at \textit{ca} 100\textdegree C. On occasion colloidal silica was added to the starting material to ensure good mechanical strength. The final dried pastes obtained by these methods were then calcined at temperatures between 400\textdegree C and 600\textdegree C before being used for catalytic reaction. During these studies it was observed that there was a correlation between the calcination temperature and the final crystal structure. In general for a stoichiometrically mixed iron phosphate catalyst prepared by the above methods the crystallographically well-known quartz/berlinite like phase of FePO$_4$ was observed to crystallize at temperatures above 500\textdegree C.\textsuperscript{2,20} However, when calcination took place between 400\textdegree C and 500\textdegree C it was noted that along with an amorphous phase a tridymite-type phase formed.\textsuperscript{19,20} Both the tridymite-type and quartz type phases have been observed to crystallize even when 1<P/Fe<2, with the amount of the tridymite phase increasing with phosphorus content.\textsuperscript{2,16} Irrespective of which co-precipitation method is used all as prepared catalysts were shown to only contain Fe$^{3+}$ ions.

As mentioned previously most of the synthesis procedures reported are variations of the co-precipitation technique. However, iron phosphate catalysts have been successfully synthesised using other methods such as the 'Vivianite method' reported by Bonnet et al.\textsuperscript{21} which utilises the mineral Vivianite (Fe$_3$(PO$_4$)$_2$.8H$_2$O) and H$_3$P$_2$O$_7$ refluxed in acetone.

Many studies have reported that the method of preparation, calcination temperature and stoichiometry can affect catalytic performance.\textsuperscript{6,22} In particular, it has been noted that the most active catalysts have a Fe/P ratio of 1:1.2 in the starting material.\textsuperscript{23} But although stoichiometry has been shown to play an important role, in addition to the overall crystal structure of the catalyst, a general conclusion is that the charge-state of iron (including a Fe$^{3+}$/Fe$^{2+}$ redox couple) is critical to the catalytic mechanism (via a Mars and Van Krevelen type mechanism) and performance.\textsuperscript{13,24-26}
Most catalytic studies have focused upon iron phosphate catalysts with a P/Fe ratio of 1.2 since this has been shown to produce the most active form,\textsuperscript{19} with the best catalytic performance occurring at temperatures between 200 and 450°C depending upon the reactants used. For the production of MAA from IBA it has been possible to achieve conversions as high as 83% (within five hours) with a selectivity of 80% but with doping selectivity can reach as high as 85%.\textsuperscript{17} Comparable performance is observed for the production of pyruvic acid from lactic acid however the selectivity to methacrolein and methacrylonitrile never exceeds 65%.\textsuperscript{3,9} Crucial to the selective conversions achievable over the catalyst is the presence of large amounts of water (10-12 times the amount of IBA) in the feed (as well as controlled and well-defined ratios of both oxygen and IBA) since it is thought that it acts as a thermal diluent, contributes to the desorption of MAA and prevents coke formation.\textsuperscript{27,28} It has also been suggested that water plays a role in stabilizing the hydroxylated form of the active phase as will be discussed later.

3.2.2) Phase formation and transformation in iron phosphates

It has been observed that the as prepared catalysts undergo various phase transformations under the conditions of catalytic testing. A number of well characterised iron phosphate phases have been identified by XRD as being present after reaction including the tridymite and quartz FePO\textsubscript{4} types (which are also formed after activation), the mixed valence Fe\textsuperscript{2+}/Fe\textsuperscript{3+} species \(\alpha\) and \(\beta\)Fe\textsubscript{3}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} and the Fe\textsuperscript{2+} containing Fe\textsubscript{2}P\textsubscript{2}O\textsubscript{7}.\textsuperscript{2} Although the structure of the tridymite form of iron phosphate has never been solved, the presence of this phase was initially inferred from the similarity of the diffraction pattern to the tridymite form of SiO\textsubscript{2}.\textsuperscript{19} However the diffraction pattern for this phase also looks very similar to the recently recorded pattern for the AlPO\textsubscript{4} tridymite phase\textsuperscript{29-31} in which the proposed crystal structure contains alternating Al\textsuperscript{3+}O\textsubscript{4} and P\textsuperscript{5+}O\textsubscript{4} tetrahedra and therefore it seems most likely therefore that tridymite FePO\textsubscript{4}, like the quartz form, also contains alternating Fe\textsuperscript{3+}O\textsubscript{4} and P\textsuperscript{4+}O\textsubscript{4} tetrahedra.

It has been proposed that the most active phase for both MAA and pyruvic acid formation is the mixed valence phase designated \(\alpha\)Fe\textsubscript{3}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} which forms via a
transformation of the tridymite-type phase during catalytic reaction in catalysts with 1<P/Fe<2. This newly formed phase crystallizes in the C2/c space group and is thought to be very different in structure to the stoichiometrically identical and well known form of mixed valence iron phosphate designated βFe₃(P₂O₇)₂. Rietveld refinement of this αFe₃(P₂O₇)₂ phase suggested that the structure consisted of trimeric clusters of face sharing mixed valence FeO₆ octahedra separated by P₂O₇ groups (figure 3.1) and it has been proposed that this sort of arrangement is likely to be the ‘isolated active site’ for partial oxidation as it is able to facilitate limited electron mobility. Such a property was supported by theoretical calculations using extended Hückel molecular orbital theory. Conversely when the structure contained mixed valence Fe₃O₁₂ clusters with the central ion possessing trigonal prismatic coordination as in βFe₃(P₂O₇)₂, electron hopping between the clusters was shown to be energetically unfavourable and the structure was shown to have very poor partial oxidation properties.

Although it has been determined that the αFe₃(P₂O₇)₂ phase is the most active for oxidative dehydrogenation of IBA the ‘true’ active phase is believed to be a hydrated form of this formed as shown in equation (3.3).

\[ \alpha \text{Fe}_3(\text{P}_2\text{O}_7)_2 + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}_3(\text{PO}_3\text{OH})_4 \]  

(3.3)

However despite the discovery that the αFe₃(P₂O₇)₂ appears to be the most active phase a study by Muneyama et al. determined that there was very little difference in the catalytic performance between any of the phases listed in Table 3.2 which suggests that the actual catalytic action can be ascribable to a surface phenomena rather than a bulk one.
Figure 3.1 Arrangements of FeO₆ octahedra isolated by P₂O₇ groups in αFe₆(P₂O₇)₂ (left) and βFe₆(P₂O₇)₂ (right). The black and white dots represent Fe³⁺ and Fe²⁺ ions respectively and the arrow in the left cluster illustrates how electron exchange can take place in αFe₆(P₂O₇)₂ and not βFe₆(P₂O₇)₂ as determined by Hückel molecular orbital calculations. Diagram adapted from Vedrine et al.⁵⁶

Table 3.2. Catalytic performances of iron phosphate phases at 400°C from Muneyama et al.⁵²

<table>
<thead>
<tr>
<th>Phase observed in XRD</th>
<th>Conversion of IBA (%)</th>
<th>Selectivity to MAA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major</td>
<td>Minor</td>
<td></td>
</tr>
<tr>
<td>FePO₄ (Q)</td>
<td>FePO₄ (T)</td>
<td>86.2</td>
</tr>
<tr>
<td>βFe₆(P₂O₇)₂</td>
<td>FePO₄ (Q)</td>
<td>84.0</td>
</tr>
<tr>
<td>αFe₆(P₂O₇)₂</td>
<td></td>
<td>83.0</td>
</tr>
<tr>
<td>Fe₂₃P₂O₇</td>
<td>αFe₆(P₂O₇)₂</td>
<td>85.0</td>
</tr>
<tr>
<td>Fe₃P₂O₇</td>
<td></td>
<td>79.0</td>
</tr>
</tbody>
</table>

(T) = Tridymite, (Q) = Quartz

3.2.3) Aims and objectives

Although some structural studies have been undertaken on both the calcined materials and the catalysts after catalytic reaction¹³⁄²⁰ it appears that there has been little attempt to characterise the starting material and no attempt to determine the phase formation during the calcination process. The few efforts that have been made in order to characterise the starting material, have often revealed that an XRD amorphous phase is produced directly after synthesis. Since it is understood that the structure and physicochemical properties of the as prepared solids greatly influences the nature, texture or amount of the phases present in the catalyst during activation⁸ it was felt that a detailed in situ study of the catalysts prepared by two popular methods and a new, efficient and simpler method of preparing the catalyst precursor by employing hydrothermal methods, normally employed for the synthesis of microporous materials,³⁷ would yield important
information with regard to understanding the crystallisation of particular phases under certain conditions. The decision to employ this new synthetic approach came in the light of the reported success of employing such techniques for the synthesis of a number of phase pure mixed oxide and sulfide materials.\textsuperscript{58,43} Therefore it was anticipated that by using such a procedure the problems with the formation of catalytically inactive phases associated with the conventional preparation procedures might be avoided.\textsuperscript{2}

### 3.3) Experimental

#### 3.3.1) Preparation of iron phosphate catalysts.

Although there have been many attempts to synthesise iron phosphate catalysts using various co-precipitation methods and different iron and phosphorus sources, for this study we concentrated on the methods that utilized ferric nitrate and phosphoric acid only. The catalysts were prepared by three different methods details of which are given below. Two of the methods have been used previously to prepare the catalysts and hereon in these will be designated as the precipitation and ammonia gel catalysts. The third is a new efficient and simpler method of preparing the catalyst precursor by employing hydrothermal methods.

#### 3.3.1.1) Precipitation method

We followed procedures similar to the one described in the literature.\textsuperscript{15} In a typical synthesis, 6.1 g of iron nitrate nonahydrate (Aldrich) was dissolved in 100 ml of water (Fluka). 2.08 g of 85\% orthophosphoric acid (Aldrich) (giving a P/Fe ratio of 1.2/1) was slowly added to this solution and the mixture was stirred for four hours at ca 100°C. The excess water was evaporated and the final paste (white in colour) was dried in an oven for six hours at 100°C.
3.3.1.2) Ammonia-gel method

Once again, we followed the procedures given in the literature.\textsuperscript{20} In a typical synthesis, 6.1 g of iron nitrate nonahydrate (Aldrich) was dissolved in 100 ml of water (Fluka) and to this 1.5 M ammonium hydroxide solution (Aldrich) was added drop wise to precipitate an iron hydroxide gel. The gel was filtered and washed before being dissolved in 2.08 g of 85% orthophosphoric acid (Aldrich) (giving a P/Fe ratio of 1.2/1). This mixture was then stirred and heated for four hours at ca 100°C before the excess water was removed. The resultant catalyst precursor paste (between pale brown to white in colour) was dried for six hours at 100°C. Additional experiments were also undertaken where the stirring/heating time was reduced from four to two hours. After only two hours synthesis time the dried catalyst was light brown/orange in colour.

3.3.1.3) Hydrothermal method

In this new procedure, 6.1 g of iron nitrate nonahydrate (Aldrich) was dissolved in 100 ml of water (Fluka) and to this 1.5 M ammonium hydroxide solution (Aldrich) was added drop wise to precipitate an iron hydroxide gel. The resulting gel was again dissolved in 85% orthophosphoric acid (Aldrich) (2.08 g giving a P/Fe ratio of 1.2/1) before the mixture was transferred to a Teflon liner. The liner was filled to 30% of its capacity with the mixture before being sealed in an autoclave and heated at 175°C for four hours. The autoclave was cooled and the contents (a white powder) were washed and dried at 100°C for six hours. Additional experiments were also undertaken where the synthesis time was extended from four to twenty hours. After a synthesis time of twenty hours the dried catalyst was pale pink in colour.

3.3.1.4) Metastrengite preparation

For the synthesis of this reference compound a recipe previously reported by Trobajo et al. was used.\textsuperscript{44} 5.41 g of FeCl\textsubscript{3}.6H\textsubscript{2}O (Aldrich) was dissolved in water (Fluka) and to this was added 2.31 g of orthophosphoric acid (Aldrich) to give a P/Fe ratio equal
to unity. The mixture was stirred before being transferred to a Teflon liner. The liner was filled to 30% of its capacity with the mixture before being sealed in an autoclave and heated at 175°C for three days. The autoclave was cooled and the contents (a white powder) were washed and dried at 100°C for six hours.

3.3.2) Characterisation

XRD patterns of all the as-synthesised materials (dried at 100°C) were recorded using both a Siemens D500 and FR571 Enraf Nonius diffractometer (both of Bragg-Brentano geometry) utilizing Cu-Kα1 radiation. TGA and DSC measurements were carried out by the ULIRS thermal methods service using a Shimadzu TGA/DSC 50 with the samples heated in aluminium pans in flowing air at a rate of 10°C/minute over a temperature range of 25°C - 600°C. The BET surface area measurements were carried out on both the as prepared and on the catalysts calcined at 400°C and 600°C employing a Micromeritics Gemini III. All samples were subjected to degassing at 100°C in N2 prior to surface area measurement using N2 at -196°C as the adsorbate. SEM pictures were taken using a Hıtachi S-570 SEM. For this work an accelerating voltage of 20 kV was used. Online mass spectrometry experiments were carried out using a VG quadrupole mass spectrometer used in electron impact (EI) mode (ionization energy 70 eV) to monitor the gaseous decomposition products that evolved during the calcination of the as prepared catalysts at a rate of 5°C/minute to 600°C in flowing air.

In situ XRD/QuEXAFS measurements were carried out at station 9.3 of Daresbury Synchrotron radiation source, which operates at 2 GeV with a typical current of 150 to 250 mA. A schematic of the experimental arrangement for this in situ study can be seen in figure 2.7 in chapter 2 with the details of this setup having been published elsewhere. The station was equipped with a Si(111) double crystal monochromator, and ion chambers for measuring incident and transmitted beam intensities for recording X-ray absorption spectra. For diffraction measurements, a position sensitive INEL detector was used. In a typical experiment, about 40 mg of the precursor iron phosphate material was pressed in to a disc of 13 mm diameter. This sample was placed into an in situ cell that permits the measurement of combined XAS and XRD data. The samples
were heated at 5°C/minute from room temperature to 400°C and held at this temperature for 30 minutes before heating further to 600°C. Fe K-edge XAS and XRD data were collected sequentially, during this activation process. The time taken for the Fe K-edge XAS pattern was 380 seconds and 180 seconds for XRD data resulting in a total cycle time of 10 minutes, which included 40 seconds dead-time to move the monochromator back to the starting point. XRD data were collected at a wavelength of 1.775 Å, well below the Fe K-edge absorption to avoid fluorescence effects. The INEL detector was calibrated using a NBS silicon standard and a 10 μm Fe foil was used to calibrate the monochromator position.

Fe K-edge XAS measurements were also carried out on stations 7.1 and 8.1 at the SRS. Both stations were equipped with a Si(111) double crystal monochromator, and ion chambers for measuring incident and transmitted beam intensities for recording X-ray absorption spectra. Again in a typical experiment, about 40 mg of iron phosphate sample was pressed in to a disc of 13 mm diameter.

Detailed Fe K-edge XANES measurements on several reference compounds and on the iron phosphate precursors were also recorded on station 8.1. Data were recorded in transmission mode with a resolution of 0.214 keV between an energy range of 7.10 keV and 7.15 keV.

Phosphorus K-edge data were collected on station 3.4 of the Daresbury Synchrotron radiation source. The station was equipped with an InSb double crystal monochromator and an ion chamber for measuring incident radiation and a Canberra fluorescence detector. Typically a few milligrams of sample was mixed with graphite and mounted onto a sample mount, which, was placed into the experimental chamber, before measurements were carried out under vacuum.

XAS data were processed using the suite of programs available at Daresbury laboratory, namely EXCALIB (for converting the raw data to energy vs. absorption coefficient), EXBROOK (to obtain normalised XANES part of the spectra and for background subtraction to extract EXAFS) and EXCURV98 (to perform detailed refinement using multiple scattering procedures to extract more detailed local structural details of the catalysts).
In situ EDXRD measurements were carried out on station 16.4 of Daresbury Synchrotron radiation source. A schematic of the experimental arrangement for these in situ hydrothermal studies can be seen in figure 2.10 in chapter 2 with the details of this setup having been published elsewhere.\textsuperscript{48-50} In a typical experiment, an autoclave containing the appropriate gel mixture was introduced into an oven, pre-heated to a specific temperature. EDXRD measurements were carried out at a temperature of 175°C. Data collection was started two minutes after the introduction of the autoclave and a data collection time of one minute per scan was employed for this work. The middle detector, used to record data with a range of d-spacing between 6-2 Å, was placed at a fixed 2θ angle of 4.619 degrees. The other reflections that appeared in the top detector at lower d-spacings are not shown here due to their lack of intensity. Integrated areas of all of the reflections detected in the EDXRD spectra were determined using a Gaussian curve fitting routine using the XFIT programme available from CCP14.
3.4) Results and discussion

3.4.1) Ex-situ studies of as prepared catalysts

3.4.1.1) XRD measurements

In figure 3.2 is shown the X-ray diffraction patterns of the as prepared catalysts synthesised by the three methods and the reference compound metastaengite. The XRD patterns of the as synthesized catalysts are very similar to the one reported in the literature for a FePO$_4$.2H$_2$O type phase.$^{51,52}$ Although some of the reflections can be indexed to the iron phosphate mineral, metastaengite, it appears that these as-synthesised solids are not the same as this mineral form. Furthermore, the extra reflections seen in the ammonia gel catalyst suggest that an additional phase co-exists along with the FePO$_4$.2H$_2$O type phase.

![XRD patterns](image)

**Figure 3.2** XRD patterns of (a) metastaengite (complete with indexing lines),$^{51}$ (b) iron phosphate catalyst prepared by hydrothermal method, (c) iron phosphate catalyst prepared by precipitation method and (d) iron phosphate catalyst prepared by the ammonia gel method complete with indexing lines for NH$_4$Fe$_6$(PO$_4$)(OH)$_{10}$(O$_{0.66}$O$_{0.33}$)$_3$(PO$_4$(OH))$_2$. 
This second phase could well be \( \text{NH}_4\text{Fe}_3(\text{PO}_3(\text{OH})_{0.666}\text{O}_{0.333})_3(\text{PO}_2(\text{OH})_2)_3.6\text{H}_2\text{O} \) (ICSD database entry 21266)\(^{54}\) as the indexing lines included in figure 3.2 appear to match closely with the extra reflections that do not appear to be due to the FePO₄·2H₂O type phase.

3.4.1.2) SEM images

The SEM images (magnification x2000) of the as prepared catalysts are shown in figure 3.3. The main difference between the three materials seems to be the particle uniformity in that the hydrothermally treated material appears to consist of small but highly uniform particles whereas the materials produced by the other two methods contain particles of varying size.

Figure 3.3 SEM images of the as prepared catalysts (magnification x 2000): (a) ammonia gel method; (b) prepared by precipitation method and (c) hydrothermal method.
This variation in particle size for the catalysts prepared by conventional methods is not clear although it is most probably due to the presence of additional phase(s) in these materials along with the FePO$_4$·2H$_2$O phase. EDAX analysis confirmed the presence of both iron and phosphorus in all three materials in the ratio of 1:1.2.

3.4.1.3) Fe K-edge XANES

In figure 3.4 we show a comparison plot, concentrating on the pre-edge peak (see inset in figure 3.4), of the Fe K-edge XANES for each of the as-prepared materials and for various model iron phosphate compounds (FeSO$_4$·6H$_2$O, metastrengite (FePO$_4$·2H$_2$O) and FePO$_4$) known to contain octahedral Fe$^{2+}$, octahedral Fe$^{3+}$ and tetrahedral Fe$^{3+}$ respectively.$^{53,55,56}$ Due to the rarity of tetrahedral Fe$^{2+}$ containing species it was not possible to obtain XANES data for this sort of iron environment.

![Figure 3.4](image)

**Figure 3.4** Fe K-edge XANES of the as-prepared iron phosphate materials, employing various synthesis procedures. Also included, for comparison, are the reference compounds FeSO$_4$·6H$_2$O containing octahedral Fe (II), FePO$_4$·2H$_2$O (metastrengite structure) possessing octahedral Fe(III) ions and the tetrahedral Fe(III) ion containing quartz form of FePO$_4$. Feature “A” highlights the absorption edge position and “B” the white line intensity. The inset shows the pre-edge part of the spectra for clarity.
It is well known that there are particular features in the XANES, which reveal information on both the oxidation state and co-ordination of the absorbing species.\textsuperscript{57} These include the presence of a pre-edge peak and both the shape and position of the edge. In figure 3.4 it is clear that the position of the edge for the octahedral Fe(II) containing FeSO\textsubscript{4}.6H\textsubscript{2}O reference compound\textsuperscript{65} is at a lower energy (ca 5 eV lower) as compared to the Fe(III) containing metastrengite and FePO\textsubscript{4} structures. This shift to a higher edge energy is a result of the increased energy required to remove a 1s electron from a 3+ ion as compared to a 2+ species due to an increase in nuclear attraction.\textsuperscript{58} It is also clear from figure 3.4 that the edge position of all of the as prepared catalysts were very similar to metastrengite (FePO\textsubscript{4}.2H\textsubscript{2}O) which suggests that the as-prepared catalysts contain predominately Fe\textsuperscript{3+} ions. It is also well known that the pre-edge intensity is sensitive to the local coordination geometry with a non centro-symmetric tetrahedral environment showing a higher intensity than an octahedral or a distorted geometry.\textsuperscript{59-63} Although this pre-edge intensity, which is due to a 1s-3d transition is dipole forbidden, it has been interpreted as due to the mixing of p orbitals of both from ligand and the 4p state of the cation, allowing this transition to take place.\textsuperscript{64,65} It was also shown that the intensity of the transition not only depended on the coordination geometry but also with metal-oxygen distances.\textsuperscript{66,67} Correspondingly the white line intensity labeled feature B (due to a 1s-4p transition) is lower in intensity for a system with a non centro-symmetric tetrahedral environment. There are two reasons why this occurs. The first is that whilst the transition is dipole allowed the mixing of d and p-orbitals (which results in enhanced pre-edge peak intensity) results in a partly forbidden transition. Furthermore since none of the local atoms are aligned in a collinear way there will be no multiple scattering effects which normally give rise to a higher white line intensity for octahedral compounds as opposed to tetrahedral systems. Thus a combination of these effects, which are due to the change in coordination geometry, can give rise to a higher pre-edge intensity and a lower white line intensity for a tetrahedrally coordinated system as compared to an octahedral one. It is clear from figure 3.4 that the spectra of all of the as prepared catalysts were very similar to metastrengite (FePO\textsubscript{4}.2H\textsubscript{2}O), which suggests that the as-prepared catalysts contain predominantly octahedral Fe\textsuperscript{3+} ions.
3.4.1.4) TGA and DSC

Although it appeared that all of the as-prepared catalysts have a similar octahedral environment to that of metastrengite (FePO₄·2H₂O), it is difficult to determine whether water molecules contribute in the formation of this octahedral geometry in all of the as-prepared catalysts. In order to determine the nature of various loosely bound species present in the catalyst, first we carried out a thermogravimetric analysis (TGA) and differential scanning calorimetry study on metastrengite and all three of the catalysts. Figures 3.5 and 3.6 (below) show the TGA and DSC data recorded for all three of the as-prepared catalysts and for the reference material metastrengite.

![Figure 3.5](image-url)  
*Figure 3.5 Thermogravimetric measurements of metastrengite and the iron phosphate catalysts prepared by the three different methods.*
Figure 3.6 Differential scanning calorimetry measurements of metastrengite and the iron phosphate catalysts prepared by the three different methods.

For all four samples a major weight loss and a large exotherm was observed between 100 and 200°C. This weight loss corresponds to approximately 20 percent of the starting mass and can be explained as the loss of two water molecules from a FePO$_4$.2H$_2$O type species. For all three of the catalysts independent online mass spectrometry experiments confirmed the loss of water on heating up to ca 200°C. Beyond this temperature only the ammonia gel sample continued to loose weight until the temperature reached ca 400°C. This continued weight loss also appears associated with a smaller second exotherm between 300-400°C. This behaviour may be due to the NH$_4$Fe$_3$(PO$_3$(OH)$_{0.666}$O$_{0.333}$)$_3$(PO$_2$(OH)$_2$)$_3$.6H$_2$O phase undergoing a phase change as this exotherm is not seen for the other catalysts.
3.4.1.5) Mass spectrometry

In order to determine the nature of the volatilites associated with this second exotherm in the ammonia gel catalyst, an online mass spectrometry experiment was carried out. In figure 3.7 is shown the mass spectrometer response for m/z 17 and 18. The major peak at ca 130°C for both masses is associated with the loss of water; the responses are generated from OH$_2^+$ and OH$^+$ ions. However a second peak which is present in the m/z 17 trace (ca 170°C) is absent in the m/z 18 plot suggesting that this is not due to further water loss and is most likely to be a result of ammonia release (NH$_3^+$ ion). It is therefore likely that the larger overall mass loss associated with this catalyst is a result of both ammonia and water loss from the second phase. The apparent difference between the temperatures at which these losses took place may be explained with reference to the different temperature rates employed for the TGA/DSC (10°C/min.) and the mass spectrometry (5°C/min.) experiments as the higher ramp rate used for the TGA/DSC may not allow the sample to reach thermal equilibrium. The loss of ammonia from this catalyst has previously been observed in a previous investigation Ai et al. 19

For the precipitation catalyst the percentage weight loss is less than that observed for the metastrengite phase. This is also thought to be due to the presence of additional phase(s) present in this material which XRD/TGA/DSC measurements suggest are of a different nature to the ammonia gel additional phases.
Figure 3.7 Mass spectrometry traces for m/z 18 (top) and m/z 17 (bottom) during calcination in air of the iron phosphate catalysts prepared by the ammonia gel method.
3.4.1.6) EXAFS analysis

Having established the octahedral nature of the iron species in the as prepared material from the XANES and the presence of two water molecules by TGA, we analysed the EXAFS data of the as-prepared catalysts and metastrengite using both the single scattering curved wave approximation\textsuperscript{68} and the full cluster multiple scattering (MS) procedure using Rehr-Alber small atom theory.\textsuperscript{69,70} Taking the reported structure for metastrengite a refinement was first performed on this structure. In this MS method all the oxygen and phosphorous atoms were taken as individual shells resulting in a set of neighbours containing six oxygen and four phosphorous atoms. Among the six oxygens attached to the iron center, four were treated as bridging oxygens linking iron and phosphorous atoms and the other two as being part of two water molecules. Because of the complexity of the model, it is necessary to treat them in C\textsubscript{1} symmetry for MS calculations. In order to avoid the refinement of too many independent parameters a set of constraints and restraints were imposed, taking chemical knowledge into account. All of the Fe-O distances and Debye-Waller factors were constrained to be the same value, since a first shell analysis and crystal structure study showed that they are likely to be similar. However, in the case of Fe-P distances, it should not be taken as the same values, since the bond-angles are likely to be different and hence they may have different MS effects. The coordination numbers of the P-atoms were fixed to be one as this multiple scattering approach requires integer values for the shell occupancies and it is not possible to determine these for each of the derived Fe-O-P arrangements. A coordination number of one was also employed for each of the oxygen atoms although this data was determined from a first shell analysis. These particular restraints avoid any correlation effects between the coordination numbers and Debye-Waller factors. Thus the refinement of the Fe-P shells and the Fe-O-P bond angles were carried out independently with the Fe-P Debye-Waller factor of all the shells constrained to be the same.

To determine whether the multiple scattering procedure produced a better description of the local coordination sites a goodness of fit index (R) (equation (3.4)) was used. This index is the difference between the calculated and experimental EXAFS at each point.
\[ R (\%) = \sum_{i}^{N} \frac{1}{\sigma_i} |\chi_i^{\exp}(k) - \chi_i^{\text{th}}(k)| \times 100 \]  

(3.4)

Since the coordination number is fixed a Debye-Waller factor greater than 0.025\,\text{Å}^2 for 2\sigma^2 is thought to be indicative of the absence of that particular shell whereas a value of < 0.001\,\text{Å}^2 for 2\sigma^2 is thought to be indicative of a higher coordination number or lower bond angle.

Tables 3.3 and 3.4 (overleaf) show the refined EXAFS parameters for metasstrengite using both the single scattering and multiple scattering refinement approaches. Also shown is the best fit between the experimental Fe K-edge EXAFS data and the calculated EXAFS in figure 3.8. It is clear (from both a comparison of both the derived R-factors and the reported crystallographic data) that the better fit is achieved using the multiple scattering approach despite all of the Fe-O-P angles being less than 150°.
Table 3.3 (top) and 3.4 (bottom). Structural parameters obtained from the EXAFS data for metastrenite using multiple scattering (Table 3.3) and single scattering approaches (Table 3.4).

*O\textsubscript{w} represents the two oxygen neighbours associated with water molecules

*O\textsubscript{b} represents the oxygen neighbour bridging Fe(III) and P(V) centres.

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<tr>
<th>K-Edge</th>
<th>Atom pair</th>
<th>N</th>
<th>R (Å)</th>
<th>2σ(^2) (Å(^2))</th>
<th>Fe-O-P angle (^{\circ})</th>
<th>R Factor</th>
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<th>R (Å)</th>
<th>2σ(^2) (Å(^2))</th>
<th>Fe-O-P angle (^{\circ})</th>
<th>R Factor</th>
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Figure 3.8 Best fit between experimental (a) Fe K-edge EXAFS data and the calculated EXAFS and (b) the associated FT's for metastrengite derived using the MS analysis procedure. In (d) and (e) is shown the best fit between Fe K-edge experimental and calculated EXAFS and their associated FT's for metastrengite using the single scattering approximation. The solid line and the dashed curve represent the experimental and calculated data, respectively.

However it has been shown previously that this approach is necessary in order to achieve the most appropriate site description. Similar such MS procedures have been used successfully in determining the structure of transition metal ions in framework substituted microporous solids. In order to determine the local coordination of the iron in the FePO$_4$.2H$_2$O starting material prepared by hydrothermal methods the final
model derived from the refinement of the metastrengite structure was used as a starting model. Considering that the XANES for both the as prepared iron phosphate catalyst and metastrengite were very similar it was postulated that the local environments should also be very similar therefore it was decided also to use the multiple scattering approach again to model the local structure.

Table 3.5. Structural parameters obtained from the EXAFS data of the as-prepared iron phosphate material, synthesised using hydrothermal methods.

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<th>K-Edge</th>
<th>Atom pair</th>
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<th>R (Å)</th>
<th>2σ² (Å²)</th>
<th>Fe-O-P angle (°)</th>
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<td>0.013</td>
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*O₆ represents the oxygen neighbour associated with water molecules
*O₆ represents the oxygen neighbour bridging Fe(III) and P(V) centres

The refinement was carried out in the same way as used for the metastrengite although this time the O-P distances were restrained to be ca 1.532Å, obtained from the analysis of the P K-edge data (see Table 3.5 and figure 3.9(a) and 3.9(b)); P K-edge data were analysed using a simple single scattering approximation due to a limited data range. The final refinement yielded the local structure of the Fe³⁺ centre for the as prepared catalyst and the resulting structural parameters are given in Table 3.5.
Figure 3.9  Best fit between experimental (a) P K-edge EXAFS data and the calculated EXAFS and (b) associated FT of the as-prepared iron phosphate catalyst prepared by hydrothermal method. In (c) and (d) is shown the best fit between Fe K-edge experimental and calculated EXAFS and the associated FT. The solid line and the dashed curve represent the experimental and calculated data, respectively. The local structural model derived by employing the MS analysis procedure is given in (e).
The best fit between experimental Fe K-edge EXAFS data and the calculated EXAFS using parameters in Table 3.5 with the associated Fourier transforms (FT’s) are shown in figures 3.9 (c) and (d). A model of the local structure derived from the analysis of the P K-edge and Fe K-edge EXAFS data is shown in figure 3.9(e). The local structure of this FePO₄·2H₂O species is determined to consist of tetrahedrally coordinated P⁵⁺ ions which are connected via four bridging oxygen atoms to octahedrally coordinated Fe³⁺ ions. The octahedra of the Fe³⁺ ions then consist of the four bridging oxygens and two water molecules resulting in a slightly distorted coordination similar to the one present in the metastrengite structure. Both the Fe K-edge EXAFS and the associated FT’s for the iron phosphate catalysts prepared by other methods were found to be very similar to that of the one synthesised by hydrothermal procedure and the local structural arrangements were determined to be closely similar to that shown in figure 3.9(e).

3.4.2) In situ studies

In order to follow the structural modifications that occurred during catalyst calcination to produce an active catalyst we carried out in situ combined XRD/QuEXAFS in order for us to be able to follow changes in both long and short range ordering. In figure 10 is shown the stacked plot of the XRD data recorded, using the combined XRD/QuEXAFS measurement procedure, during the activation process of the as-prepared iron phosphate catalyst (prepared by hydrothermal methods) between room temperature and 600°C.

It was observed that the XRD pattern underwent considerable changes during the activation process (see figure 3.10(a)). In figure 3.10(b) we show the variation in the intensity of non-overlapping intense reflections appearing at 2θ angles of 36.39, 23.11, 29.43, which represent the as-prepared, tridymite and quartz phases, respectively, of the iron phosphate catalyst. It is clear from figure 3.10(a) and 3.10(b) that the reflections associated with the as-prepared material appeared to remain intact until the temperature reached ca 150°C and above which new reflections started to appear at the expense of
those present in the starting material. The loss of these reflections belonging to the starting material and the appearance of new reflections were almost instantaneous. These new reflections have been identified as due to the formation of a tridymite type phase.

Figure 3.10 (a) Stacked XRD patterns of the hydrothermally prepared iron phosphate material, recorded during calcination in air from room temperature to 600°C. The data were collected employing the combined XRD/QuEXAFS method and the patterns were collected below the Fe K-edge, at λ=1.775Å. Regions A, B and C correspond to the as-prepared, tridymite and quartz phases, respectively. (b) Variation in the intensities of the reflections appear at 2θ values of 36.39, 23.11 and 29.43, that represent as-prepared, tridymite and quartz phases of iron phosphate material. (c) Variation in the FWHM of the reflection at 24.3 2θ belonging to the tridymite phase, as a function of temperature.
Although there is no crystallographic information available for the tridymite phase of FePO₄, this phase was identified based on an AlPO₄ analogue. The only changes observed in the XRD pattern recorded between ca 150°C and ca 500°C is the increase in intensity and decrease in full-width at half maximum (FWHM) of the reflections corresponding to the tridymite phase. The FWHM extracted from the reflection, which appeared at a 2θ value of 24.3, is plotted against temperature in figure 3.10(c). This change in FWHM clearly suggests the growth of bigger particles upon calcination at elevated temperatures; we estimate that the average particle size grows from ca 25 nm to ca 35 nm (using the well-known Scherrer equation (3.5)) before the material undergoes a second transformation.

\[ t = \frac{0.9\lambda}{B\cos\theta} \]  

(3.5)

Where:

- \( t \) = crystallite size
- \( \lambda \) = x-ray wavelength
- \( B \) = Bragg peak width
- \( \theta \) = diffraction angle

On reaching ca 500°C the well-known phase of FePO₄ (quartz type) appears and the transformation from tridymite to quartz phase was complete at 600°C (see figure 3.10(b)). No other reflections were detected other than those that belonged to the stoichiometric phases despite the inclusion of excess phosphorus during the initial stages of the synthesis.

Close inspection of the stacked XAS data in figure 3.11 (a) clearly indicated that a change in both the XANES and EXAFS data took place when the calcination temperature exceeded ca 150°C. In particular, in the XANES region an abrupt increase in the intensity of the pre-edge peak, a decrease in the white line intensity and a shift in the frequency of the EXAFS oscillations can be seen. Analysis of the EXAFS data obtained from the dynamic measurement, were performed taking a simple average local structural
arrangement consisting of oxygen atoms around the iron as the first neighbours to determine the change in local structural parameters with temperature.

Figure 3.11 (a) Stacked plot of the Fe K-edge XAS data recorded during calcination of the hydrothermally prepared iron phosphate, from room temperature to 600°C. Note that this data set is collected sequentially with the XRD data shown in figure 10(a). An expanded region is also given to show clearly the change in the intensity of the pre-edge peak. In (b) we show the variation of pre-edge intensity (PI), coordination number (N), Fe-O distance (R) and 2σ (Debye-Waller factor) with the calcination temperature. The coordination number, Fe-O distance and 2σ were extracted from the analysis of the EXAFS data using single scattering approximation. Note that more than one point appears at 400°C, which is because the temperature was maintained at 400°C for 30 minutes before continuing the heating process to 600°C.
In figure 3.11 (b) has been plotted the variation in coordination number, average Fe-O distance, Debye-Waller factor (which consists of contributions from static and thermal disorder) and intensity of the pre-edge peak with temperature, for the hydrothermally prepared catalyst.

The most striking feature seen in the result is the dramatic change that occurs at ca 150°C. At this point the coordination number, average Fe-O distance and Debye-Waller factor decreased, which coincided with an increase in the XANES pre-edge peak intensity. These changes reflect the formation of a four coordinated Fe$^{3+}$ site. In particular, a decrease in coordination number from ca 6 to 4, a change in Fe-O distance from 1.98 Å to 1.86 Å and an increase in pre-edge intensity is consistent with the XRD observation that a tetrahedral Fe$^{3+}$ containing tridymite phase is formed above 150°C and therefore like the AlPO$_4$ analogue (known to contain tetrahedrally coordinated Al$^{3+}$ centers) so the FePO$_4$ tridymite phase was seen to contain tetrahedrally coordinated Fe$^{3+}$ centers. On heating above 150°C only the Debye-Waller factor was seen to increase as a function of temperature; the coordination number, Fe-O distance and the pre-edge intensity remained the same value (within the experimental error). This indicated that the local structure remained intact during the process of calcination, since both the tridymite and quartz type phase of FePO$_4$ consist of tetrahedrally coordinated iron centers. The changes in the Debye-Waller factors, which consisted of both static and dynamic disorder, can be rationalised as follows. In the initial stages, the octahedral coordination has a large static disorder due to the presence of loosely bound water molecules in addition to the bridging oxygen atoms. Upon removal of the water molecules, a decrease in the Fe-O distances occurred and the change to tetrahedral coordination resulted in an abrupt decrease in the Debye-Waller factor, despite the data being collected at a higher temperature as compared to the as-prepared sample. Subsequent increase in the Debye-Waller factor can be explained as being simply due to an increase in the thermal disorder of the Fe-O pairs present in the tetrahedral arrangement.

In order to show the effect of dynamic disorder, we carried out a combined XRD/QuEXAFS measurement of FePO$_4$ quartz phase at various temperatures using an identical procedure to that of the typical calcination process. As can be seen in figure
3.12, the Debye-Waller factor indeed coincided with that of the data recorded above *ca* 150°C.

**Figure 3.12** Variation in $2\sigma^2$ for FePO$_4$ quartz form and hydrothermally prepared FePO$_4$·2H$_2$O (after the transformation to the tridymite form at *ca* 150°C) with temperature to demonstrate that a systematic increase is seen with temperature. Note that meaningful data can only obtained up to three decimal places and hence the scatter in the plot.

A more complex picture emerged for the catalysts prepared using the precipitation and ammonia gel methods. Although a plot of the relative intensity of the major reflections (similar to the one shown in figure 3.10(b)) present in the stacked XRD patterns (figure 3.13 (a) and (c)) revealed that the transformation of the starting material to the FePO$_4$ tridymite and quartz phases occurred between 150°C and 600°C (see figure 3.13 (a-d)) similar to that which had been observed for the hydrothermally prepared sample (see figure 3.10(b)), the Fe K-edge XAS results were found to be different. In figure 3.14 we have plotted the variation of the structural parameters with temperature, derived from the analysis of the XANES and EXAFS for the catalysts prepared by precipitation and ammonia gel methods. Similar to the observation made for the material prepared by hydrothermal procedure (see figure 3.11), both these materials underwent a considerable change on reaching *ca* 150°C.
Figure 3.13 Stacked XRD plots (also collected at \( \lambda = 1.775 \text{Å} \)) and intensity plots for the variation in the intensities of the reflections that appear at 2\(\theta\) values of 36.39, 23.11 and 29.43, that represent as-prepared, tridymite and quartz phases of iron phosphate material prepared by (a) and (b) precipitation method and (c) and (d) the ammonia gel method. The discontinuity and multiple points observed in the data recorded at 400°C is likely to be due to shrinkage in the sample resulting in the change in the intensity when the temperature was held at 400°C for 30 minutes.

However, beyond 150°C both catalysts continued to experience a gradual decrease in the average Fe-O bond length. This slow decrease in Fe-O distance was also seen to coincide with a gradual increase in the XANES pre-edge peak intensity. Furthermore for the precipitation catalyst the Debye-Waller factor tended to remain fairly constant with
increasing temperature and showed no obvious increase as a direct result of increase in dynamic disorder (see figure 3.14 (a)).

Figure 3.14 Variation of pre-edge intensity (PI), coordination number (N), Fe-O distance (R) and $2\sigma^2$ (Debye-Waller factor) with the calcination temperature, for iron phosphate materials prepared by (a) precipitation method and (b) ammonia gel method. The coordination number, Fe-O distance and $2\sigma^2$ were extracted from the analysis of the EXAFS data using single scattering approximation.

For the ammonia gel catalyst a slightly different behaviour in the Debye-Waller factor was observed (figure 3.14 (b)). Beyond the abrupt fall at ca 150°C the Debye-Waller factor was seen to continue to decrease but on exceeding ca 450°C it was seen to stabilize and remain relatively constant until calcination finished at 600°C. The final Fe-O average bond length, coordination number, pre-edge peak intensity and Debye-Waller factor values for all three catalyst types at 600°C are identical to the values found for quartz at the same temperature. This deviation in the behaviour of the these two conventionally prepared materials from that seen for the hydrothermal catalyst is probably due to the presence of small amounts of the additional phase(s) in both the starting materials.
3.4.2.1) Calcination of metastrengite

An in situ combined XRD/QuEXAFS experiment was also conducted on metastrengite in order to follow and compare the structural modifications that took place during calcination to 600°C. In figure 3.15 (a) and (b) is shown the stacked plot of the combined XRD and QuEXAFS data recorded between room temperature and 600°C. It appeared that both the XRD pattern and the EXAFS only changed once during the heating process. This occurred when the temperature reached ca 150°C but up until this point the XRD reflections and EXAFS associated with the starting metastrengite phase had remained unchanged. The transformation of both the XRD and EXAFS was to a new and unidentified phase(s), which was still present when the calcination study had finished. In a further ex-situ study it was discovered that eventually the quartz form of FePO₄ crystallised from metastrengite after prolonged calcination for several hours at 600°C but even then other phases were still present in small amounts.

On a closer inspection of the stacked XAS data in figure 3.15 (b) it became apparent that both the XANES and EXAFS had changed when the calcination temperature exceeded ca 150°C. In particular, an abrupt increase in the intensity of the pre-edge peak, a decrease in the white line intensity and a shift in the frequency of the EXAFS oscillations can be seen. Analysis of this EXAFS data obtained from the dynamic measurements, was performed assuming a single oxygen shell as the first neighbours around the iron atom.
Figure 3.15 Stacked XRD patterns (a) for metastrengite recorded during calcination in air from room temperature to 600°C. The data were collected employing the combined XRD/QuEXAFS method and the patterns were collected below the Fe K-edge, at λ=1.775Å. In (b) the stacked plot of the Fe K-edge XAS collected sequentially with the XRD data.

In figure 3.16 the variation in coordination number, average Fe-O distance, Debye-Waller factor and intensity of the pre-edge peak with temperature, were plotted. It can be seen that dramatic changes occurred at ca 150°C and at this point the coordination number, average Fe-O distance and Debye-Waller factor decreased. These
transformations coincided with the changes observed in the XRD and the XANES pre-edge peak intensity. In particular, a decrease in coordination number from ca 6 to 4, a change in Fe-O distance from 1.98 Å to 1.87 Å and an increase in pre-edge intensity suggests that the unidentified phase(s) present as observed by XRD contain four coordinate Fe$^{3+}$ species. These results are consistent with a recent publication by Song et al. which proposed that this new XRD pattern was due to a previously unidentified monoclinic form of FePO$_4$ containing tetrahedral Fe$^{3+}$ centres (space group P2$_1$/n with lattice parameters a = 5.4802 Å, b = 7.4802 Å, c = 8.0537 Å and β = 95.708°) which formed after dehydration to remove two water molecules attached to the Fe$^{3+}$ ions in metastroenite.$^{75}$ On heating beyond 150°C only the Debye-Waller factor was seen to increase as a function of temperature; the coordination number, Fe-O distance, pre-edge peak intensity and XRD pattern remained intact (within the experimental error) suggesting that no further phase transformations took place.

![Graph](Figure 3.16 Variation of pre-edge intensity (PI), coordination number (N), Fe-O distance (R) and 2σ$^2$ (Debye-Waller factor) with the calcination temperature, for metastroenite. The coordination number, Fe-O distance and 2σ$^2$ were extracted from the analysis of the EXAFS data using a single scattering approximation.)
3.4.3) Local structure of the calcined catalysts determined from full cluster multiple scattering calculations.

Full cluster multiple scattering calculations were also carried out for the calcined catalysts, stabilised in either the tridymite or quartz phase. The phosphorus EXAFS results for only the tridymite phase (since the P-O distance in the quartz phase is known) is shown in figure 3.17.

![Graph](a)

![Graph](b)

**Figure 3.17** Typical best fit to the P K-edge EXAFS data of the tridymite phase material and the associated FT's are shown in (a) and (b), respectively. The solid line and the dashed curve represent the experimental and calculated data, respectively.
Analysis of the data resulted in an average P-O distance of 1.534 Å (see Table 3.6), which is consistent with a four co-ordinate phosphorus species. The Fe K-edge data were analysed using a similar procedure as described for the as-prepared catalyst and the only difference for the analysis of this data is the exclusion of the water molecules from the starting model. Structural parameters obtained from the analysis of the Fe K-edge EXAFS data (employing the multiple scattering approach) of the tridymite and quartz structure types formed during calcination of the hydrothermally prepared catalyst are given in Table 3.6 and the corresponding best fit to the EXAFS and FT’s are shown in figure 3.18 along with the local structure arrangements of the Fe$^{3+}$ centers for the tridymite and quartz FePO$_4$ type phases respectively. The results are in very good agreement with the crystallographic data for the FePO$_4$ quartz type phase.$^{56}$

<table>
<thead>
<tr>
<th>K-Edge</th>
<th>Atom pair</th>
<th>N</th>
<th>R (Å)</th>
<th>2σ² (Å$^2$)</th>
<th>Fe-O-P angle (°)</th>
<th>R factor</th>
</tr>
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<tr>
<td>P</td>
<td>P-O</td>
<td>3.74</td>
<td>1.534</td>
<td>0.0040</td>
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<td>34.61</td>
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<tr>
<td>Fe(Tridymite)</td>
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<td>0.008</td>
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<tr>
<td></td>
<td>Fe-P</td>
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<td>11.98</td>
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<tr>
<td></td>
<td>Fe-P</td>
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<tr>
<td></td>
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<td>3.054</td>
<td>0.06</td>
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<td></td>
</tr>
<tr>
<td>Fe (Quartz)</td>
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<td>1.857</td>
<td>0.006</td>
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<td>3.154</td>
<td>0.11</td>
<td>137</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6. Structural parameters obtained from the analysis of the P K-edge and Fe K-edge EXAFS data of the tridymite and quartz phases of iron phosphate material prepared by heating the hydrothermally synthesised sample.
Figure 3.18 In (a), (b) is shown the best fit to Fe K-edge EXAFS data of tridymite and quartz phases, respectively, obtained by heating the hydrothermally prepared material. The associated FT’s are given in (c) and (d). The solid line and the dashed curve represent the experimental and calculated data, respectively. The local structural models obtained from the final refinement are shown in (e) and (f).
In Table 3.7 the BET surface area results are shown for the as prepared catalyst precursors and after calcination at 400°C and 600°C respectively. From these measurements it is clear that the hydrothermally prepared iron phosphate catalyst has a larger surface area than the other two catalysts. This initial surface area remains intact for all three catalyst types on calcination to 400°C but begins to diminish on reaching 600°C. This reduction in surface area is probably related to the growth in the tridymite particle size before the final transformation to the quartz phase.

**Table 3.7.** Surface area (in m² g⁻¹) of the catalyst heated at 100°C (as synthesised), 400°C and 600°C. Results are accurate to within ± 2 m² g⁻¹.

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>As Synthesised</th>
<th>Calcined at 400°C</th>
<th>Calcined at 600°C</th>
</tr>
</thead>
<tbody>
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<td>Hydrothermal method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia Gel method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrothermal method</td>
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<td>14</td>
<td>8</td>
</tr>
<tr>
<td>Precipitation method</td>
<td>9</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Ammonia Gel method</td>
<td>8</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>

Preliminary catalytic studies for the conversion of isobutyric acid to methacrylic acid undertaken using the same amount of each of the catalysts indeed suggested that the catalyst prepared by the hydrothermal method possesses a higher activity for methacrylic acid production than the catalysts prepared by the conventional methods.

**3.4.4) Effect of preparation conditions on the as prepared catalysts.**

It has been demonstrated that the method of preparation of the iron phosphate catalyst can affect the final crystal structure, which, in turn affects its final catalytic properties.¹⁹,²⁰,²² Parameters that have previously been altered include calcination temperature and conditions and ingredient sources but during the course of this study it has been discovered that the effect of synthesis time employed for the preparation of both the hydrothermally prepared and the ammonia gel catalyst is critical to the formation of the iron phosphate phases identified in this study.
3.4.4.1) Effect of synthesis time on the iron phosphate catalysts prepared by hydrothermal methods.

In figure 3.19 is shown the XRD patterns for the iron phosphate catalysts prepared by hydrothermal methods after a synthesis time of 4 and 20 hours respectively. It is clear from this figure that after twenty hours of hydrothermal treatment that FePO$_4$.2H$_2$O, metastrengite had formed – this is despite using a synthesis mix containing an excess of phosphorus. This suggested that the FePO$_4$.2H$_2$O phase formed after only four hours of reaction might be an intermediate that forms before metastrengite under these conditions of reaction. A close comparison of the two XRD patterns reveals that there are certain reflections inherent to both phases. From the crystal structure solution for metastrengite$^{53}$ the four strongest reflections are the 110, 002, 120 and 013/130/-221 at 19.16, 20.28, 24.64, and 31.92 degrees 2θ respectively and although the FePO$_4$.2H$_2$O phase contains reflections at similar 2θ values these are both lower in intensity and more broad.

![XRD patterns](image)

Figure 3.19 XRD patterns for iron phosphate materials produced via hydrothermal treatment after (a) 4 hours and (b) 20 hours.

In order to determine whether the FePO$_4$.2H$_2$O phase observed after 4 hours reaction time was an intermediate forming before metastrengite an EDXRD study was
undertaken. The stacked EDXRD pattern (the data were recorded from the middle detector at 185°C is shown in figure 3.20) recorded during the hydrothermal crystallisation and transformation of the FePO₄·2H₂O phase clearly showed that during the initial stages, five distinct reflections appear in the gel (after an induction period ca 17 minutes), which become narrow very quickly. An extent of reaction $^{73,74}$ ($\alpha_{hkl}$) vs. time plot for the growth in peak intensity and decrease in Full Width at Half Maximum (FWHM) of a particular Bragg reflection $I_{hkl}$ with time ($t$) (equation (3.6)) is shown in figure 3.21 for the five previously identified reflections.

$$\alpha_{hkl}(t) = \frac{I_{hkl}(t)}{I_{hkl}(t_{\infty})}$$  \hspace{1cm} (3.6)

![Figure 3.20 Stacked EDXRD pattern recorded in situ during the hydrothermal transformation of the FePO₄·2H₂O phase to metastrengsite. The time zero corresponds to the start of the data-collection, which was two minutes after introduction of the autoclave in to a pre-heated oven. A data collection time of one minute was employed for this work. For clarity, only data obtained from the middle detector (the detector was placed at a fixed 2θ angle of 4.997 degrees) is shown over a short range of d-spacing. Data collection was halted for ca 15 minutes after one hour of reaction after the synchrotron beam was lost.](image)

It appeared that the FePO₄·2H₂O phase remained stable and intact for some time after it had first crystallised (ca 60 minutes). After this time had elapsed the five
reflections all began to gradually increase in intensity whilst at the same time their FWHM gradually decreased (figure 3.21 (b)). This was taken as evidence that the slow transformation to metastrengite had begun since the reflections recorded for this phase were both more intense and narrower than the reflections in the FePO$_4$.2H$_2$O phase.

![Graph](image)

**Figure 3.21** (a) Normalised (with respect to the last data set collected during measurement at a specific temperature) extent of reaction $\alpha$(hkl) curves for the most intense reflections (110, 002, 120, 013/130/-221) for metastrengite versus time. (b) Decline in FWHM vs. time for the same peaks. The decline in FWHM after ca two hours reflects the transformation from FePO$_4$.2H$_2$O to metastrengite. We have plotted the 131 and 200/002 reflections for the γ-phase and the −221, 023, 040 and −204 peaks for the α-phase. The large gap (ca 15 minutes) in the plot is due to the loss of beam.
After two hours it appeared that only reflections corresponding to metastrengite remained. No evidence of the tridymite phase was observed after calcination of this metastrengite material at 400°C for six hours.

3.4.4.2) Effect of synthesis time on the iron phosphate catalysts prepared by the ammonia gel method.

In figure 3.22 is shown the XRD patterns of the as prepared ammonia gel catalysts after mixing for two and four hours respectively. As previously observed by Ai et al. 19 when a mixing time of only 2 hours is employed in order to prepare this catalyst an XRD amorphous iron phosphate material is produced which is orange in colour. However a much closer inspection of the XRD pattern for this material reveals that it is possible to make out reflections (asterisked) corresponding to NH₄Fe₅(PO₄(OH)₀.₆₆₆(OH)₃·₆H₂O (ICSD database entry no. 21266) which suggested that this phase crystallizes before the FePO₄·2H₂O phase.

![Figure 3.22 XRD patterns of ammonia gel catalysts prepared after 2 and 4 hours respectively. Also included are the indexing lines for the NH₄Fe₅(PO₄(OH)₀.₆₆₆(OH)₃·₆H₂O phase, for clarity the presence of this phase in the top XRD pattern is asterisked.](image-url)
The *in situ* calcination of the ammonia gel material, which had been mixed for 2 hours, to 600°C was followed in separate XRD and XAS experiments. The stacked XRD plots detailing the changes that took place in the long-range ordering in the material are shown in figure 3.23 along with a plot of the intensity of the non-overlapping intense reflections appearing at 2θ angles of 21.51 and 26.05 degrees which represent the tridymite and quartz phases respectively (figure 3.23 (b)). Unlike the previous dynamic study undertaken on the first ammonia gel catalyst in figures 3.13 (a) and (b) the reflections for the starting material could not be tracked as these were both very weak and difficult to make out from a noisy background. However it is clear from figure 3.23 (a) and (b) that the reflections associated with the tridymite phase do not appear until the temperature reached ca 400°C. This has been observed many times previously.¹⁹,²⁰,²²,³² Beyond this temperature the intensity of the reflection at 21.51 degrees 2θ continued to increase until the calcination conditions reached ca 500°C and the most intense reflection for the quartz phase (012 reflection at 26.05 degrees 2θ) was first observed. On completion of calcination at 600°C this was the only phase remaining. Again no other reflections were detected other than those that belonged to either the tridymite or quartz phases despite the presence of the NH₄Fe₃(PO₅(OH)₀.⁶₆₆O₀.₃₃₃)(PO₂(OH)₂)₃.₆H₂O phase in the starting material and an inclusion of excess phosphorus during the initial stages of the synthesis.
Figure 3.23 Stacked XRD plots (a) and intensity plots (b) for the variation in the intensities of the reflections that correspond to the tridymite and quartz phases of iron phosphate material prepared by the second ammonia gel method. The presence of a high background at the lower angles is responsible for the apparent high intensity of the tridymite phase before the temperature reached 400°C.

Analysis of the EXAFS data obtained from the dynamic measurement were performed as before assuming a single oxygen shell as the first neighbours around the iron atoms, and these results are shown in figure 3.24. Unlike the ammonia gel sample prepared over four hours the changes that were observed to have occurred during activation were less dramatic. Instead there was a gradual decrease in coordination number from ca six to four, Fe-O distance from ca 1.98Å to 1.87Å and Debye-Waller factor from 0.013 Å² to 0.009 Å² throughout the course of the calcination. These changes coincided with a gradual increase in the XANES pre-edge peak intensity. As with the previous iron phosphate catalysts studied it is thought that these changes reflect a transformation of the local coordination in the starting material from six coordinated Fe³⁺ to a four coordinated Fe³⁺ site in the calcined catalyst at the end of the experiment, although the change in this material is much more gradual. Although the tetrahedral Fe³⁺ containing tridymite phase is seen from the XRD to crystallize at ca 400°C analysis of the EXAFS parameters (an Fe-O distance greater than 1.86Å and coordination number greater than four) suggested that this is not the only phase present. This observation is consistent with previous studies that have shown that after calcination at ca 400°C this
catalyst often contained along with reflections corresponding to the tridymite phase, an XRD amorphous part. However both the EXAFS parameters and XRD suggest that on reaching 600°C the majority phase present is the tetrahedral Fe\(^{3+}\) containing quartz phase.

Since no trace of the FePO\(_4\).2H\(_2\)O phase was detected by XRD the origin of the Fe\(^{3+}\) octahedral species detected by XAS is not totally clear. However the presence of a pre-edge peak higher in intensity than for the FePO\(_4\).2H\(_2\)O samples might be indicative of the presence of a phase(s) either containing a distorted octahedral environment or a mixture of octahedral/tetrahedral Fe\(^{3+}\) species.

![Graph showing variation of pre-edge intensity (PI), coordination number (N), Fe-O distance (R) and 2\(\sigma^2\) (Debye-Waller factor) with the calcination temperature, for the second ammonia gel sample. The coordination number, Fe-O distance and 2\(\sigma^2\) were extracted from the analysis of the EXAFS data using single scattering approximation.]

The TGA and DSC results for the second ammonia gel catalyst heated to 600°C are shown in figure 3.25. Unlike the first ammonia gel catalyst the second looses weight steadily throughout the course of heating although the rate begins to slow on reaching the end of the experiment. The DSC trace is punctuated with small exotherms at ca 100, 200, 250 and 500°C. A separate online mass spectrometry experiment confirms a loss of water at ca 100°C whereas the largest exotherm at ca 250°C coincides with an increase in
weight loss in the TGA although no further volatilites were detected by mass spectrometry. The last exotherm at ca 500°C coincides with the formation of the quartz phase as observed by XRD.

Figure 3.25 Thermogravimetric (a) and differential scanning calorimetry (b) measurements for the second ammonia gel sample.
3.5) Summary and conclusions

In summary, all three synthesis procedures employed here to produce an iron phosphate catalyst resulted in the formation of an FePO$_4$.2H$_2$O type phase, in the as-prepared state which is crystallographically different to the well-known mineral form of FePO$_4$.2H$_2$O known as metastergite. In the case of the hydrothermally treated iron phosphate catalyst this was the only phase that formed whereas for the catalysts produced using the precipitation and ammonia gel methods it appears that additional (minority) phases are formed, which also contain octahedral Fe$^{3+}$ centers. For the ammonia gel catalyst a second phase has been identified as being due to the presence of NH$_4$Fe$_3$(PO$_3$(OH)$_{0.666}$O$_{0.333}$)$_3$(PO$_2$(OH)$_2$)$_3$.6H$_2$O. The detailed in situ study of iron phosphate catalysts prepared by conventional methods as well as a new approach using hydrothermal techniques, found that the as prepared form transformed into a quartz type phase via the formation of tridymite phase (first observed at ca 150ºC) with both these phases containing iron in the 3+ state and in a tetrahedral coordination. This was despite the presence of small amounts of secondary phase(s) in the catalysts prepared using conventional co-precipitation techniques.

A comparative in situ study of the calcination of metastergite revealed no evidence of the tridymite structure between ca 150 – 500ºC but instead a previously unidentified monoclinic form of FePO$_4$ also containing tetrahedral Fe$^{3+}$ centred was produced before this transformed to the quartz form of FePO$_4$ after several hours of heating at 600ºC. This difference in activation behaviour provided further evidence of the difference between the FePO$_4$.2H$_2$O and meetastergite phase and that it would appear that the presence of the FePO$_4$.2H$_2$O phase in the as prepared catalysts is necessary in order to form the tridymite phase. This observation could well be useful when determining the best catalysts for ODH reactions since it has been shown that the active phase (αFe$_3$(P$_2$O$_7$)$_2$) forms via a transformation of the tridymite phase during catalysis.

It was also discovered that the activation behaviour of the as prepared ammonia gel and hydrothermal materials varied with the preparation/reaction time. For the ammonia gel catalyst a halving of the synthesis time resulted in the formation of small amounts of the NH$_4$Fe$_3$(PO$_3$(OH)$_{0.666}$O$_{0.333}$)$_3$(PO$_2$(OH)$_2$)$_3$.6H$_2$O phase along with an
amorphous part. On activation the tridymite phase was not observed in the XRD until the temperature reached ca 400°C although on reaching 600°C this had transformed into the quartz form. Throughout the whole heating process the shortening of the average Fe-O bond length, coordination number and increase in the pre edge peak intensity was taken as evidence of a slow solid state reaction/transformation to the various FePO₄ phases. For the hydrothermal catalysts an increase in the hydrothermal reaction time from 3.5 to 20 hours resulted in the transformation of the FePO₄.2H₂O phase to metastrengite as confirmed in an EDXRD study. Although this metastrengite material was not subjected to an in situ calcination study ex situ measurements confirmed the absence of the tridymite phase and presence of quartz phase only after several hours heating at 600°C.

The finding of the presence of additional phases in the as prepared state of the conventionally prepared catalysts could have important consequences in the understanding of structure-catalytic property relationships of these materials. This observation is particularly poignant when considering that a number of different phases (most of which are thought to be inactive) have been identified as being present after catalytic testing. But perhaps the most important finding in this investigation is the applicability of hydrothermal synthesis techniques for the preparation of phase pure iron phosphate catalysts, in a short period of time, with a surface area higher than that obtainable for the iron phosphate materials produced by conventional methods and this finding may have important implications for catalytic performance.
3.6) References


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(74) Millange, F.; Walton, R. I.; O'Hare, D. J. Mater. Chem. 2000, 10, 1713.

Chapter 4

An *in situ* study following the crystallisation of bismuth molybdate catalysts prepared by hydrothermal methods

4.1) Chapter overview

The three well-known and catalytically important phases of bismuth molybdate have been prepared, in a phase pure form, employing hydrothermal methods at temperatures below 200°C. An *in situ* study of the formation of these phases using the time-resolved energy dispersive X-ray diffraction (EDXRD) technique revealed that the alpha and gamma crystalline phases are formed directly from the amorphous gel mixture without forming any intermediate phases. Kinetic data analysis using the Avrami-Erofe’ev nucleation-growth model suggested that the mechanisms for formation were different for each phase. For the gamma phase it appears that the growth process can be separated into two distinct parts; a first stage involving the formation of Bi₂O₂²⁺ layers which is followed by incorporation of MoO₄ units. In contrast the alpha phase was observed to grow in three directions but in both cases this hydrothermal method of preparation yielded materials with a higher surface area as compared to the solids prepared by conventional techniques.

4.2) Introduction

Some of the most industrially important α and β-unsaturated aldehydes and nitriles are produced via the gas phase catalytic reaction of lower olefins.¹ The most simple and widely used olefin in this process is propylene, which undergoes catalytic oxidation to produce acrolein and catalytic ammoxidation to form acrylonitrile (equation (4.1)).

\[
C_3H_6 + O_2 \xrightarrow{350^\circ C} C_3H_4O \text{ (acrolein)} + H_2O
\]  

(4.1)

\[
C_3H_6 + 1.5O_2 + NH_3 \xrightarrow{450^\circ C} CH_2CHCN \text{ (acrylonitrile)} + 3H_2O
\]
A measure of the industrial importance of these chemical processes was conveyed by the following recently published quotation: ‘According to current statistics for every man, woman and child on this planet approximately one kilogram of acrylonitrile is produced throughout the world annually’ J. M. Thomas (2001).\(^2\) Apart from the sheer volume of production both of these processes share another pertinent similarity: the catalyst used for their reaction, which in both cases are multicomponent mixed oxide catalysts consisting predominantly of bismuth and molybdenum.

The first patent for these so-called allylic oxidations of lower olefins was filed by Shell in 1948 for the reaction between propene and molecular oxygen to produce acrolein over a copper oxide catalyst.\(^3\) However this allylic oxidation process wasn’t industrialised until after 1959 when the first patent was filed for this same reaction this time using a bismuth molybdate system in the form of a heteropoly compound (Bi\(_3\)PMo\(_{12}\)O\(_{40}\)) supported on SiO\(_2\).\(^4\) It was soon realised that certain binary oxide phases of bismuth and molybdenum showed considerable activity for these types of reaction as well as for the oxidative dehydrogenation of \(n\)-butene to butadiene\(^5\) and a potential for gas sensing.\(^6\) Three phases specifically were identified as being particularly active: Bi\(_2\)Mo\(_3\)O\(_{12}\), Bi\(_2\)Mo\(_2\)O\(_6\), Bi\(_2\)MoO\(_6\) designated as the \(\alpha\), \(\beta\) and \(\gamma\)-phases respectively.\(^7\)

Since the early commercialisation, the processes for acrolein and acrylonitrile production have been vastly improved as a result of drastic changes to catalyst preparation, composition and the reaction process with yields of the two products now commonly exceeding 80%.\(^8\) The advances made in enhancing catalytic activity alone has witnessed an improvement of over 100 times and resulted in a lowering of reaction temperatures by as much as 70°C.\(^8\) The main factor responsible for bringing about this significant catalyst improvement is a change in its composition by the inclusion of a number of additional elements such as magnesium, manganese, nickel, cobalt, iron, potassium, sodium and aluminium as well as bismuth and molybdenum giving rise to the modern day multicomponent commercial catalysts.\(^8\) A consequence of the inclusion of additional elements in the multicomponent system is a plethora of metal molybdate phases in the final catalyst, since molybdenum often makes up \(ca\) 50% of the total cation ingredient.\(^8\) Hence the term multicomponent molybdates or MCMs has been coined in order to describe these multicomponent systems. However
despite the inclusion of a number of different elements and the presence of a multitude of phases it is still thought that the important catalytic activity originates from the simple bismuth molybdate phases. For example in the multicomponent molybdate (MCM) system $\text{K}_x\text{Ni}_x\text{Co}_x\text{Fe}_y\text{BiMoO}_x$, $\alpha$-$\text{Bi}_2\text{Mo}_3\text{O}_{12}$ containing small amounts of iron is thought to be the actual catalytic phase\(^9\). It has been proposed, that MCM systems are more active due to the phenomena of phase cooperation between the various constituent phases contained within catalytic particles consisting of a ‘core’ containing various doped binary divalent and trivalent metal molybdates, which impart an enhanced oxide ion diffusivity, and a surface enriched in structurally/electronically modified bismuth molybdates (normally the $\alpha$-phase): structural modification often occurs in the form of enhanced surface area.\(^8,10\)

### 4.2.1) Structure of the active phases

As mentioned previously only the $\alpha$-$\text{Bi}_2\text{Mo}_3\text{O}_{12}$, $\beta$-$\text{Bi}_2\text{Mo}_2\text{O}_9$ and $\gamma$-$\text{Bi}_2\text{MoO}_6$ phases have been found to be active for oxidation and ammoxidation ((amm)oxidation) reactions despite the establishment of detailed phase diagrams detailing the existence of a number of bismuth molybdate phases\(^11,12\).

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\alpha$-$\text{Bi}_2\text{Mo}<em>3\text{O}</em>{12}$</th>
<th>$\beta$-$\text{Bi}_2\text{Mo}_2\text{O}_9$</th>
<th>$\gamma$-$\text{Bi}_2\text{MoO}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>$P2_1/c$</td>
<td>$P2_1/n$</td>
<td>$Pca2_1$</td>
</tr>
<tr>
<td>$a$ Å</td>
<td>7.7104 (3)</td>
<td>11.972 (3)</td>
<td>5.4822 (3)</td>
</tr>
<tr>
<td>$b$ Å</td>
<td>11.5313 (4)</td>
<td>10.813 (4)</td>
<td>16.1986 (8)</td>
</tr>
<tr>
<td>$c$ Å</td>
<td>11.9720 (5)</td>
<td>11.899 (2)</td>
<td>5.5091 (3)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$</td>
<td>115.276 (3)</td>
<td>90.13 (2)</td>
<td>90</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Reference</td>
<td>13</td>
<td>14</td>
<td>15</td>
</tr>
</tbody>
</table>

Although it is still not clear exactly why these particular phases are active many studies suggest that the origin of this activity is related to the presence of cationic and anionic vacancies which can easily be accommodated within the structures of all three phases which have, according to both diffraction and HREM
studies, \(^\text{16}\) traits in common with the fluorite structure (CaF\(_2\)) known to possess a capability for rapid oxygen transport, \(^\text{17}\) Both the \(\alpha\)-Bi\(_2\)Mo\(_3\)O\(_{12}\) and \(\beta\)-Bi\(_2\)Mo\(_2\)O\(_9\) phases have often been described as defective fluorite structures containing Mo\(^{6+}\) ions in tetrahedral coordination, although \(\alpha\)-Bi\(_2\)Mo\(_3\)O\(_{12}\) is more commonly described as having a defect scheelite structure possessing an asymmetric Mo-O\(_5\) arrangement with four short and one intermediate Mo-O bond. \(^\text{18}\) Conversely it is the Bi\(^{3+}\) ions that possess similar coordination in both the \(\gamma\)-Bi\(_2\)MoO\(_6\) and \(\beta\)-Bi\(_2\)Mo\(_2\)O\(_9\) structures with both phases containing BiO\(_8\) polyhedra. \(^\text{16,18}\) However the \(\gamma\)-Bi\(_2\)MoO\(_6\) phase is commonly referred to as an Aurivillius type structure consisting of alternate Bi\(_2\)O\(_2\)\(^{2+}\) sheets and layers of corner sharing MoO\(_6\) octahedra. \(^\text{19}\) More recently an attempt has been made to draw parallels between structural similarities characterised by the presence of a reflection in the XRD patterns of all three phases at \(\text{ca} d = 3.2\ \text{Å}\). It has been proposed that the enhanced oxygen transport capability in these phases is related to the close arrangement of oxygen sublattices to similar cationic planes whose separation is \(\text{ca} 3.2\ \text{Å}\) with the only difference between the three phases being the presence of cationic vacancies (particularly in the \(\alpha\) and \(\beta\)-phases). Also cited has having possible effects upon the physical properties was the occurrence of Bi-Mo substitutional disorder affecting the oxygen sublattice and therefore the ionic conductivity of the phase(s) and metal-metal interactions brought about via cationic clustering. \(^\text{20}\)
4.2.2) Reaction mechanism

The reaction mechanism for (amm)oxidation has been extensively investigated with detailed experimental catalytic studies yielding many proposed total catalytic cycles which differ in the proposed roles of the various components. However the most widely accepted concept is that of the ‘dual-site’ where it has been proposed that the first step for both oxidation and ammoxidation of propene involves the abstraction of hydrogen from a methyl group by the bismuth-oxygen species leaving a π-allyl intermediate attached to the molybdenum dioxo species. For ammoxidation it was further proposed that ammonia is able to first reversibly attach to the molybdenum dioxo species in order to form an imido type species (Mo=NH) before NH is inserted into the allyl group. Further isotope labelling studies using both deuterium and $^{18}$O were used to identify both the likely intermediates formed during reaction and the role that structural oxygen from the catalyst was to play. More recently \textit{ab initio} calculations (using first principles quantum mechanical methods) have been used to verify both catalytic cycles.
4.2.3) Preparation history

Since the first patent dealing with bismuth molybdate catalysts was published in 1948, several research articles and patents have appeared in the literature, many of which detail new preparative methods or catalyst formulations (particularly for the addition of dopants to form MCMs). For the most part, however, these catalysts have been synthesised using co-precipitation techniques in which appropriate amounts of a bismuth source, normally bismuth nitrate, is dissolved in water, and to this is added a source of molybdenum ions in solution normally achieved after the dissolution of ammonium heptamolybdate. At this stage the pH of the resultant precipitate is adjusted before the mix is aged, washed and dried to yield a precursor material, which is then calcined at elevated temperatures (between ca 400-700°C) to remove any volatillites and to form the final active form of the catalyst. This method is preferred to the mixing and heating of the solid oxides since it is both quicker and allows for reactant mixing at the atomic level and thus avoids sample inhomogeneity problems that can arise if two oxides are not mixed together properly. One of the main drawbacks of this approach is that some of these oxides, particularly the \( \gamma \)-\( \text{Bi}_2\text{MoO}_6 \) form, undergo a further transformation to the catalytically inactive \( \gamma'\)-\( \text{Bi}_2\text{MoO}_6 \) phase. The transformation takes place in two stages and involves the formation of an intermediate \( \gamma''\)-phase. The transformation to \( \gamma''\)-phase begins at 570°C but this is reversible up to ca 610°C. This may be because there is little difference between the two structures (a study by Sankar et al. demonstrated no change in the space group (\( Pca2_1 \)) and only a slight increase (\( \approx 4 \text{Å}^2 \)) in unit cell volume on going from \( \gamma - \gamma'' \)). However between 610 – 750°C the gradual irreversible transformation of \( \gamma''\)-\( \text{Bi}_2\text{MoO}_6 \) takes place via a progressive increase in the octahedral distortion around the \( \text{Mo}^{6+} \) ions to leave a tetrahedral arrangement on reaching ca 750°C, characteristic of the \( \gamma'\)-\( \text{Bi}_2\text{MoO}_6 \) phase. Typical synthesis conditions for the preparation of each of the three catalytically active phases using co-precipitation techniques are given in Table 4.2.
Table 4.2 Typical synthesis conditions employed for the preparation of the three phases using co precipitation techniques.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Molybdenum source</th>
<th>Bismuth source</th>
<th>Final pH range</th>
<th>Bi:Mo Ratio</th>
<th>Calcination Temp. Range (°C)</th>
<th>Calcination Time (Hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Normally (NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>Acidified Bi(NO₃)₃·5H₂O</td>
<td>1.2-7.0</td>
<td>2:3</td>
<td>300-620</td>
<td>5-48</td>
</tr>
<tr>
<td>β</td>
<td>Normally (NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>Acidified Bi(NO₃)₃·5H₂O</td>
<td>2.0-8.0</td>
<td>1:1</td>
<td>400-650</td>
<td>2-48</td>
</tr>
<tr>
<td>γ</td>
<td>Normally (NH₄)₆Mo₇O₂₄·4H₂O</td>
<td>Acidified Bi(NO₃)₃·5H₂O</td>
<td>5.0-7.0</td>
<td>2:1</td>
<td>400-620</td>
<td>5-48</td>
</tr>
</tbody>
</table>

The effects of varying a number of synthesis parameters on the final crystal structure have been thoroughly investigated over the years.²²,35-38 During this time it has been suggested that the variables reactant source, concentration, stoichiometry, pH and calcination temperature are important in determining the purity of the final crystalline product. The most commonly used source of bismuth is bismuth nitrate as Bi(NO₃)₃·5H₂O which is normally acidified using nitric acid. However as it is highly hygroscopic (which can affect the reaction stoichiometry) this is now more frequently prepared by the reaction of Bi₂O₃ with nitric acid.³⁸ For molybdenum ions the most favoured source is the highly soluble ammonium heptamolybdate (NH₄)₆Mo₇O₂₄·4H₂O although molybdcic acid is occasionally used.³⁶ At this point the two solutions are normally mixed and the pH is adjusted between the ranges of 1.0-7.0 accordingly, using dilute ammonium hydroxide. It has been proposed that this pH adjustment is important since it is known that this affects the stability of various polymeric molybdates present in solution (as detailed in table 4.3) which, it was concluded, can influence the type (including stoichiometry) of precipitate formed.³⁸,3⁹ For example it has been proposed that the alpha and beta phases form under conditions where the Mo₃O₁₂²⁻ and Mo₂O₇⁻ anions are stable.³⁸,3⁹
Table 4.3 Proposed polymeric molybdate and bismuth species as a function of pH, temperature and concentration adapted from Trifiro et al. and Keulks et al.\textsuperscript{36-39}

<table>
<thead>
<tr>
<th>Species</th>
<th>pH</th>
<th>100°C</th>
<th>[Conc.]</th>
<th>1.5</th>
<th>6</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>cisMoO\textsubscript{4}\textsuperscript{2+}</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMO\textsubscript{6}\textsuperscript{6-}(Mo\textsubscript{2}O\textsubscript{4}\textsuperscript{2+}Mo\textsubscript{3}O\textsubscript{10}\textsuperscript{2-})</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo\textsubscript{4}O\textsubscript{13}\textsuperscript{2-}</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo\textsubscript{6}O\textsubscript{24}\textsuperscript{2-}</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo\textsubscript{7}O\textsubscript{24}\textsuperscript{2-}</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoO\textsubscript{4}\textsuperscript{2-}</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(OH)\textsubscript{3}</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In contrast, the chemistry of bismuth under various pH conditions is less well known with a number of species having been proposed to possibly exist including bismuthyl ions (BiO\textsuperscript{+}), bismuth oxinitrate (BiO(NO\textsubscript{3})) bismuth oxyhydrate (BiO(OH)) and bismuth hydroxide Bi(OH)\textsubscript{3}. However it has been proposed that it is most likely that bismuth exists as Bi(OH)\textsubscript{3} above a pH of 1.5.\textsuperscript{22,35-38,40} However it has also been postulated that a low pH is important for the precipitation of a heteropolymolybdate of bismuth, which is necessary for the formation of the alpha phase.\textsuperscript{37}

Stoichiometry and calcination temperature are also known to be particularly important and the effects of varying these parameters is displayed in a phase diagram adapted from Snyder et al. (figure 4.2).\textsuperscript{12} Below the minimum temperature displayed in the figure (450°C) it is known to be difficult to form pure crystalline bismuth molybdate phases although temperatures as low as 400°C have been reportedly used to form the \(\beta\)-phase and 300°C for the \(\alpha\)-phase.\textsuperscript{12} However the use of such a low calcination temperatures often results in the formation of mixed phase materials, which are thermally unstable.\textsuperscript{12}
4.2.4) Aims and objectives

In order to overcome some of the difficulties encountered in the preparation of crystalline bismuth molybdate phases, in this study hydrothermal methods have been employed to produce phase pure, crystalline binary oxide phases, under mild conditions. Hydrothermal methods are traditionally used to obtain meta-stable zeotype materials, which include aluminosilicates, aluminophosphates, mesoporous silicas and their metal ion substituted variants although more recently have been used for the preparation of several advanced oxide materials.\textsuperscript{41-44}

During this study the $\alpha$, $\beta$ and $\gamma$-phases of bismuth molybdate have been prepared employing mild hydrothermal conditions (temperatures \textit{ca} 150$^\circ$C) over short reaction times (\textit{ca} 20 hours). The formation of the $\alpha$ and $\gamma$-phases from an amorphous gel to the crystalline solid was followed using time-resolved energy dispersive X-ray diffraction (EDXRD) and for the $\gamma$-phase combined X-ray diffraction (XRD) and extended X-ray absorption spectroscopy (EXAFS, also referred to as QuEXAFS) was also used. In order to form the $\beta$-phase it was necessary to apply further heat treatment to the solid extracted from the hydrothermally treated gel, at \textit{ca}. 560$^\circ$C and the formation of this pure $\beta$-phase was also followed using the \textit{in situ} combined
XRD/QuEXAFS technique. For comparative purposes the three phases were also synthesised using both precipitation and solid-state techniques.

4.3) Experimental

4.3.1) Preparation of bismuth molybdate catalysts

For the hydrothermal, co-precipitation and solid-state preparations of the bismuth molybdate phases the following procedures were adopted:

4.3.1.1) Hydrothermal preparation

Stoichiometric amounts of acidified bismuth nitrate solution were mixed with ammonium heptamolybdate (Aldrich) dissolved in ammonium hydroxide (Aldrich) and the pH of this mixture was adjusted to a specific range (see Table 4.4). The resultant precipitate was then introduced into a Teflon lined autoclave for hydrothermal treatment. The autoclave was placed in a pre-heated oven for several hours before the reaction was quenched and the contents were filtered, washed and dried.

Table 4.4 Synthesis conditions for the hydrothermal preparation of α-Bi$_2$Mo$_3$O$_{12}$, β-Bi$_2$Mo$_2$O$_9$ and γ-Bi$_2$MoO$_6$.

<table>
<thead>
<tr>
<th>Amount Bi$_2$O$_3$ (g)</th>
<th>Amount (NH$_4$)$_6$Mo$<em>7$O$</em>{27}$·4H$_2$O (g)</th>
<th>Amount HNO$_3$ (g)</th>
<th>Amount NH$_4$OH (ml)</th>
<th>Gel pH</th>
<th>Reaction Temp. (°C)</th>
<th>Prep. Time (Hrs)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.16</td>
<td>1.32</td>
<td>4.08</td>
<td>5</td>
<td>&lt; 2.0</td>
<td>140</td>
<td>20</td>
<td>α</td>
</tr>
<tr>
<td>1.16</td>
<td>0.88</td>
<td>4.08</td>
<td>3.75</td>
<td>= 4.0</td>
<td>140</td>
<td>20</td>
<td>γ-type &amp; amor- phous</td>
</tr>
<tr>
<td>1.16</td>
<td>0.44</td>
<td>4.08</td>
<td>2.5</td>
<td>&gt; 6.0</td>
<td>140</td>
<td>20</td>
<td>γ</td>
</tr>
</tbody>
</table>
4.3.1.2) Coprecipitation preparation

Stoichiometric amounts of acidified bismuth nitrate solution were mixed with ammonium heptamolybdate (Aldrich) dissolved in ammonium hydroxide (Aldrich) and the pH of this mixture was adjusted to a specific range (see Table 4.5). The resultant precipitate was aged for two hours at 80°C before the precipitate was filtered, washed and dried. The resultant solids were calcined at between 560-610°C for 8 hours.

Table 4.5 Synthesis conditions using the co precipitation approach to prepare α-Bi$_2$Mo$_3$O$_{12}$, β-Bi$_2$Mo$_2$O$_9$ and γ-Bi$_2$MoO$_5$.

<table>
<thead>
<tr>
<th>Amount Bi$_2$O$_3$ (g)</th>
<th>Amount (NH$_4$)$_6$Mo$<em>7$O$</em>{24}$ 4H$_2$O (g)</th>
<th>HNO$_3$ /H$_2$O (g)</th>
<th>NH$_4$OH/ H$_2$O (ml)</th>
<th>Final Gel pH</th>
<th>Calcination Temperature (°C)</th>
<th>Time (Hrs)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.16</td>
<td>1.32</td>
<td>4.08/5</td>
<td>5/5</td>
<td>&lt; 2.0</td>
<td>560</td>
<td>8</td>
<td>α</td>
</tr>
<tr>
<td>1.16</td>
<td>0.88</td>
<td>4.08/5</td>
<td>3.75/5</td>
<td>= 2.0</td>
<td>610</td>
<td>8</td>
<td>β</td>
</tr>
<tr>
<td>1.16</td>
<td>0.44</td>
<td>4.08/5</td>
<td>2.5/5</td>
<td>&gt; 6.0</td>
<td>560</td>
<td>8</td>
<td>γ</td>
</tr>
</tbody>
</table>

4.3.1.3) Solid-state preparation

Stoichiometric amounts of bismuth oxide (Aldrich) were mixed with molybdenum oxide (Alfa) before the mix was pelleted and subjected to calcination at 560°C for 182 hours (see Table 4.6).

Table 4.6 Synthesis conditions for the solid-state preparation of α-Bi$_2$Mo$_3$O$_{12}$, β-Bi$_2$Mo$_2$O$_9$ and γ-Bi$_2$MoO$_5$.

<table>
<thead>
<tr>
<th>Amount Bi$_2$O$_3$ (g)</th>
<th>Amount MoO$_3$ (g)</th>
<th>Calcination Temperature (°C)</th>
<th>Calcination Time (Hrs)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.16</td>
<td>1.08</td>
<td>560</td>
<td>182</td>
<td>α</td>
</tr>
<tr>
<td>1.16</td>
<td>0.72</td>
<td>560</td>
<td>182</td>
<td>β</td>
</tr>
<tr>
<td>1.16</td>
<td>0.36</td>
<td>560</td>
<td>182</td>
<td>γ</td>
</tr>
</tbody>
</table>
4.3.2) Characterisation

XRD patterns of all the as-synthesised materials (dried at 100°C) were recorded using both a Siemens D500 and FR571 Enraf Nonius diffractometer (both of Bragg-Brentano geometry) utilizing Cu-Kα₁ radiation. The BET surface area measurements (using a Micromeritics Gemini III) were carried out on all samples after calcination at temperatures between 400-610°C. A temperature of 400°C was employed to calcine the hydrothermal catalysts (a typical temperature used for catalytic reaction), whereas between 560-610°C was used for all the others in order to form the final phases. All samples were subjected to degassing at 100°C in N₂ prior to surface area measurement using N₂ at -196°C as the adsorbate. SEM pictures were taken using a Hitachi S-570 SEM and for this work an accelerating voltage of 20 kV was used.

*In situ* EDXRD measurements were carried out on station 16.4 of Daresbury Synchrotron radiation source, which operates at 2 GeV with a typical current of 150 to 250 mA. A schematic of the experimental arrangement for these *in situ* hydrothermal studies can be seen in figure 2.10 in chapter 2 with the details of this set-up having been published elsewhere.⁴⁵ In a typical experiment, an autoclave containing the appropriate gel mixture was introduced in to an oven, pre-heated to a specific temperature. EDXRD measurements were carried out at temperatures between 110-150°C. Data collection was started two minutes after the introduction of the autoclave and a data collection time of one minute per scan was employed for this work. The middle detector, used to record data with a range of d-spacing between 6-2Å, was placed at a fixed 2θ angle of 4.619 degrees. The other reflections that appeared in the top detector at lower d-spacings are not shown here due to their lack of intensity. Integrated areas of all of the reflections detected in the EDXRD spectra were determined using a Gaussian curve fitting routine using the XFIT programme available from CCP14.

*In situ* XRD/QuEXAFS measurements were carried out at station 9.3 of Daresbury Synchrotron radiation source. The station was equipped with a Si(220) double crystal monochromator and ion chambers for measuring incident and transmitted beam intensities for recording X-ray absorption spectra. For diffraction measurements, a position sensitive INEL detector was used. About 40 mg of the
bismuth molybdate precursor, was pressed into a 13 mm pellet and mounted in to the in situ cell that permits the measurement of combined XAS and XRD data chapter 2 figure 2.7 and 2.8). The sample was heated at 5°C minute from room temperature to 560°C (610°C for the β-precursor prepared by co-precipitation) and held at this temperature for 60 minutes. For hydrothermal crystallisation studies of the γ-phase a different set-up was used details of which can be found below in figure 4.3. For this work a few millilitres of the γ-gel was used and measurements began when the temperature of the apparatus reached 85°C. The Mo K-edge XAS and XRD data were collected sequentially, during this activation process. The time taken for the Mo K-edge XAS pattern was 380 seconds and 180 seconds for XRD data resulting in a total cycle time of 10 minutes, which includes 40 seconds of dead time to move the monochromator back to the starting point. XRD data were collected at a wavelength of 0.928 Å or 1.517 Å to avoid fluorescence effects. The INEL detector was calibrated using a NBS silicon standard and a 10 μm Mo foil was used to calibrate the monochromator position.

![Image](image.jpg)

**Figure 4.3** Liquid cell in the brass furnace (A) set-up on station 9.3 for combined QuEXAFS/XRD measurements. A more detailed picture of the liquid cell is shown in Figure 4.4.

Liquid samples containing molybdate anions in solution of different pH were measured in an in situ cell (figure 4.4) in transmission mode on station 9.2 of the
Daresbury Synchrotron radiation source. The station was equipped with a Si(220) double crystal monochromator and ion chambers for measuring incident and transmitted beam intensities for recording X-ray absorption spectra. In a typical experiment 0.44 g of ammonium heptamolybdate was dissolved in 5 ml of water at pH 1.0, 4.0, 6.0 and 7.0.

![Sample](image.jpg)

**Figure 4.4** In situ cell used in the furnace in Figure 4.3 and for liquid sample measurements on station 9.2. The liquid gel was first placed between two mica sheets separated by a teflon ring, before this was placed between two metal flanges and clamped together.

XAS data were processed using the suite of programs available at Daresbury laboratory, namely EXCALIB (for converting the raw data to energy vs. absorption coefficient), EXBROOK (to obtain normalised XANES part of the spectra and for background subtraction to extract EXAFS) and EXCURV98 (to perform a first coordination shell analysis).
4.4) Results and discussion

Firstly, the results obtained from the *ex situ* study for the hydrothermal, co precipitation and solid state synthesis of the three bismuth molybdate phases are discussed followed by the results obtained from the *in situ* study of the crystallisation of these phases using EDXRD and combined XRD/QuEXAFS.

4.4.1) *Ex situ* studies

4.4.1.1) XRD patterns and surface area measurements

The diffraction patterns of the as-prepared material using hydrothermal methods are shown in figure 4.5. It is clear from the XRD patterns that the solids prepared using gel compositions that correspond to $\alpha$ and $\gamma$-phases can be readily identified as the crystalline $\alpha$-Bi$_2$Mo$_5$O$_{12}$ and $\gamma$-Bi$_2$MoO$_6$ (JCPDS Card Nos. 21-103 (a) & 21-102 (b)) phases, respectively. The gel prepared with $\beta$-phase (Bi$_2$Mo$_2$O$_9$) stoichiometry did not yield a phase pure material. The XRD pattern of this sample (d) appears to have reflections that correspond to the $\gamma$-type phase in addition to an amorphous phase. However, the pure form of the $\beta$-phase can be prepared from this hydrothermally treated material by calcining in air at temperatures between 500 and 560°C. The XRD pattern of this calcined material is also shown in Figure 4.5 (c) along with the index lines for $\beta$-phase (JCPDS Card No. 33-209).

Confirmation that all three phases have been prepared in a pure form using both co precipitation and solid-state methods can be found in figures 4.6 and 4.7. Although the solid state route has been successful for producing all three phases in a pure form it has taken 182 hours which is a very long time even for a solid state reaction. The results obtained from the surface area measurements for all of the samples are shown in Tables 4.7 and 4.8. It is clear that all of the hydrothermally prepared materials show a much larger surface area than the materials prepared by the conventional sol-gel and solid state methods; even after calcination at a typical reaction temperature of 400°C, employed for propylene ammoxidation.⁸
Figure 4.5 X-ray diffraction patterns of (a) Bi$_3$MoO$_{12}$ – α-phase, (b) Bi$_2$MoO$_6$ – γ-phase (c) Bi$_2$Mo$_2$O$_9$ – β-phase are shown along with the lines representing the patterns reported in the JCPDS database, card nos. 21-103, 21-102 and 33-209, respectively. All three materials were prepared by employing hydrothermal methods at 140°C for 20 hours although in order to form the β-phase it was necessary to heat the material further to ca 560°C. In (d) is shown the product from the hydrothermal treatment of the β-gel, which appears to have reflections that correspond to the γ-phase.

Figure 4.6 X-ray diffraction patterns of (a) α-phase, (b) β-phase and (c) γ-phase prepared using co precipitation techniques after calcination at 560°C for 8 hours for the α and γ-phases and 610°C for 8 hours for the β-phase.
Figure 4.7 X-ray diffraction patterns of (a) α-phase, (b) β-phase and (c) γ-phase prepared using solid-state techniques after calcination at 560°C for 182 hours.

Table 4.7. Surface area measurements for the hydrothermally synthesised bismuth molybdate phases before and after calcination. Results are accurate to within ±2m²/g.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Calcination Temperature (°C)</th>
<th>Calcination Time (Hours)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha</td>
<td>As prepared</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Alpha</td>
<td>400</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Gamma</td>
<td>As prepared</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Gamma</td>
<td>400</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Beta</td>
<td>560</td>
<td>8</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4.8. Surface area measurements for the phase pure bismuth molybdate phases prepared via coprecipitation (denoted (c)) and solid-state routes. Results are accurate to within ±2m²/g.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Preparation Temperature (°C)</th>
<th>Preparation Time (Hours)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha(c)</td>
<td>560</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Alpha</td>
<td>560</td>
<td>182</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Gamma(c)</td>
<td>560</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Gamma</td>
<td>560</td>
<td>182</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Beta(c)</td>
<td>610</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Beta</td>
<td>560</td>
<td>182</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
4.4.2) SEM images

In figure 4.8 is shown the SEM pictures for the \( \alpha \) and \( \gamma \)-phases prepared by hydrothermal methods over a temperature range of 110-150°C. It appears that the particle shapes are very different for the two phases. The \( \alpha \)-phase particles at 120-130°C look very small and round but they seemed to lose this definition when this phase is hydrothermally prepared at 140°C becoming more rectangular. Conversely the gamma phase particles appear to have grown predominantly in only two dimensions and can best be described as irregularly shaped platelets.

In figure 4.9 are shown the SEM images after calcination for all three phases prepared by co-precipitation, solid state and the hydrothermally treated \( \beta \)-phase. It is clear that the particles produced by the conventional methods (particularly the solid state route) tend to be much larger (which is probably due to particle coalescence during calcination) than those produced via the hydrothermal route and this probably explains the much smaller surface area for these samples. For the \( \beta \)-phase there does not appear to be an obvious difference in particle size between the hydrothermally treated material and the material produced using the co precipitation route, which accounts for the relatively small difference in surface area measurements. However the hydrothermally treated \( \beta \)-phase appears to have more uniformly shaped particles than the co precipitation sample, which appears to contain small amounts of impurity phases.
Figure 4.8 Scanning electron micrograph (SEM) images (magnified x 20,000) of the bismuth molybdate solids prepared by hydrothermal methods (a-c) Bi₂Mo₆O₁₉ – α-phase at prepared at 393, 403 and 413 K and (d-e) Bi₂MoO₆ – γ-phase prepared at 383, 413, and 423 K. The γ-phase particles appear to be irregular shaped platelets whereas below 413 K the α-phase particles look small and round. Above 413 K the α-phase particles seem more rectangular. The white scale bar = 1 μm.
Figure 4.9 Scanning electron micrograph (SEM) images (magnified x 8,000) of the bismuth molybdate solids prepared by various methods. In (a) is shown the $\beta$-phase prepared by hydrothermal methods and calcined at ca 560°C. From (b-d) (b) $\alpha$-phase, (c)$\beta$-phase (d) $\gamma$-phase) are shown all three phases prepared by co-precipitation routes and (e-g) ((e) $\alpha$-phase, (f) $\beta$-phase (g) $\gamma$-phase) by solid-state methods. The white scale bar = 5 $\mu$m.
4.4.2) **In situ** EDXRD studies

In order to determine whether the \( \alpha \) and \( \gamma \)-phases are produced via the formation of any other intermediate phases during the hydrothermal treatment a detailed *in situ* study was carried out at various reaction temperatures. This study would also enable us to obtain details on the kinetics of the crystallisation process, which could provide important information in any attempt to propose a reaction mechanism.\(^{46}\) Furthermore a detailed understanding of these crystallization mechanisms would enable us to control and optimise the synthesis conditions so that it might be possible to tailor the final properties of the material to suit a particular application.

The stacked EDXRD patterns (typical data recorded at 140°C is shown in figure 4.10) recorded during the hydrothermal treatment clearly showed that during the initial stages, two very broad but distinct reflections appear in the gel with \( \gamma \) stoichiometry (figure 4.10(a)) and four broad reflections appear in the gel with \( \alpha \) stoichiometry (figure 4.10(b)), which, over a period of time, become narrow. These reflections have been identified as the –221, 023, 040 and –204 peaks for the gel with \( \alpha \) stoichiometry and the 131 and 200/002 reflections for the \( \gamma \) gel. The other reflections that appeared at lower d-spacings are not shown here due to the limited d-spacing range of the detector and their lack of intensity.

For the subsequent kinetic analysis of this gel-to-solid reaction, the growth of the integrated peak intensity of a particular Bragg reflection \( I_{hkl} \) with time \( t \) (equation (4.2)) is used to represent the extent of reaction \( \alpha_{hkl} \).

\[
\alpha_{hkl}(t) = \frac{I_{hkl}(t)}{I_{hkl}(t_\infty)}
\]  

(4.2)

Similar analysis procedures have been used for several systems (see, for example references 29, 32, 42-45). In figure 4.11 the extent of reaction \( \alpha \), for the previously identified reflections (–221, 023, 040 and –204 peaks for the gel with \( \alpha \) stoichiometry and the 131 and 200/002 reflections for the \( \gamma \) gel) for both phases seen in the EDXRD
Figure 4.10 Typical stacked EDXRD patterns recorded in situ during the hydrothermal synthesis, at 140°C, of (a) γ-phase and (b) α-phase. The time zero correspond to the start of the data-collection, which was two minutes after introduction of the autoclave into a pre-heated oven. A data collection time of one minute was employed for this work. For clarity, only data obtained from the middle detector (the detector was placed at a fixed 2θ angle of 4.619 degrees) is shown over a short range of d-spacing.
data, are plotted as a function of time. It appears that the growth curves obtained from various reflections are superimposable (within experimental error) and it is concluded that uniform crystal growth had taken place with no obvious favoured crystallographic direction. The sigmoidal curves seen here are typical for a crystallisation process consisting of an initial period of induction followed by a slow nucleation step before a rapid acceleration of the reaction occurs as the nuclei grow at a constant rate. The reaction then decelerates as the reactants are consumed and a continuous growth of the crystallites is observed until a constant value is reached reflecting a tendency towards completion.

Figure 4.11 Normalised (with respect to the last data set collected during measurement at a specific temperature) extent of reaction ($\alpha$) curves for the most intense reflections for the bismuth molybdates (top) $\gamma$-phase and (bottom) $\alpha$-phase versus time. For the $\gamma$-phase the most intense reflections are the 131 and 200/002 reflections whereas for the $\alpha$-phase the −221, 023, 040 and −204 reflections have been plotted.
Due to the uniformity of the growth process, for the subsequent kinetic analysis the most intense peaks (-221 for $\alpha$-phase and 131 for $\gamma$-phase) were used. The extent of reaction curves for both $\alpha$ and $\gamma$-phases recorded at various temperatures are compared in figure 4.12. It is clear from figure 4.12 that an increase in synthesis temperature results in a reduction in the rate and onset of crystallisation for both phases. It is interesting to note that, although the induction period for $\alpha$-phase growth is longer, the rate at which the crystallisation took place was faster compared to the $\gamma$-phase.

**Figure 4.12.** Plots of the area under the reflection (131) for the $\gamma$-phase (top) and (-221) for the $\alpha$-phase (bottom), as a function of reaction time. The various curves in this figure represent the data recorded at different temperatures. Note that the time zero corresponds to the start of the data collection, two minutes after introducing the autoclave into the pre-heated oven held at a specific temperature.
The different nature of the growth curves seen for the two phases suggests that the crystallisation processes are likely to be different. Furthermore the growth profiles for each phase showed little variation with temperature, which we conclude, is evidence that the growth mechanism is not temperature dependent for the range of temperatures studied.

In figure 4.13 is plotted the full width at half maximum (FWHM), of the same reflections shown in figure 4.12 in order to determine the variation in particle size with temperature. The FWHM values for both systems decreases very sharply with the rate at which the decrease takes place dependent upon the reaction temperature. The interesting feature of these plots is that the FWHM decreases up to a point, which coincides with the change in rate seen in figure 4.12. Beyond this point the FWHM remains more or less constant (within the experimental error), whilst further increase in the extent of reaction (\(\alpha\)) is observed. Due to such variation in the \(\alpha\) vs. time plot and FWHM with time, and to extract meaningful kinetic information of the initial stages of crystallisation, we have analysed only the first part of the crystallisation curve where with an upper limit of \(\alpha\) close to ca 0.6.

Using the well-known nucleation and growth approximation proposed by Avrami and Erofe’ev\textsuperscript{47-50} the rate of growth of both the \(\alpha\) and \(\gamma\)-phases was obtained. The Avrami-Erofe’ev equation (4.3) was originally derived in order to determine the kinetics of phase change in solids but has since been more widely applied to model decomposition, crystallisation and intercalation reactions.\textsuperscript{51-55} It assumes that solid state reactions occur via a two stage process of nucleation and growth and proposes that the nuclei necessary for transformation (ie. the desired end phase) are initially present in the reactants and that their number increases with both temperature and duration of reaction. These nuclei can either consist of ‘foreign’ matter with an external surface of the newly forming phase or tiny crystals of the new phase.\textsuperscript{47} It is proposed that these then become growth nuclei growing at a steady rate or else they are ingested by the growing nuclei or dissolve back into the reactant mixture. These growth nuclei then continue to grow (assumed to be isotropically) until there is no more reactant left and the reaction effectively stops.

\[
\alpha = 1 - \exp\left(-kt\right)^n
\]  

(4.3)
The exponents \( k \) and \( n \) correspond to the rate constant and the mechanism for both nucleation and growth. Common values used for \( n \) range from \( n = 0.5 - 4 \) and is known to contain information on both the dimensionality and the process of crystallisation.\(^{51,56}\) However, the interpretation of the Avrami exponent is very rarely straightforward since the above expression does not take into account that different stages of crystal growth may take place by different mechanisms.\(^{51}\) However despite the obvious weaknesses in the determination, the Avrami-Erofe’ev approximation does allow for a comparative study to be made between processes that occur under
similar conditions. Previous work documents the successful application of this equation to model a variety of solid state reactions, but it was generally found to be most appropriate over a data range of $0.15 < \alpha < 0.6$.$^{54}$ If the Avrami-Erofe’ev nucleation-growth model is valid for the reaction of interest a plot of $ln(-ln(1-\alpha))$ vs. $ln(t)$ should result in a straight line of slope $n$ and intercept $n \ ln(k)$ as derived from equation (4.4), otherwise known as a Sharp–Hancock plot.$^{57}$

$$ln[-ln(1-\alpha)] = n \ ln \ (t) + n \ ln \ k \quad (4.4)$$

The resultant Sharp – Hancock plots for both phases for the three different temperatures are shown in figure 4.14 and the kinetic data and Avrami exponent ($n$) derived from this plot are given in Table 4.9. The $n$ values (close to 1.0 for the $\gamma$-phase and between 3-4 for the $\alpha$-phase) for both phases are also in agreement with the observations made in figure 4.14, which suggest that the growth mechanism for the two phases is different and is not dependent upon temperature over the range of temperatures studied. For the $\alpha$-phase the exponent values are higher than that determined for the $\gamma$-phase. According to the analysis of Hulbert the difference in the exponent values corresponds to very different growth mechanisms.$^{58}$ In the analysis Hulbert proposed that it is possible to obtain some idea of solid state growth processes by comparing the Avrami exponent $n$ with a tabulated ‘ideal’ set of values derived from mathematical models. For the $\gamma$-phase the derived values being close to 1.0 is thought to be indicative of a system experiencing growth in two dimensions which is diffusion controlled and with a decreasing rate of nucleation. This proposed mechanism appears reasonable given that the $\gamma$-phase is often described as consisting of $\text{Bi}_2\text{O}_3^2+$ layers in an Aurivillius$^{19}$ type structure and furthermore is supported by the presence of platelets in the SEM pictures for all three the samples synthesised at temperatures between 110-150°C (see figure 4.8(a)).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature (K)</th>
<th>N</th>
<th>k/m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha</td>
<td>393</td>
<td>3.13</td>
<td>0.0339</td>
</tr>
<tr>
<td></td>
<td>403</td>
<td>3.80</td>
<td>0.0603</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>3.83</td>
<td>0.0693</td>
</tr>
<tr>
<td>Gamma</td>
<td>383</td>
<td>1.06</td>
<td>0.0270</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>1.19</td>
<td>0.0471</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>0.97</td>
<td>0.0634</td>
</tr>
</tbody>
</table>

Table 4.9. Avrami exponent ($n$) and rate of crystallisation ($k$) as derived from a Sharp-Hancock analysis of the data in figure 4.11.
Figure 4.14 Sharp-Hancock plots for the data recorded at various temperatures for the γ-phase (top) and the α-phase (bottom) over a data range of 0.15 < α < 0.6.

For the α-phase the values of between 3-4 are thought to be representative of three-dimensional growth, which is proposed to be via a phase-boundary controlled mechanism with a decreasing nucleation rate.\textsuperscript{58} Again this is also seems plausible from the SEM pictures of the α-phase (see figure 4.8(b)) (as it is proposed that 3 dimensional growth should result in spherical particles), when the synthesis temperature is below 140°C. It is interesting to note that the similar FWHM values at completion for both γ and α-phases appears to indicate that within the temperature
range of the investigation, changing the temperature has very little affect on the final crystallites’ size. Furthermore based on these findings for both γ and α-phases, it should be possible to arrest the reaction at any given time to produce smaller particle sizes with potentially a larger surface area.

4.4.3) Mo K-edge X-ray absorption spectroscopy

Although it appeared from the EDXRD that a poorly crystalline phase of the final product was formed at the initial stages of the reaction, Mo K-edge X-ray absorption spectroscopy revealed that the coordination environment of the molybdenum is completely different for the starting gel as compared to the final phase. Typical Mo K-edge X-ray absorption near edge structure (XANES) of the starting gel and the final product for γ-Bi₂MoO₆ are compared with Mo(VI) containing model compounds in figure 4.15. The features A and B (marked in figure 4.15) are related to the pre-edge and edge and correspond to 1s-4d (A) and the 1s-5p (B) quadrupole transitions respectively.¹⁸ Their intensities are known to be sensitive to the local coordination around molybdenum with non-centrosymmetric environments (ie. tetrahedral) resulting in a larger pre-edge feature A (due to better d-p orbital mixing relaxing the transition’s symmetry requirements) than octahedral environments. Consequently feature B in octahedral systems is more prominent as the lower degree of d-p orbital mixing in these environments will allow for a stronger transition. It is clear from a comparison of the Mo K-edge XANES that for the γ-Bi₂MoO₆ phase tetrahedrally coordinated Mo(VI) ions are present in the starting gel but the presence of a smaller pre-edge intensity (feature A) for the final, hydrothermally prepared crystalline γ-Bi₂MoO₆ is consistent with the crystallographically determined structure of Mo(VI) ions in a distorted octahedral coordination. Similarly the pre-edge and edge features of the crystalline α-Bi₂Mo₃O₁₂ catalyst are also consistent with the suggestion that a five-coordinated molybdenum species is present in the final material.¹⁸

A more thorough investigation of the as prepared gel and the γ-Bi₂MoO₆ material prepared by hydrothermal methods was undertaken by analysing the EXAFS from both samples. The analysis was performed taking a simple average local
structural arrangement consisting of oxygen atoms around molybdenum as the first neighbours and in figure 4.16(a-b) and 4.16(c-d) are shown the best fit between experimental and calculated Mo K-edge EXAFS data and associated Fourier transforms (FTs) with the results of this analysis shown in Table 4.10.

![Graph with intensity vs energy](image)

**Figure 4.15** Mo K-edge XANES of starting gel mixture of Bi$_2$MoO$_6$ crystalline Bi$_2$MoO$_6$, crystalline Bi$_2$Mo$_3$O$_{12}$, Bi$_2$MoO$_6$ gel, MoO$_3$, and Na$_2$MoO$_4$ are compared with model compounds containing tetrahedrally coordinated Mo(VI) (Na$_2$MoO$_4$) and octahedrally coordinated Mo(VI) (MoO$_4^{2-}$) compounds. The pre-edge feature “A” dominates the spectra in the materials possessing four-coordinated molybdenum whereas feature “B” is more prominent for six coordinated species.

Clearly the data recorded for the γ-gel are consistent with the XANES observation (as shown in figure 4.15) that the molybdenum is tetrahedral with an average bond length close to 1.78 Å. In contrast the best fit for the γ-Bi$_2$MoO$_6$ material formed after hydrothermal reaction, is obtained for a distorted octahedral environment with 2 long Mo-O bonds ca 2.25 Å and 4 short bonds at 1.76 Å.\(^{33,59}\) This is also consistent with the XANES measurement (also shown in figure 4.15), which shows the presence of octahedral molybdenum in this phase. Thus it has been clearly shown (in both cases) that these materials form directly from the respective gels and there is no evidence for the formation of any other crystalline phase during the course of the hydrothermal synthesis.
Table 4.10 Structural parameters determined from Mo K-edge EXAFS of the γ-gel and crystalline γ-Bi₂MoO₆.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo-O distance (Å)</th>
<th>N</th>
<th>$2\sigma^2$ (Å²)</th>
<th>R-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-gel</td>
<td>1.78</td>
<td>3.8</td>
<td>0.011</td>
<td>28.7</td>
</tr>
<tr>
<td>γ-Bi₂MoO₆</td>
<td>1.76</td>
<td>4</td>
<td>0.010</td>
<td>31.6</td>
</tr>
<tr>
<td></td>
<td>2.25</td>
<td>2</td>
<td>0.012</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.16 Best fit between experimental Mo K-edge EXAFS data and the calculated EXAFS and associated FT’s for the γ-gel (a-b) and crystalline Bi₂MoO₆ (c-d) is shown using the single scattering approximation. The solid line and the dashed curve represent the experimental and calculated data, respectively.
4.4.4) \textit{In situ} combined QuEXAFS/XRD study of the hydrothermal crystallisation of \(\gamma\)-Bi\(_2\)MoO\(_6\).

In order to obtain more information on the hydrothermal crystallisation of the \(\gamma\)-Bi\(_2\)MoO\(_6\) phase a combined QuEXAFS/XRD study was undertaken. In figure 4.17(a) and 4.17(b) the stacked Mo K-edge XANES data recorded during the formation of the \(\gamma\)-phase is shown along with the variation in the two commonly used signatures (marked A and B) employed for the interpretation of the Mo K-edge XANES data. The intensities of both the A and B features are seen to decrease and increase, respectively during the hydrothermal reaction, which is indicative of a coordination change from predominantly Mo(VI) in tetrahedral geometry of the starting gel to the distorted octahedron in \(\gamma\)-Bi\(_2\)MoO\(_6\). In contrast the XRD patterns (figure 4.16 (c)) already contained reflections corresponding to \(\gamma\)-Bi\(_2\)MoO\(_6\) suggesting that the phase had already formed even before data collection had begun. However as the experiment progressed it appeared as though there was a gradual shift of all of the reflections to lower d-spacings and that this shift coincided with a gradual change in the Mo(VI) coordination observed in the Mo K-edge XANES data, from tetrahedral to distorted octahedral. Assuming that these changes are related it is possible to propose that the transformation from tetrahedral to octahedral occurs as the Mo(VI) establishes Mo-O-Bi links with the Bi\(_2\)O\(_2\)\(^{2+}\) layers and pulls them closer together.
Figure 4.17 In (a) is shown the stacked Mo K-edge XANES data (for clarity only a small region is shown, although the entire Mo K-edge XAS pattern was recorded within 380 seconds) recorded sequentially with the XRD (which took 180 seconds resulting in a total interval time of 10 minutes between measurements). In (b) is shown the variation in the intensity of the features A and B with temperature. The main change was seen to occur at temperatures above 130°C, which is clearly due to formation of the \( \gamma \)-Bi\(_2\)MoO\(_6\) phase with molybdenum in six coordination. (c) Stacked XRD plots (recorded at 0.928 Å) obtained sequentially with the XAS data shown in (a). It appears from the XRD pattern that the \( \gamma \)-Bi\(_2\)MoO\(_6\) phase has already formed before data collection began. On heating to 130°C there is a shift in the position of all of the reflections to a lower d-spacing which coincides with a change in the intensity of the XANES features plotted in (a) and (b).
4.4.5) *In situ* combined QuEXAFS/XRD study of the crystallisation of the β-phase from the solid obtained after hydrothermal treatment.

A combined QuEXAFS/XRD study was also undertaken in order to follow the formation of the β-phase from the solid obtained after hydrothermal treatment. The facile formation of β-Bi₂Mo₂O₉ during heating of the solid obtained from the hydrothermally treated beta gel is shown in figure 4.18. Both the XRD pattern and the X-ray absorption spectra can be seen to change during the calcination process. In figure 4.18(a) the XRD pattern changes from the initial mixed phase material (amorphous and γ-phase) to the β–Bi₂Mo₂O₉ phase above 500°C. In figure 4.18 (b) and (c) the stacked Mo K-edge XANES data recorded during the formation of β phase is shown along with the variation of the two commonly used signatures in the XANES data (marked A and B) employed in the interpretation of the Mo K-edge XANES data. The intensities of both the A and B features are seen to increase and decrease, respectively, suggesting the coordination changes from the predominantly octahedral geometry of the starting gel (due to presence of γ-phase) to the tetrahedrally coordinated Mo(VI) indicative of β–Bi₂Mo₂O₉.
Figure 4.18 (a) Stacked XRD plot obtained using the position sensitive INEL detector, during the course of heating the solid obtained from hydrothermal synthesis (appropriate gel mixture containing chemical composition related to the β-phase was first hydrothermally treated at 140°C for 20 hours), from room temperature to 560°C at a rate of 5°C per minute. Results are shown from 200°C onwards as below this temperature the material condenses on losing water resulting in a distortion in the data. XRD patterns were collected at 0.928 Å. In (b) we show the stacked Mo K-edge XANES data (for clarity we show only the small region, although the entire Mo K-edge XAS pattern was recorded within 380 seconds) recorded sequentially with the XRD pattern shown in (a) (which took 180 seconds resulting in a total interval time of 10 minutes between measurements). In (c) we show the variation in the intensity of the features A and B with temperature. The main change was seen to occur at temperatures above 500°C, which is clearly due to the loss of the distorted six coordinate geometry resulting from the presence of γ-phase and the formation of β-phase with molybdenum in four coordination, consistent with the XRD data.
4.4.6) In situ EXAFS study of hydrothermally synthesised $\gamma$-Bi$_2$MoO$_6$ during calcination to 700°C.

In order to determine whether the hydrothermally prepared $\gamma$-Bi$_2$MoO$_6$ phase was susceptible to a phase transformation to form $\gamma'$-Bi$_2$MoO$_6$ during calcination to 700°C, as has been previously been observed for this material, an in situ EXAFS study was undertaken. Two graphs detailing the changes in local coordination with temperature are shown in figures 4.19 (a) (change in Mo-O bond lengths) and 4.19 (b) (change in disorder). The refinement of the data was carried out using a simple two-shell Mo-O model (to represent the distorted Mo-O$_6$ octahedron in $\gamma$-Bi$_2$MoO$_6$) to avoid correlation effects between the coordination number and Debye-Waller factors. The first shell was comprised of four oxygens with an average Mo-O bond length of 1.79 Å whilst a second shell of two oxygens was constructed with a bond length ca 2.25 Å. Initially a gradual increase in both bond length and disorder (figure 4.19) for both Mo-O shells was observed as the temperature increased which reflected an increase in the thermal disorder of the system. On reaching 700°C the Debye-Waller factor for the second shell had reached a value of 0.035 $2\sigma^2$ which coincided with a maximum average Mo-O distance of 2.31 Å. Such a high disorder and bond length value for the Mo-O$_2$ shell at this temperature has previously been reported as evidence of the complete or near complete dissociation of these two oxygens from molybdenum leaving the tetrahedral coordination typical of molybdenum in the $\gamma'$-Bi$_2$MoO$_6$ structure. An XRD pattern recorded on the material after the in situ calcination had finished confirmed the transformation to $\gamma'$-Bi$_2$MoO$_6$ phase (figure 4.19 (c)).
Figure 4.19 (a) Change in bond distances and (b) mean square displacement derived from EXAFS measurements carried out during heating of γ-Bi$_2$MoO$_6$ to 700°C using a two shell model to represent the distorted Mo-O$_6$ octahedra. The smooth upward trend up to 650°C in both data plots corresponds to the effects of heat on the Mo-O bond lengths. The sudden increase in the first shell average distance between 100 and 200°C is most likely to be an artefact of the data collected/data fitting at this temperature rather than any real change in the system (it is noted however that the values recorded are within the error limits of the technique). On reaching ca 700°C the average bond length and Debye-Waller factor for the second shell reached 2.31 Å and 0.04 Å$^2$ respectively suggesting that this shell has disappeared leaving a tetrahedral Mo-O$_4$ arrangement indicative of γ-Bi$_2$MoO$_6$. An XRD pattern taken (complete with indexing lines from the ICSD database entry number 40215) after calcination of γ-Bi$_2$MoO$_6$ at 700°C (c) in a separate experiment confirms the formation of γ-Bi$_2$MoO$_6$.

4.4.7) Effects of reactant gel pH upon the final crystal structure

For hydrothermal reactions it has been demonstrated that careful control of pH is important when trying to prepare a phase pure material. With respect to the synthesis of bismuth molybdates it has been suggested that pH is important since a
variety of polymeric molybdates have been proposed to exist in solution\textsuperscript{36,38}. Therefore a study on the effects of pH on the final crystal structure was undertaken. The study was broken down into two parts. The first part involved an XRD study of the three bismuth molybdate phases prepared at 140°C for 20 hours between a pH range of 1.0 - 7.0. For the second part a Mo K-edge XANES study was undertaken on the molybdate anions in solution and precursor gel in order to determine if it was possible to distinguish between any polymeric molybdate species. The results of this study are shown in Table 4.11. It appears that, as with other hydrothermally prepared materials, pH is also important when trying to prepare a phase pure form of the three bismuth molybdate catalysts by such methods. Arguably it is the most important factor with particular reference to the preparation of the γ-phase where even a gel with α-stoichiometry at pH 7.0 forms γ-Bi\textsubscript{2}MoO\textsubscript{6}. Furthermore it is the dominant phase present in gels with α and β-stoichiometry above pH 4.0 and is also present for every synthesis carried out using the γ-gel over the entire pH range used in this study. However as the pH drops from 7.0 to 1.0 the crystallinity of the phase decreases. Conversely for the α-phase a combination of both the correct reactant stoichiometry and pH is necessary in order for it to form. Thus far the attempts to form the β-phase have been unsuccessful and with respect to this study it appears that even the careful control of pH is not enough to form this phase.

<table>
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<tr>
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<th>γ-gel</th>
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<td>α</td>
<td>Unknown + α</td>
<td>Amorphous + γ</td>
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<tr>
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Table 4.11 Detailing the effects of pH and reactant stoichiometry on the final crystal structure. All samples were hydrothermally treated at 140°C for 20 hours.

In figures 4.20 and 4.21 is shown the Mo K-edge XANES measurements taken for a series of molybdenum ions in solution under various pH conditions. Spectra were recorded on solutions containing a typical amount of dissolved ammonium heptamolybdate used for the preparation of the gamma phase (0.44 g), at pH 1.0, 4.0, 6.0, 7.0 and 9.0. Due to the limited time in which we had to record synchrotron data the Mo K-edge XANES measurements were limited to these solutions only.
Plotted in figure 4.20 are the Mo (VI) XANES measurements on three solutions of molybdate anions at pH 1.0, 4.0 and 7.0 and three reference spectra for tetrahedral Mo (VI) containing sodium molybdate, the as prepared α-phase containing five coordinated Mo (VI) ions and the octahedral Mo (VI) containing ammonium heptamolybdate. It is clear from this figure that the Mo (VI) XANES features for the molybdenum ions in solution at pH 1.0 and 4.0 are very similar to that of the octahedral Mo(VI) containing ammonium heptamolybdate whereas in comparison the spectra recorded at pH 7.0 is more similar to the tetrahedral coordinated Mo (VI) ions of sodium molybdate. In a second Mo K-edge XANES (figure 4.21) study conducted on solutions at pH 4.0, 6.0, 7.0 and 9.0 it was observed this time that the 7.0 and 9.0 solutions contained tetrahedral molybdate species whereas the 4.0 and 6.0 samples appeared octahedral. Furthermore it was also possible to convert the Mo (VI) anions at pH 1.0 from octahedral to tetrahedral by increasing the pH of the solution to 7.0. From the results of this Mo K-edge XANES study it is possible to identify a clear boundary between the types of molybdate species as a function of pH. Samples dissolved in water at pH 6.0 to pH 1.0 contained octahedral Mo(VI) species whereas between 7.0 and 9.0 the molybdate species were tetrahedral. This seemed to correlate well with the results obtained in the hydrothermal crystallisation study of the gamma phase (Table 4.9) where it was observed that it was difficult to form this phase below a pH of 7.0.
Figure 4.20 Mo K-edge XANES for Mo(VI) reference compounds and for ions in solution at pH 1.0, 4.0 and 7.0. Under low pH conditions the molybdenum coordination appears to be octahedral but under neutral conditions the coordination seems to drop to tetrahedral.

Figure 4.21 Mo K-edge XANES for Mo(VI) ions in solution at pH 4.0, 6.0, and 7.0. The XANES spectra identified as pH 7.0 (adjusted) has undergone pH adjustment up to 7.0 after dissolution in low pH (1.0) conditions. Again it appears that for pH < 7.0 molybdenum appears to be in octahedral coordination but when > 7.0 appears tetrahedral.

In order to obtain more information on the nature of the Mo(VI) environment at pH 7.0 the Mo K-edge EXAFS was analysed. Analysis of the EXAFS data were performed taking a simple average local structural arrangement consisting of oxygen atoms around the molybdenum as the first neighbours and in figure 4.21 is shown the
best fit between experimental and calculated Mo K-edge EXAFS data and FTs. As with the previous XANES study the EXAFS analysis confirms the existence of four coordinated molybdenum with an average bond length of 1.78 Å. Since there is no change in the frequency of the isolated EXAFS oscillations out to 15 Å⁻¹ it appears that the tetrahedral Mo (VI) containing species are isolated MoO₄ type units (possibly MoO₄²⁻ type anions).

![Figure 4.22](image)

**Figure 4.22.** (a) Mo K-edge EXAFS (solid lines) and the calculated EXAFS (dotted lines) and associated FT’s (b) for Mo(VI) ions in solution at pH 7.0 recorded up to 15 Å⁻¹.

A comparison of the EXAFS data obtained from both the γ-gel and in solution at pH 7.0 is shown in figure 4.23 and their identical oscillation frequency confirms the suggestion that a similar molybdenum environment is present in both samples. This would tend to suggest that the simple mixing of the acidified bismuth nitrate with the molybdate anions in solution at pH ≈ 7.0 does not significantly alter the molybdenum (VI) coordination environment.
4.5) Summary and conclusions

In summary, it has been possible to produce, employing hydrothermal methods, over a short reaction period, crystalline Bi$_2$Mo$_n$O$_{3n+1}$ (where $n=1,2,3$) phases with higher surface areas as compared to those synthesised by conventional preparative methods. The in situ time resolved EDXRD studies (and XRD/QuEXAFS in the case of γ-phase) clearly suggest that there are no intermediate phases involved in the formation of highly crystalline α and γ phase bismuth molybdate solids. Furthermore it has been shown that it is conceivable to tailor the material’s properties by controlling the synthesis conditions, namely, temperature, time and stoichiometry. The crystallisation data were modelled using the Avrami-Erofe’ev nucleation-growth model and it is concluded that the growth mechanisms for the two phases are different. For all three of the temperatures studied for the α-phase, it is thought that the phase undergoes three-dimensional growth whereas for the γ-phase, initially, two-dimensional growth was observed. Both of these observations seemed to be confirmed by SEM images, which suggested that the α-phase consisted predominantly of round particles whereas the γ-phase was made up of platelet like particles. In both cases, the overall rate of reaction was seen to increase with temperature. Although it was not possible to prepare β-phase directly using hydrothermal methods, employing the
composition and conditions described here, it has been possible to produce a phase pure material from a hydrothermally produced precursor material by heat treatment at ca 500°C.

Further studies on the hydrothermally prepared materials suggested that particular combinations of both stoichiometry and pH are necessary to form phase pure α and γ-phases. However in the case of γ-phase the more important of the two variables is pH since at pH ≥ 7.0 no matter which Bi:Mo stoichiometry is used, phase pure γ-phase always forms. The XANES/EXAFS investigation into the effect of pH on Mo (VI) coordination may hold the clue as to why this is so. At a pH = 7.0 it is clear that tetrahedral molybdenum predominates and is probably due to the existence of MoO$_4^{2-}$ species. This molybdenum environment remains intact even after mixing with acidified bismuth nitrate in the γ-gel before hydrothermal reaction. With only a small drop in pH to 6.0 the coordination changes to octahedral and a hydrothermally treated γ-gel at this pH results in poorly crystalline γ-phase. However little is known how pH can affect the type of bismuth species present before reaction although many studies have suggested that Bi(OH)$_3$ is the most likely form to exist above a pH of 1.5.$^{38}$ Since the preparation of the γ-phase can be conducted at pH 7.0 or above it is possible to propose the following generalised reaction scheme (equation 4.5):

$$2 \text{Bi(OH)}_3 + \text{H}_2\text{MoO}_4 \rightarrow \text{Bi}_2\text{MoO}_6 + 4\text{H}_2\text{O}$$  \hspace{1cm} (4.5)

This reaction scheme is given further credibility by the fact that the pH of the filtrate after reaction was determined to be at ca 7.0.

The in situ EDXRD and combined XRD/QuEXAFS measurements suggest that the hydrothermal formation of the γ-phase takes place in two distinct stages. The first part is thought to be the growth of Bi$_2$O$_5^{2+}$ type layers and this is then followed by a reaction with MoO$_4^{2-}$ to produce the final γ-Bi$_2$MoO$_6$ phase. Similar behaviour has been observed for the crystallisation of this phase from a co precipitation/calcination procedure.$^{63}$

Although similar hydrothermal methods for the formation of the γ-phase have previously been reported in the literature,$^{64,65}$ these have normally been undertaken over a much longer time period, at higher temperatures or in metal halide solutions. This present study offers a more convenient and reproducible route, without the use of
any metal halide solutions, for the formation of a superior industrially important bismuth molybdate catalyst.
4.6 References


(47) Avrami, M. *Journal of Chemical Physics* 1939, 7, 1103.
(48) Avrami, M. *Journal of Chemical Physics* 1940, 8, 212.
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Chapter 5

A study of the redox behaviour of cobalt and manganese substituted into the framework of MAIPO-5 and MAIPO-18

5.1) Chapter overview

This chapter contains the results from an investigation into the redox behaviour of cobalt and manganese ions substituted into the microporous aluminophosphate structures AIPO-5 and AIPO-18. Results obtained from EXAFS, EPR measurements and the catalytic conversion of methanol to olefin (MTO), suggested that the transition metal centres were initially incorporated into the tetrahedral sites of both AIPO frameworks as $M^{2+}$ (where $M = \text{Co and Mn}$) species in the high spin state. On calcination to remove the structure directing agent a decrease in EPR signal intensity and the shortening of the average M-O bond lengths, as determined by EXAFS, strongly supported the notion of oxidation of $M^{2+}$ to $M^{3+}$. However, the extent of oxidation was found to be dependent upon both the metal centre and structure type with the manganese ions in AIPO-18 determined to have undergone the greatest degree of oxidation.

5.2) Introduction

Since zeolites are used in the petrochemical industry for a variety of different cracking, isomerisation and alkylation reactions$^{1,2}$ they are perhaps the most important of all of the inorganic oxides used in catalytic reactions today. However it is not just in catalysis that zeolites have found an application since they are also used for water softening, gas separation and desiccation.$^{1,2}$ The application of these microporous aluminosilicates centres around their large and sometimes intricate internal structure consisting of a framework of Si(IV)O$_4$ and Al(III)O$_4$ tetrahedra (arranged in a way that avoids the formation of tetrahedral Al-O-Al linkages)$^3$ containing channels and/or cages of molecular dimension$^3$ and these ‘voids’ are normally filled with a variety of charge balancing cations (such as alkaline earth metals) and water. They occur naturally within the Earth’s crust but with such a wide range of applications having
already been identified it is perhaps unsurprising that a great deal of research effort has focussed on the preparation of synthetic analogues of these natural constructions and on the design of new topologies altogether. With time this principle was extended further to include the preparation of new zeolite like structures (or Zeotypes) by substituting other elements of the periodic table for either aluminium or silicon. In particular a whole new class of zeotypes were synthesised by replacing the silicon with varying amounts of phosphorus to produce either silicoaluminophosphates (abbreviated as SAPOs) or when all of the silicon is replaced, aluminophosphates (AlPOs). Since the initial discovery a whole variety of aluminophosphate structures have been synthesised some of which are structural analogues of either minerals or zeolites (eg. SAPO-42 possessing the zeolite A structure) whilst others (such as AlPO-5 and −18) are novel open framework species and are shown in figure 5.1.

![Structural characteristics of two microporous aluminophosphate structures.](image)

**Figure 5.1** Structural characteristics of two microporous aluminophosphate structures. The aluminate \((\text{AlO}_3\text{)}_6\) tetrahedra are coloured red and \((\text{PO}_4)\) tetrahedra purple. The nomenclature used to describe these structures has been standardised to AlPO-n where the suffix refers to a particular framework code number and a three letter code (applicable to all zeolite/zeotype structures). The AlPO-5 (AFI) structure is composed of 4, 6 and 12-ring straight channels interconnected by 6-ring windows to produce near circular channels with a diameter of 7.3 Å whereas AlPO-18 (AEI) contains ellipsoidal cages either side of an 8-ring window with a much smaller diameter of approximately 3.8 Å.

It was soon discovered that it was possible to substitute other chemical elements including transition metals such as iron into the framework to produce another class of material, the metal substituted aluminophosphates or MAIPO. However it appears as though there is generally a limit on how much of these metal substituents can be incorporated before the material becomes thermally unstable after the structure directing agent (SDA) is removed; a necessary procedure in order to free up the internal area for any potential application.
5.2.1) Synthesis of (M)AlPOs

As with the synthesis of microporous aluminosilicates, (M)AlPOs are prepared under hydrothermal conditions from an alkaline gel containing a source of aluminium (typically Al(OH)₃), phosphorus (normally as H₃PO₄) and a SDA, which is typically either an amine or a quaternary ammonium salt. At this stage metal substituents (if required to make an MAIPO) are added in the form of a soluble salt. Reactions are normally carried out in a Teflon lined autoclave for anything up to 2 weeks over a temperature range of 125-200°C. However extremes of both temperature and time often produce a variety of condensed phases including berthierite (structurally analogous to quartz SiO₂), tridymite type AlPO₄ and the dihydrates (AlPO₄·2H₂O) variscite and metavariscite. The optimum conditions required to create a phase pure form is not just dependent upon time and temperature but also the nature of the SDA, the species of metal salt and pH of the reactant gel. However perhaps the most critical ingredient for the formation of microporous AlPOs is the SDA since without this only dense phases are formed.

The substitution of different metal ions in place of either Al³⁺ or P⁵⁺ to create a MAIPO can change the chemical properties of the AlPO framework. For example when divalent ions such as Zn²⁺ or Mg²⁺ are incorporated in place of Al³⁺ a high surface area shape selective acid catalyst is produced (figure 5.2) when the SDA is removed and H⁺ ions are introduced in order to maintain the electroneutrality of the framework.

![Figure 5.2 Schematic illustrating the formation of a Brønsted acid centre in various MAIPO-n structures. The centre is created when the SDA is removed during calcination (at ca 550°C) and H⁺ ions are introduced to maintain the electroneutrality of the framework. Such acid centres have been implicated as being necessary for the catalytic conversion of methanol to olefin and gasoline (MTO/MTG).](image-url)
Other successful applications of MAIPOs, which make use of the different chemical properties imparted by the metal substituent, include the catalytic isomerisation of butene, the oxyfunctionalisation of alkanes and an ion exchange capacity.\textsuperscript{9-13}

5.2.2) The nature of the active site in MAIPOs

Thus far perhaps the most important successful application of MAIPOs (\(M = \text{Co, Mn and Fe}\)) has been as catalysts for the oxyfunctionalisation of alkanes.\textsuperscript{10,11,14,15} However the nature of the active site (which is normally the substituted metal since the corresponding AlPO-n structures do not show such catalytic activity) is not so well known or understood. For example for the cobalt substituted aluminophosphates (CoAlPOs) there is disagreement over whether cobalt exists as Co\(^{2+}\) or Co\(^{3+}\) after SDA removal. Most of the previous studies have used EPR to determine the cobalt oxidation state since the technique is thought to be sensitive to the amount of paramagnetic tetrahedral Co\(^{2+}\) present but insensitive to tetrahedral Co\(^{3+}\). As such the reduction in the EPR signal intensity observed in a variety of CoALPOs has been rationalised in terms of the oxidation Co\(^{2+}\) to Co\(^{3+}\). However, this conclusion has been disputed.

5.2.3) Summary of previous work on CoAlPOs

Initially work carried out by Iton et al.\textsuperscript{16} on CoAIPO-5 and CoSAPO-34 proposed that the drop in the integrated EPR signal intensity at 4 K after calcination was due to oxidation of tetrahedral Co\(^{2+}\) to the EPR inactive tetrahedral Co\(^{3+}\). This drop of between 70 and 80% for both samples was accompanied by a colour change in both samples (from blue to yellow/green) and changes in the UV-Vis spectrum. However, both Kurshev et al.\textsuperscript{19} and Prakash et al.\textsuperscript{20} disputed this redox behaviour of cobalt in CoAIPOs in work on CoAIPO-5 and on CoAIPO-41 and -44, where in both studies it was observed that the difference in the integrated signal intensity at 4 K had practically vanished at 20 K. Furthermore the calcined CoAIPO-5 sample showed unusual non Curie-Weiss like temperature-dependent behaviour and it was concluded
therefore that the reduction in signal intensity was due to a change in the symmetry of the Co$^{2+}$ coordination environment from $T_d$ to $D'_{2d}$ as a result of an interaction with molecular oxygen.

Barrett et al.$^{18}$ also proposed a change in the cobalt oxidation state to account for the change in the average first neighbour Co-O distances, observed using EXAFS, after calcination of structure types CoAlPO-5, -36, -18, and CoSAPO-44. They proposed that the extent of Co$^{2+}$ oxidation depended upon structure type and that this could be estimated from the changes in Co-O bond lengths by using the Vegard relationship. By using this method the degree of Co$^{2+}$ oxidation was calculated to be only ca 20% for CoAlPO-5 species but almost 100% for the CoAlPO-18 material. However it was also noted in the study that the coordination numbers for all of the CoAlPOs dropped after calcination. In the case of the partially oxidised -5 and -36 structures this was explained as being due to the introduction of oxygen vacancies within the framework (figure 5.3) whereas for the totally oxidised -18 structure it was proposed that the newly formed tetrahedral Co$^{3+}$ species tended to distort to produce a coordination environment of one long and three short Co-O bonds.$^{18}$ The partial redox behaviour of cobalt in some of the CoAlPO structures was also confirmed by Weckhuysen and coworkers$^{17}$ for a number of CoAlPO-n (where n = 5, 11, 41 and 44) materials although the difference between the two EPR signals at 10 K was estimated to be closer to 30% for all of the materials studied. However, when Thompson et al.$^{21}$ compared the EXAFS and EPR data in a separate study on CoAlPO-5 they proposed that there was no actual decrease in the EPR signal intensity but that it merely became more broad after calcination and that this broadening, coupled with the reduction in the average EXAFS Co-O bond lengths, could be explained by the production of vacancies in the CoAlPO framework as described by Barrett et al.$^{18}$ and shown in figure 5.3(a).
Figure 5.3 (a) Proposed local atomic environment around cobalt in calcined CoAIPO-5 & -36. The cobalt shown in this figure remains as Co$^{2+}$ and is associated with the formation of a vacancy (formed via a dehydroxylation reaction) represented by the empty box. However up to 30% is thought to oxidise to Co$^{3+}$. In contrast for CoAIPO-18 it has been proposed that almost total oxidation to Co$^{3+}$ takes place on calcination with the formation of a distorted tetrahedral site as detailed in (b). The distortion involves an elongation of one of the Co-O bonds to 2.04 Å whilst the other three remain at 1.83 Å$^{18}$.

5.2.4 MnAIPO-n structures

As with the CoAIPO-n structures so there are many questions that exist with respect to manganese incorporation in MnAIPO-n samples. Thus far substitution attempts have been limited to only a handful of AIPO-n structures with evidence for the successful incorporation of manganese elucidated mainly from EPR (including electron spin echo modulation (ESEM)) studies although other techniques such as EXAFS, XRD and IR have also been applied$^{5,22-26}$. In general it appears as though the successful isomorphous substitution of manganese into a framework site is not always assured with factors such as structure type and concentration thought to play a role. For example it has been proposed by Brouet et al.$^{27}$ using EPR and ESEM to study MnAIPO-11, that when using a high concentration of manganese (ie. 10% of the phosphorus content) in the synthesis, the majority of the manganese exists as extraframework species. However, when the concentration was lowered to ca 0.1% the successful incorporation of all of the manganese takes place as evidence by ESEM.$^{27}$ Similar observations have been made with regard to MnAIPO-5 where it has been generally accepted that a small proportion of manganese used in the synthesis mix does substitute into the AIPO-5 framework (whether this is for phosphorus or aluminium is disputed$^{23}$ but the majority of the metal is thought to exist as extraframework species.$^{26,28}$
A question mark also exists over the coordination of the framework substituted manganese in as prepared MnAlPOs with many studies suggesting that the EPR fine structure observed for these materials is due to high spin octahedral Mn$^{2+}$. This has been inferred from the hyperfine coupling values derived from these spectra although more recently it has been suggested that these values could also be indicative of manganese in tetrahedral coordination.\textsuperscript{47} Either way it is clear that thus far the nature of the manganese species in these materials is unclear.

Like CoAlPOs, MnAlPO-n types (where n = 18, 34 and 36) have been successfully employed as catalysts for the oxyfunctionalisation of alkanes and it has been proposed that the catalytic activity is related to the amount of Mn$^{3+}$ (formed from the oxidation of Mn$^{2+}$) present in the framework after calcination.\textsuperscript{10} Evidence for the formation of Mn$^{3+}$ in calcined MnAlPOs has been proposed on the basis of a reduction of average Mn-O bond lengths as observed from EXAFS measurements and a reduction in EPR signal intensity (with reference to MnAlPO-5)\textsuperscript{28,29} since Mn$^{3+}$ like Co$^{3+}$ is also thought to be EPR inactive. However as with the CoAlPOs the degree of oxidation appears to dependent upon structure type.

5.2.5) Aims and objectives

In this thesis chapter the results are reported from a combined EXAFS, EPR and catalytic study on some cobalt and manganese substituted AIPOs. For these experiments small amounts (0.5% of the total aluminium content) of the two transition metals have been isomorphously substituted into the structure types AIPO-5 and \textsuperscript{18}. Small amounts of dopant were used since this avoids some of the problems mentioned previously when too much substituent is used in the synthesis mix, such as the formation of extraframework species and structural instability. These AIPO-5 and \textsuperscript{18} structure types were chosen since it has been shown by the determination of bond length measurements from EXAFS that the apparent degree of oxidation from M$^{2+}$ to M$^{3+}$ is much greater for metals in the MAIPO-18 (\approx 85%) structure than in \textsuperscript{5} (20-65%). Therefore a systematic EPR study comparing the signals obtained before and after calcination for the two structure types and metal substitutes, when considered along with the EXAFS data, should provide further evidence for redox behaviour for
these samples. In addition to this the catalytic conversion of methanol to olefin (MTO) was performed since it is well-known that SAPO-34, and its nickel substituted analogue are very effective in converting methanol to both ethylene and propylene\textsuperscript{30,31} and AIPO-18 is structurally very similar (the main difference being the way in which the double six rings are stacked, otherwise their pore dimensions are identical). The majority of synthesis and catalytic studies in the literature are concerned with SAPO-34 and a variety of metal substituted analogues, such as CoAIPO-34, NiSAPO-34 and FeSAPO-34\textsuperscript{32,33} and it is therefore and somewhat surprising to see that only a few studies have been devoted to the hetero-atom substituted AIPO-18 structure\textsuperscript{34,35} since although the overall architecture and thermal stability of both AIPO-34 and AIPO-18 related structures are very similar, a greater number of different hetero-atom compositions are possible. For example, it has been shown that SAPO-18 can be prepared with Si/Al ratio ranging from 0.0 to at least 0.1, whereas in contrast SAPO-34 can only be prepared over a much smaller composition range of between 0.09 and 0.11.\textsuperscript{34}

Because of this flexibility in the composition of the MAIPO-18 structure, we have carried out a systematic investigation of two transition metal ion substituted AIPO-18 materials for the production of light olefins from methanol. To do so pure AIPO-18 was synthesised as well as cobalt and manganese substituted analogues (CoAIPO-18 and MnAIPO-18) with a concentration of metal substituent ranging from 0.05 – 4 atom percent of the total aluminium content, and carried out detailed catalytic studies to investigate the nature of selectivity and activity as a function of both transition metal incorporation. The results clearly show that manganese and cobalt substituted systems are very good catalysts for the selective conversion of methanol to both ethylene and propylene and that the catalytic conversion improved with increasing amounts of metal substitution.
5.3) Experimental

5.3.1) Preparation of MAIPOs (where M = Co, Mn).

As mentioned previously MeAlPOs are normally prepared via the hydrothermal treatment of a synthesis gel containing a source of metal ions, aluminium, phosphorus, template and water. Similar procedures were used to prepare both Mn/CoAlPOs with varying degrees of metal incorporation as detailed below.

5.3.1.1) Preparation of CoAlPO-5

For the preparation of 0.5% cobalt substituted CoAlPO-5 the following procedure was used. 0.995 molar equivalents of aluminium hydroxide (1.55 g) (Aldrich) was dissolved in 8 ml of water (Fluka) and to this was added 1.0 molar equivalents (2.31 g) of 85% orthophosphoric acid (Aldrich). To this mix 0.02 g of cobalt acetate tetrahydrate (0.005 molar equivalents) (Aldrich) dissolved in 1 ml of water was added and the contents were thoroughly mixed. Finally 2.02 g (1.0 molar equivalent) of triethylamine (TEA) (Aldrich) was added as a SDA and once again this mixture was well mixed together. The pH of the final gel was adjusted to ca 3.5 before it was transferred to a Teflon liner, which was then filled to 30% of its capacity with the mixture before it was sealed in an autoclave and heated at 175°C for four hours. The autoclave was cooled and the contents (a blue powder) were washed and dried at 100°C for six hours. The same experimental procedure was used for the preparation of CoAlPO-5 with increasing amounts cobalt (up to 4%), details of which are given below in table 5.1.

Table 5.1 molar compositions used in the preparation of AFI structure Co$_{0.5x}$Al$_{1-x}$PO$_4$,SDA$_y$ with increasing cobalt concentration.

<table>
<thead>
<tr>
<th>Cobalt (x)</th>
<th>Al(OH)$_3$ (1-x)</th>
<th>H$_3$(PO)$_4$</th>
<th>SDA (y)</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.99</td>
<td>1.0</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>0.02</td>
<td>0.98</td>
<td>1.0</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>0.04</td>
<td>0.96</td>
<td>1.0</td>
<td>1</td>
<td>25</td>
</tr>
</tbody>
</table>
5.3.1.2) Preparation of CoAlPO-18

For the preparation of 0.5% cobalt substituted CoAlPO-18 we used the following procedure. 0.995 molar equivalents (1.55 g) of aluminium hydroxide (Aldrich) was dissolved in 8 ml of water (Fluka) and to this was added 2.31 g (1.0 molar equivalent) of 85% orthophosphoric acid. To this mix 0.02 g of cobalt acetate tetrahydrate (Aldrich) (0.005 molar equivalents) dissolved in 1 ml of water was added before the contents were thoroughly mixed. Finally 2.2 g (0.85 molar equivalents) of N’N-diisopropylethylamine (DIPE) (Aldrich) was added as the SDA and once again this mixture was well mixed together. The pH of the final gel was adjusted to ca 8.0 before it was transferred to a Teflon liner (30% fill) before it was sealed in an autoclave and heated at 150°C for 96 hours. The autoclave was cooled and the contents (a blue powder) were washed and dried at 100°C for six hours. The same experimental procedure was used for the preparation of CoAlPO-18 with increasing amounts cobalt (up to 4%), details of which are given below in table 5.2.

Table 5.2 molar compositions used in the preparation of AEI structure Co$_x$Al$_{(1-x)}$PO$_4$, SDA$_y$, with increasing cobalt concentration.

<table>
<thead>
<tr>
<th>Cobalt (x)</th>
<th>Al(OH)$_3$ (1-x)</th>
<th>H$_3$(PO)$_4$</th>
<th>SDA (y)</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.99</td>
<td>1.0</td>
<td>0.85</td>
<td>25</td>
</tr>
<tr>
<td>0.02</td>
<td>0.98</td>
<td>1.0</td>
<td>0.85</td>
<td>25</td>
</tr>
<tr>
<td>0.04</td>
<td>0.96</td>
<td>1.0</td>
<td>0.85</td>
<td>25</td>
</tr>
</tbody>
</table>

5.3.1.3) Preparation of MnAlPO-5

For the preparation of 0.5% manganese substituted MnAlPO-5 the procedures that were followed were similar to those described above for CoAlPO-5 except that 0.027 g of manganese acetate tetrahydrate (0.005 molar equivalents) (Aldrich) were used instead of cobalt acetate tetrahydrate and the autoclave contained a white powder after reaction. The same experimental procedure was used for the preparation of MnAlPO-5 with increasing amounts manganese (up to 4%), details of which are given below in table 5.3.
Table 5.3 molar compositions used in the preparation of AFI structure Mn_{\alpha}Al_{(1-x)}PO_{4}.SDA_{y} with increasing manganese concentration.

<table>
<thead>
<tr>
<th>Manganese (x)</th>
<th>Al(OH)_{3} (1-x)</th>
<th>H_{3}(PO)_{4}</th>
<th>SDA (y)</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.99</td>
<td>1.0</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>0.02</td>
<td>0.98</td>
<td>1.0</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>0.04</td>
<td>0.96</td>
<td>1.0</td>
<td>1</td>
<td>25</td>
</tr>
</tbody>
</table>

5.3.1.4) Preparation of MnAlPO-18

For the preparation of 0.5% manganese substituted MnAlPO-18 the procedures that were followed were similar to those described above for CoAlPO-18 except that 0.027 g of manganese acetate tetrahydrate (0.005 molar equivalents)(Aldrich) were used instead of cobalt acetate tetrahydrate and the autoclave contained a white powder after reaction. The same experimental procedure was used for the preparation of MnAlPO-18 with increasing amounts manganese (up to 4%), details of which are given below in table 5.4.

Table 5.4 molar compositions used in the preparation of AEI structure Mn_{\alpha}Al_{(1-x)}PO_{4}.SDA_{y} with increasing manganese concentration.

<table>
<thead>
<tr>
<th>Manganese (x)</th>
<th>Al(OH)_{3} (1-x)</th>
<th>H_{3}(PO)_{4}</th>
<th>SDA (y)</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.99</td>
<td>1.0</td>
<td>0.85</td>
<td>25</td>
</tr>
<tr>
<td>0.02</td>
<td>0.98</td>
<td>1.0</td>
<td>0.85</td>
<td>25</td>
</tr>
<tr>
<td>0.04</td>
<td>0.96</td>
<td>1.0</td>
<td>0.85</td>
<td>25</td>
</tr>
</tbody>
</table>

5.3.2) Characterisation

The phase purity of the as-synthesised materials (dried at 100°C) were verified by X-ray diffraction measurements recorded using a Siemens D500 (of Bragg-Brentano geometry) utilizing Cu-K\(\alpha\) radiation. EPR measurements were carried out on a Bruker ESP 300 operating at X-band frequencies with a typical microwave power output of 1 mW. In a typical experiment 0.5 g of MAIPO sample was placed in a specially designed in situ cell (figure 5.4) which allowed for either calcination of the sample at 550°C in flowing nitrogen followed by an oxygen atmosphere to remove the template or for simple dehydration of the as prepared sample at 150°C. The heat treated sample was then transferred to the attached quartz EPR tube which was filled
to a depth of at least 2.5 cm before it was sealed under vacuum since the presence of either oxygen and or organics in the atmosphere could affect the sensitivity of the measurements. Measurements were carried out from 7 to 50 K in order to obtain information on the paramagnetic species in the framework. For this work a magnetic field sweep width of 7000 Gauss (G) (~1000 to 6000 G) was employed with a resolution of 50 mG to produce a first derivative trace for the rate of change of absorption vs. field strength as shown in figure 5.12. The area under the first derivative plot was determined using a double integration approach, which allowed for a direct comparison of signal intensity for the dehydrated and as prepared samples. A well characterised reference EPR spectra (CuSO₄ in KCl) was also recorded for each measurement (at room temperature) and the integrated area measurements normalised with respect to this value in order to correct for any variation in instrument response.

Figure 5.4 In situ apparatus for EPR sample preparation. Gas flows from the arrow marked ‘Gas in’ through the sample (held at elevated temperatures during both calcination and dehydration) and out through the tap at ‘Gas out’. The EPR tube into which the sample is transferred for measurement is connected from the right hand side.
5.3.2.1) Theory of EPR spectroscopy

Electron Spin or Paramagnetic Resonance (ESR/EPR) spectroscopy is a technique that is used to probe the electron spin state of paramagnetic species by observing the interaction of unpaired electrons in a magnetic field with microwave radiation. The technique works on the principle that electrons in a paramagnetic sample when placed in a magnetic field, will either align themselves with the field (parallel to) or against it (antiparallel to it). This energy splitting is known as the Zeeman splitting and is demonstrated in figure 5.5. The lower energy (parallel) arrangement of these two states is more populated than the higher energy state (the distribution between the two being given by the Maxwell-Boltzmann expression (equation. 5.1)) and the technique of EPR is to induce electronic transitions between the two spin states by the process of radiation absorption equal to the splitting energy $\Delta E$.

$$\frac{N_2}{N_1} = \exp \left( - \frac{\hbar \nu}{kT} \right)$$  \hspace{1cm} (5.1)

The energy $\Delta E$ is a function of the following equation (5.2)

$$\Delta E = g\beta H$$  \hspace{1cm} (5.2)

Where $H$ is proportional to the strength of the magnetic field, $\beta$ the magnetic moment of the electron (in Bohr magnetons) and $g$ the spectroscopic splitting or Landé factor which is a measure of the contribution of the spin and orbital motion of the electron to its total angular momentum which for a free electron is close to 2.0 but for transition metal systems such as those that contain $\text{Co}^{2+}$ these values can be as high as 5 reflecting different spin-orbit coupling effects. Another important condition affecting the transition probability is the spin selection rule where $\Delta M_s = \pm 1$. 

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5.3.2.1.1) Nuclear hyperfine interactions

Unpaired electrons that give rise to the EPR signal are sensitive to their surroundings and are able to interact with the nuclei, which also possess quantised magnetic moments.\textsuperscript{36} This interaction is known as hyperfine coupling and arises as a result of electron resonances being split by the nuclear hyperfine interaction into a maximum of $2I + 1$ resonances where: $I$ is the nuclear spin which can for elements with odd mass numbers be equal to 1/2, 3/2, 5/2 etc.\textsuperscript{38} For example the hyperfine Zeeman splitting for low spin Mn\textsuperscript{55} (II) ($d_5$ – with one paramagnetic species) where $S = 1/2$ and $I = 5/2$\textsuperscript{39} will produce a signal characterised by 6 hyperfine interactions as shown in figure 5.5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.5.png}
\caption{Quantised energy levels arising from the hyperfine interaction between the single unpaired electron in low spin Mn\textsuperscript{55} and its nucleus with spin $I = 5/2$.}
\end{figure}

5.3.2.1.2) EPR in practice

Resonance can occur for paramagnetic species over a range of applied magnetic field for a specified incident microwave radiation. Alternatively it is possible to achieve resonance by fixing the magnetic field and applying different frequencies of microwave radiation. The first of these two arrangements is more common and was also used for this project.
5.3.2.2) XAS measurements

Co and Mn K-edge XAS measurements were carried out on stations 7.1 and 8.1 at the SRS. Both stations were equipped with a Si(111) double crystal monochromator, ion chambers for measuring incident and transmitted beam intensities and either a thirteen element (on station 8.1) or a seven (station 7.1) element Canberra fluorescence detector for collecting fluorescence data on dilute samples. In a typical experiment about 100 mg of MAIPO sample was pressed in to a disc of 20 mm diameter before being placed in a specially designed in situ cell (figure 5.6). XAS spectra were recorded on both the as prepared samples and on samples heated to 535°C at a rate of 5°C/minute firstly in a flow of nitrogen for approximately one hour and subsequently in oxygen (one hour) to yield the final activated catalyst. The sample was cooled to room temperature and the in situ cell was sealed before carrying out the respective cobalt and manganese K-edge measurements.

![Metal sample holder](image)

**Figure 5.6** In Situ cell for EXAFS measurements. Gases used to calcine the sample flow in through the joint marked 'Gas in', out through the tube marked 'Gas out' over the sample contained in the metal sample holder placed in the furnace. EXAFS measurements are made through kapton windows (orange) at the base of the cell.
XAS data were processed using the suite of programs available at Daresbury laboratory, namely EXCALIB (for converting the raw data to energy vs. absorption coefficient), EXBROOK (to obtain normalised XANES part of the spectra and for background subtraction to extract EXAFS) and EXCURV98 (to obtain information on the cobalt and manganese local coordination environments).

5.3.2.3) Catalytic tests

The gas phase conversion of methanol to olefins (MTO) in nitrogen was performed over the MeAlPO samples in order to obtain information on how increased metal ion incorporation into the sample affected the catalytic properties. For these experiments typically 200 mg of catalyst was placed into a tubular quartz reactor and calcined in a flow of nitrogen (60 ml/minute) at a rate of 5°C/minute up to 535°C and held at this temperature for two hours. At the end of the first hour the calcination gas was switched to oxygen for the remainder of the calcination. The sample was then cooled to 350°C before the gas was switched back to nitrogen and along with methanol (injection rate 0.05 ml/minute and WHSV = 10 hr⁻¹) was fed in at one end of the reactor with the reaction products analysed, using both a VG quadrupole mass spectrometer (in electron impact (EI) mode) and a Perkin-Elmer 8410 gas chromatograph equipped with a Porapak-N column and FID detector, at the other. A schematic of the experimental set-up is given in figure 5.7.
Figure 5.7 Catalysis rig designed for the online monitoring of MTO reaction. A mixture of nitrogen gas and vaporised methanol enters the quartz reactor tube containing approximately 200 mg of catalyst on the left hand side and on the right hand side the gaseous products are monitored by GC and mass spectrometry. The entire steel pipe work is heated to ca 80°C to prevent product condensation.

The mass spectrometer is able to collect an entire spectrum (from 10–100 daltons) in under 10 seconds and is sensitive enough to identify species in the parts per million (ppm) concentration, therefore allowing for the detection of very small amounts of product produced during the reaction. The technique is able to discriminate between different chemical species by their mass to positive charge ratio (m/z) by stabilising their flight down an analyser tube. Ions are focussed onto the detector by controlling their flight path down a flight tube according to equation 5.3.38

\[
V_o = \frac{\pi^2}{6} \frac{r_o^3 m v^2}{e^2} \mu \left[ \frac{k m_j}{j(j+1)} \right]^{-1}
\]  

(5.3)

Where \(V_o\) is the voltage passed through the quadrupole electromagnets of radius \(r_o\) and length \(e\) which can be controlled in order to stabilise a particular mass (m) with a processional motion described by \([k m_j/j(j+1)]^{-1}\) passing through the system at velocity (v) so it can be seen by the detector. One of the drawbacks of the technique is that the signals produced are often due to a mixture of several different chemical species. This is because electrons are fired at the chemical species at high speeds in order to create the positively charged ions, which the mass spectrometer can detect. This electron
impact (EI) energy is deliberately set at 70 eV in order to improve the sensitivity of the technique to species that have a high ionisation energy, however the downside of this is that unstable species are ‘smashed up’ into smaller more stable entities and produce a ‘cracking pattern’. Therefore it is difficult to distinguish between parent ion responses and fragment ions thus rendering the technique unsuitable for quantitative analysis.

In order to obtain quantitative information such as the degree of conversion and the selectivity of a catalytic reaction it is necessary to use the gas chromatography technique (GC). This technique works by partitioning a mixture of analytes between two phases (the stationary and mobile phases) within a chromatography column. Initially the analyte mix enters the column in the mobile phase but the components become physically separated as a result of their respective solubility difference between the two phases. Those species that show a greater affinity to the stationary phase will remain longer in the column and will elute last. The type of stationary phase, flow of the mobile phase and temperature can all be varied/controlled in order to optimise separation of analyte mixes. The technique is both quantitative (as a function of peak area) and qualitative (as a function of retention time).

5.3.2.3.1) GC detector

The exit of the column feeds directly into a Flame Ionisation Detector (FID) where the separated analytes are ionised in a H₂/air flame. A detector on the other side of the flame is sensitive to positively charged species created in the flame (such as CHO⁺) and the FID is therefore able to detect hydrocarbons but is insensitive to atmospheric gases. However this also means that the response is greater for higher molecular weight hydrocarbons such as hexane (C₆) than for low molecular weight species such as methane (C₁) and therefore it is necessary to calculate a relative response factor (RRF) from a known amount (in mass or number of moles) of standard (which in this case is methane) using equation 5.4

\[
\text{RRF} = \frac{\text{Known mass of standard}}{\text{Same mass of methane}} \times \left( \frac{1}{\frac{\text{Peak area of standard}}{\text{Peak area of methane}}} \right)
\] (5.4)
5.3.2.3.2) Qualitative information

Retention time (RT) is often best measured relative to a standard whose elution time is known (in minutes) and for this work a relative retention time (RRT) with respect to methane (the first signal and most clearly resolved) was calculated according to equation 5.5

\[
\frac{RT \text{ (analyte(s))}}{RT \text{ (Methane)}} = \text{RRT} \tag{5.5}
\]

5.3.2.3.3) Quantitative information

The calculation for the degree of methanol conversion (%) was calculated with respect to a blank (without catalyst) measurement as detailed in equation 5.6.

\[
\frac{\text{MeOH (area blank)} - \text{MeOH area}}{\text{MeOH (area blank)}} \times 100 = \% \text{ conversion} \tag{5.6}
\]

The product selectivity of the catalyst was also calculated with respect to methane. This is necessary in order to determine a response factor for the detector with respect to a known mass of methane since it produces a linear response and again it is the first signal and most clearly resolved.

\[
\frac{\text{Mass of Analyte}}{\text{Mass of Methane}} \times \frac{\text{Peak area (Methane)}}{\text{Peak area (Analyte)}} = \text{Response factor} \tag{5.7}
\]
5.4) Results and discussion

The results section is broken up into two parts. The first part will concentrate upon the CoAIPOs and will first discuss the results obtained from the XAS measurements followed by the EPR study. The same format will then be used to discuss the MnAIPO results before the catalytic test measurements are presented for both samples simultaneously.

5.4.1) CoAIPOs

5.4.1.1) XRD and XAS study of as prepared catalysts

In figure 5.8 are shown the X-ray diffraction patterns of the as prepared catalysts containing 0.5% weight of cobalt. These patterns can be readily indexed to those of the AiPO-5 and AiPO-18 structures suggesting there are no other phases present in these materials. The pale blue colour of the cobalt containing samples has previously been taken as evidence of Co$^{2+}$ into the tetrahedral sites of both the AiPO-5 and −18 frameworks.¹⁶ However in order to determine whether the cobalt had entered both AiPO frameworks it was necessary to carry out Co K-edge XAS measurements. Such measurements would also enable additional information such as oxidation state and the coordination geometry to be obtained.
The Co K-edge EXAFS data and the calculated best fit for both the as prepared CoAlPO-5 and −18 samples containing 0.5% cobalt are shown in figure 5.9 (a) and (c) along with the associated Fourier Transforms (b) and (d). The analysis was performed taking a simple average local structural arrangement consisting of oxygen atoms around cobalt as the first neighbours and the results of the analysis are shown in Table 5.5. The average first neighbour distance for both samples of 1.94Å and coordination number close to 4 is consistent with the reported crystallographic environment for high-spin tetrahedral Co$^{2+}$ ions in the spinel structure CoAl$_2$O$_4$ and is also similar to the previously reported local environment for Co$^{2+}$ ions in framework substituted AlPO-n materials.\textsuperscript{18,42} Furthermore the values of the Debye-Waller factors are similar in both materials suggesting there is no significant difference in the static disorder around the respective cobalt environments.
Figure 5.9 Co K-edge EXAFS data and the associated Fourier Transforms for as synthesised CoAlPO-5 (a) and (b) and CoAlPO-18 (c) and (d). The solid line represents the experimental data whilst the dotted curve was chosen to represent the calculated EXAFS. The structural parameters derived from the best fit are given in Table 5.5.

Table 5.5 Structural parameters determined from Co K-edge EXAFS refinement of as synthesised CoAlPO-5 and -18 data.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co-O distance (Å)</th>
<th>N</th>
<th>2σ² (Å²)</th>
<th>R-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoAlPO-5</td>
<td>1.94</td>
<td>4.0</td>
<td>0.007</td>
<td>31.7</td>
</tr>
<tr>
<td>CoAlPO-18</td>
<td>1.94</td>
<td>4.0</td>
<td>0.005</td>
<td>35.6</td>
</tr>
</tbody>
</table>

5.4.1.2) Calcined catalysts

Although there appears to be no obvious change in the long-range structures (by XRD) after calcination to remove the template, the local environments of both catalysts change dramatically. The first noticeable difference can be seen in the
XANES regions of the XAS spectra for both CoAIPO-5 and -18 as plotted in figure 5.10. Clearly there is a shift to a higher energy for the Co K-edge position for both samples, which is in the order of 0.5 eV for the CoAIPO-5 sample but is as much as \textit{ca} 1.4 eV for CoAIPO-18. It has been proposed in previous work comparing the X-ray absorption edge position of cobalt containing compounds in various oxidation states, particularly in an oxide environment, that such edge shifts are indicative of an oxidation state change from Co$^{2+}$ to Co$^{3+}$\textsuperscript{43}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure510.png}
\caption{Comparative Co K-edge XANES data of as prepared and calcined CoAIPO-5 (top) and CoAIPO-18 (bottom). The arrows indicate a shift in the edge position to a higher energy, which is more pronounced in calcined CoAIPO-18 than in CoAIPO-5.}
\end{figure}
These changes in absorption edge are also accompanied by variations in the Co K-edge EXAFS for both samples which are plotted in figures 5.11 (a) and (c) along with the calculated best fit and associated FTs (b) and (d) for a single shell oxygen with the results of this EXAFS analysis summarised in Table 5.6. As was mentioned previously the cobalt environments for both samples have changed but the degree of change is different between the two samples. For CoAlPO-5 the average Co-O bond distance and co-ordination has decreased to 1.92 Å (± 0.02) and 3.6 (± 10%), respectively, whilst for CoAlPO-18 the bond length has dropped to 1.83 Å with a coordination number of 2.8. Barrett et al have previously reported similar observations for these materials and were understood to be evidence of partial oxidation of the framework cobalt from 2+ to 3+ with the extent of this oxidation related to the AlPO-n structure type. Therefore as in this previous study the extent of oxidation of Co$^{2+}$ to Co$^{3+}$ appears much greater in CoAlPO-18 than in CoAlPO-5 as evidenced by a much shorter Co-O bond length and a greater shift in edge position. The decrease in coordination number for CoAlPO-5 to 3.6 and for CoAlPO-18 of 2.8 were also rationalised by Barrett et al. as illustrated in figure 5.3. However, for the calcined CoAlPO-18 sample used in this study it was not possible to fit a second oxygen shell at a distance of 2.04 Å. This may be due to a lack of the necessary quality of data needed to resolve such a second shell.
Figure 5.11 Co K-edge EXAFS data and the associated Fourier Transforms for calcined CoAlPO-5 (a) and (b) and CoAlPO-18 (c) and (d). The solid line represents the experimental data whilst the dotted curve was chosen to represent the calculated EXAFS data. The structural parameters derived from the best fit are given in Table 5.6.

Table 5.6 Structural parameters determined from Co K-edge EXAFS refinement of calcined CoAlPO-5 and -18 data.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co-O distance (Å)</th>
<th>N</th>
<th>$2\sigma^2$ (Å$^2$)</th>
<th>R-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoAlPO-5</td>
<td>1.92</td>
<td>3.6</td>
<td>0.004</td>
<td>33.7</td>
</tr>
<tr>
<td>CoAlPO-18</td>
<td>1.83</td>
<td>2.8</td>
<td>0.009</td>
<td>39.6</td>
</tr>
</tbody>
</table>

Due to the reliability in the determination of bond distances from EXAFS data (±0.02 Å) it is possible to use the derived Co-O distance in order to determine the extent of oxidation. By comparing the distances obtained from the first shell analysis of the CoAlPOs with compounds known to contain tetrahedral Co$^{2+}$ and Co$^{3+}$ species
it is possible to estimate the extent of oxidation using the Vegard relationship (equation 5.8). In doing so it is assumed that the cobalt species that remain as 2+ still possess an average Co-O distance of ca 1.94 Å.

\[ R_1 x + R_2 (1- x) = R \]  

(5.8)

Where \( R_1 \) represents a tetrahedral Co(III)-O distance of 1.79 Å obtained from a single crystal study of \( K_2Co(III)W_{12}O_{40-20}H_2O^{4+} \) and \( R_2 \) equal to 1.94 Å. This then leaves \( x \) as the fraction of oxidised cobalt in the sample and this has been summarised for the CoAIPO-n samples studied in table 5.7.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average Co-O distance (Å)</th>
<th>Fraction of Co(III) (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As prepared</td>
<td>Calcined</td>
</tr>
<tr>
<td>CoAIPO-5</td>
<td>1.94</td>
<td>1.92</td>
</tr>
<tr>
<td>CoAIPO-18</td>
<td>1.94</td>
<td>1.83</td>
</tr>
</tbody>
</table>

5.4.1.3) EPR measurements of as prepared catalysts

Typical first derivative EPR spectra for both the CoALPO-5 and -18 structures recorded at 10 K is shown in figure 5.12. For both samples the EPR trace and calculated g-values (for CoAIPO-5 \( g_\parallel = 5.74 \) and CoAIPO-18 \( g_\parallel = 5.80 \) and both samples containing a much weaker resonance at \( g_\parallel = 2.00 \)) are very similar to data previously reported for cobalt incorporated into AlPO-n frameworks.
Figure 5.12 EPR spectra of Co$^{2+}$ ions in as synthesised CoAlPO-5 (left) and CoAlPO-18 (right) recorded at 10K.

5.4.1.4) Calcined catalysts

A comparison of the first derivative plots recorded at 10 K for both catalysts before and after calcination in figure 5.13 revealed that there was a significant decrease in signal intensity after heat treatment. However, the signal decrease was much greater for the CoAlPO-18 sample than for the CoAlPO-5 sample. In order to make a quantitative comparison between the as prepared and calcined signals for the two samples it was necessary to perform a double integration on the EPR spectra. These integral EPR intensities recorded during a temperature study for both CoALPO-5 and CoAlPO-18 are shown in figure 5.14. The EPR absorption in both the samples (both before and after calcination) studied decreased with increasing temperature, which is associated with a decrease in the population of the energy levels involved in the EPR transition. This Curie-Weiss behaviour has been observed previously during EPR studies on CoAlPO-n materials and has been$^{17,19,21}$ directly associated with the amount of paramagnetic cobalt. Thus it would appear that in the calcined samples there are fewer paramagnetic species present and that this may well be due to Co$^{2+}$ oxidation to Co$^{3+}$. As mentioned previously$^{17}$ work on CoAlPO-5, −11, −44 and −46 have calculated that at 10 K this decrease in signal intensity after calcination was ca 30% suggesting that the cobalt in these materials underwent only a partial oxidation to Co$^{3+}$. It is estimated here from the decrease in the sample intensities at 10 K that for CoAlPO-5 after calcination ca 20% oxidation had
occurred. However a larger decrease (ca 70%) in signal intensity was observed for the CoAlPO-18 sample suggesting that a greater extent of oxidation to Co$^{3+}$ had taken place than for CoAlPO-5. These results correspond well with the EXAFS measurements, which also suggested that the cobalt in CoAlPO-18 was more susceptible to oxidation than the cobalt in CoAlPO-5.

![Comparative EPR spectra of Co$^{2+}$ ions at 10 K in as synthesised and calcined CoAlPO-5 (left) and CoAlPO-18 (right) illustrating the decrease in signal intensity after calcination. The g-values for the calcined catalysts had changed to 5.42 and 5.28 respectively for the CoAlPO-5 and CoAlPO-18 samples. After double integration of the two spectra it was determined that this decline for the calcined signal intensity was in the order of 20% for the CoAlPO-5 sample and 65% for CoAlPO-18.](image)

**Figure 5.13**

![Doubly integrated EPR spectrum intensity of Co$^{2+}$ ions in as-synthesised and calcined CoAlPO-5 (left) and CoAlPO-18 (right) from 7-50 K.](image)

**Figure 5.14**
5.4.2) MnAlPOs

5.4.2.1) XRD and XAS study of as prepared catalysts

In figure 5.15 are shown the X-ray diffraction patterns of the as prepared catalysts containing 0.5% weight of manganese. These patterns can also be readily indexed to those of the AlPO-5 and AlPO-18 structures suggesting there are no other phases were present in these materials. Whereas the pale blue colour of the cobalt containing samples has been taken as strong evidence of cobalt incorporation into tetrahedral sites it is not so easy to draw similar conclusions for the white MnAlPOs since the pure AlPOs are also white in colour. However it is possible to suggest that if manganese has been successfully incorporated it may well be as Mn$^{2+}$ since d$^5$ systems are typically colourless.$^{37}$ In order to determine whether the manganese had entered both AlPO frameworks it was necessary to carry out Mn K-edge XAS measurements.

Figure 5.15 XRD patterns of as prepared MnAlPO-5 (top) and MnAlPO-18 (bottom) complete with indexing lines from the structures reported in the literature.$^{31}$
The Mn K-edge EXAFS data and the calculated best fit for both the as prepared MnAlPO-5 and –18 samples containing 0.5% manganese are shown in figures 5.16 (a) and (c) along with the associated FTs (b) and (d). The analysis was performed taking a simple average local structural arrangement consisting of oxygen atoms around manganese as the first neighbours and the results of the analysis are shown in Table 5.8. The average first neighbour distance for both the as prepared MnAlPO-5 and –18 close to 2.02 Å and a coordination number of ca 4 is consistent with previous EXAFS and computational studies (using Density Functional Theory (DFT)) on manganese substituted AlPOs. This strongly suggested that high spin tetrahedral Mn\(^{2+}\) is present in the framework tetrahedral sites of both structures.\textsuperscript{24,47}

**Figure 5.16** Mn K-edge EXAFS data and the associated Fourier Transforms for as prepared MnAlPO-5 (a) and (b) and MnAlPO-18 (c) and (d). The solid line represents the experimental data whilst the dotted curve was chosen to represent the calculated EXAFS. The structural parameters derived from the best fit are given in Table 5.8.
Table 5.8 Structural parameters determined from Mn K-edge EXAFS of as synthesised MnAlPO-5 and -18.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co-O distance (Å)</th>
<th>N</th>
<th>2σ² (Å²)</th>
<th>R-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAlPO-5</td>
<td>2.02</td>
<td>4.0</td>
<td>0.009</td>
<td>27.8</td>
</tr>
<tr>
<td>MnAlPO-18</td>
<td>2.03</td>
<td>4.0</td>
<td>0.015</td>
<td>26.8</td>
</tr>
</tbody>
</table>

5.4.2.2) Calcined Catalysts

Although there appeared to be no obvious change in the extended structures (as observed by XRD) after calcination to remove the SDA, the local environment around the manganese of both MnAlPO-5 and -18 had changed dramatically. The first noticeable difference can be seen in the XANES regions of the XAS spectra for both samples as plotted in figures 5.17. Clearly there is a shift to a higher energy for the Mn K-edge position, which is in the order of 0.7 eV for the MnAlPO-5 sample and 1.5 eV for MnAlPO-18. Similar to the CoAlPO structures such a shift in edge position has been taken as evidence of oxidation of tetrahedral Mn²⁺ to Mn³⁺. ⁴⁵,⁴⁶

The changes in the absorption edge were also accompanied by variations in the Mn K-edge EXAFS for both samples which are plotted in figures 5.18 (a) and (c), along with the calculated best fit and associated FTs (b) and (d) for a single shell oxygen with the results of this EXAFS analysis summarised in Table 5.9. As was mentioned previously the manganese environments for both samples have changed but unlike the cobalt samples the degree of change is not as great. For MnAlPO-5 the average Mn-O bond distance has decreased to 1.93 Å (± 0.02) from 2.02 Å but the coordination number remained close to 4. Similar results were observed for MnAlPO-18 although the bond length was found to be even shorter than that of MnAlPO-5 at 1.86 Å. As with the cobalt data the change in the EXAFS parameters on calcination suggested that partial oxidation of the framework manganese from 2+ to 3+ had taken place and again the extent of this oxidation appeared to be related to the AlPO-n structure type with more Mn³⁺ forming in MnAlPO-18 than in MnAlPO-5.
Figure 5.17 Comparative Mn K-edge XANES data of as prepared and calcined MnAlPO-5 (left) and MnAlPO-18 (right). The arrows indicate a shift in the edge position to a higher energy that is more pronounced in calcined MnAlPO-18 than in MnAlPO-5.
Figure 5.18 Mn K-edge EXAFS data and the associated Fourier Transforms for calcined MnAlPO-5 (a) and (b) and MnAlPO-18 (c) and (d). The solid line represents the experimental data whilst the dotted curve was chosen to represent the calculated EXAFS. The structural parameters derived from the best fit are given in Table 5.9.

Table 5.9 Structural parameters determined from Mn K-edge EXAFS of calcined MnAlPO-5 and -18.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co-O distance (Å)</th>
<th>N</th>
<th>2σ² (Å²)</th>
<th>R-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAlPO-5</td>
<td>1.93</td>
<td>4.0</td>
<td>0.020</td>
<td>33.5</td>
</tr>
<tr>
<td>MnAlPO-18</td>
<td>1.85</td>
<td>3.8</td>
<td>0.015</td>
<td>25.9</td>
</tr>
</tbody>
</table>

Since tetrahedral Mn$$^{2+}$$ and Mn$$^{3+}$$ systems coordinated to four oxygens are rare, in order to estimate the degree of oxidation (using the Vegard rule) it was necessary to use the computationally derived Mn-O bond lengths (using Density Functional Theory (DFT)) predicted for such systems. In such circumstances a manganese-oxygen bond length of ca 2.04 Å has been predicted$^{47}$ for high spin tetrahedral Mn$$^{2+}$$.
whereas a distance of 1.87 Å has been proposed\textsuperscript{29} for high spin tetrahedral Mn\textsuperscript{3+}. Using these determined distances the extent of oxidation for the two catalysts as estimated from the reduction in the average Mn-O bond length after calcination is shown in table 5.10.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average Mn-O distance (Å)</th>
<th>Fraction of Mn(III) (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As prepared</td>
<td>Calcined</td>
</tr>
<tr>
<td>MnAlPO-5</td>
<td>2.02</td>
<td>1.93</td>
</tr>
<tr>
<td>MnAlPO-18</td>
<td>2.02</td>
<td>1.85</td>
</tr>
</tbody>
</table>

In comparison it appeared as though the extent of oxidation from 2+ to 3+ is greater for manganese in MnAlPO–5 and MnAlPO–18 than for cobalt in the corresponding CoAlPO–5 and CoAlPO–18 structures.

5.4.2.3) EPR measurements of as prepared catalysts

A typical first derivative EPR spectrum for both the MnAlPO-5 and -18 structures recorded at 10 K are shown in figures 5.19. The EPR trace for both samples appeared to be very similar to each other and to previously reported EPR spectra for Mn\textsuperscript{2+} in AlPO-n structures in which one resonance was observed at \( g \approx 2.00 \) with six resolved hyperfine lines. As mentioned previously the origin of this signal is unclear since it has been attributed to the presence of both high spin tetrahedral and octahedral Mn\textsuperscript{2+}.\textsuperscript{23,47}

5.4.2.4) Calcined catalysts

The signal intensity of the first derivative plots recorded at 10 K for both the catalysts after calcination in figure 5.20 had clearly decreased in intensity for both samples after heat treatment. Such a decrease in intensity has been previously observed for calcined MnAlPO-5 samples\textsuperscript{28} and has been ascribed to the oxidation of the Mn\textsuperscript{2+} species to EPR inactive Mn\textsuperscript{3+}. In comparison the observed signal decrease for the MnAlPO-18 sample appeared to be greater than for the MnAlPO-5 sample. In
order to make a quantitative comparison between the as prepared and calcined signals for the two samples it was necessary to perform a double integration on the EPR spectra. Based upon the assumption that the signal intensity is proportional to the number of paramagnetic species it appears that there are fewer paramagnetic species present in the calcined MnAlPO-5 and -18 samples than in the as prepared and that this may well be due Mn$^{2+}$ oxidation to Mn$^{3+}$.

**Figure 5.19** First derivative EPR spectra of Mn$^{2+}$ ions in as synthesised MnAlPO-5 (left) and MnAlPO-18 (right) recorded at 10 K. One resonance has been identified possessing a g-value of ≈ 2.00.

**Figure 5.20** First derivative EPR spectra of Mn$^{2+}$ ions in calcined MnAlPO-5 (left) and MnAlPO-18 (right) recorded at 10 K. The intensity scale is the same as was used for the as prepared samples in Figure 5.19. The decrease in signal intensity of ca 50% for MnAlPO-5 and 80% for MnAlPO-18 has been ascribed to the oxidation of Mn$^{2+}$ to Mn$^{3+}$.

It was estimated therefore, from the respective decrease in signal intensity, that ca 50% of the Mn$^{2+}$ in MnAlPO-5 and 80% of the Mn$^{2+}$ in MnAlPO-18 had oxidised to Mn$^{3+}$ after calcination.
5.4.3) Catalytic performance for methanol conversion over MAIPO-n (where M = Co and Mn and n = 5 and 18).

In figure 5.21 (a-d) are shown the results for the catalytic conversion of methanol to olefin (MTO) at 350°C as a function of transition metal incorporation ([Co/Mn]) into the AlPO-5 and AlPO-18 frameworks. Clearly over pure AlPO-5 and AlPO-18 catalysts although there is methanol conversion the only product formed is dimethyl ether (DME).\textsuperscript{35,48} The slightly higher overall conversion over AlPO-5 may be due to the larger pore size in comparison to AlPO-18 for this structure, which would allow more methanol into the catalyst to react. The absence of any olefins from the conversion reflects the lack of any strong Brønsted acid sites (as demonstrated from previous IR studies), which have been deemed necessary for the MTO reaction to prevail.\textsuperscript{35,48}

As can be seen for all four catalytic studies the successful incorporation of up to 2 atom percent of metal substituent into the framework of both structures types improved the conversion of methanol and selectivity to olefins over DME. Beyond this amount there was no significant improvement in catalytic performance. Even a small weight percent transition metal inclusion brings about a significant increase in olefin production, which continues to improve with increasing metal incorporation. However, there is an effect of pore-size upon product distribution since the smaller pore MeAlPO-18 samples showed a greater selectivity to lower olefins (C2, C3) than the larger pore MeAlPO-5 samples where a greater proportion of C4+ products were produced. The overall improvement in the selectivity of the MAIPOs with increasing metal incorporation can be rationalised with respect to the increased number of Brønsted acid sites (as demonstrated in Figure 5.3) that must result from the direct substitution of Co/Mn\textsuperscript{2+} for Al\textsuperscript{3+}. 
Figure 5.21 Catalytic conversion of methanol over CoAlPO-5 (a), CoAlPO-18 (b), MnAlPO-5 (c) and MnAlPO-18 (d) as a function of % transition metal incorporation [Co/Mn].
It is interesting to note that the methanol conversion and selectivity to olefins over the two MAIPO-18 samples is greater than for the corresponding MAIPO-5 samples. This is consistent with the observation that a greater number of Co/Mn$^{3+}$ species are formed after calcination of these structures, which can then be reduced to form the necessary Brønsted acid centres. However in view of this understanding it is somewhat surprising that the catalytic performance of the manganese substituted structures is in general only marginally better than the corresponding cobalt substituted analogue when 2-4% of the transition metal is incorporated. Only when a comparison is made between the 0.5% substituted samples does it appear that the enhanced redox capability of manganese has any dramatic affect on catalytic performance.

5.5) Summary and conclusions

It has been possible to synthesise both cobalt and manganese containing AlPO-5 and –18 structures with a weight range of transition metal incorporated from 0.5 – 4.0 atom percent. The structural studies that were carried out on the 0.5% substituted samples, in order to determine the nature of the substituted metal centres both before and after the structure direct template had been removed, suggested that initially both metals are incorporated into tetrahedral sites of both AlPO frameworks in the high spin 2+ oxidation state. For manganese such a conclusion was made based mainly upon the results of the EXAFS analysis for these samples which strongly suggests that the manganese is present with a coordination of four and a bond length of ca 2.02 Å which is consistent with computationally determined distances for such systems.

On calcination to remove the template a lowering of the average Co/Mn-O bond length and a reduction in the EPR signal intensity can be best understood in terms of oxidation of the transition metals to the 3+ oxidation state. The extent of oxidation was found to be dependent upon both structure type and the transition metal as detailed in table 5.11. Although the difference between the two types of measurement can be as high as 20% there is an obvious trend in which Mn$^{2+}$ undergoes greater oxidation to the 3+ form than the corresponding Co$^{2+}$ species.
These results are consistent with previous work in which it has been proposed that manganese containing MnAlPO systems are superior oxidation catalysts for the conversion of alkanes in comparison to the corresponding CoAlPO structures since after calcination they contain more 3+ species.14,49

Table 5.11 Summary of proposed extent of oxidation from $M^{4+}$ to $M^{3+}$ (where M = Co, Mn) as determined from EXAFS and EPR measurements.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Extent of Oxidation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EXAFS</td>
</tr>
<tr>
<td>CoAlPO-5</td>
<td>15</td>
</tr>
<tr>
<td>CoAlPO-18</td>
<td>80</td>
</tr>
<tr>
<td>MnAlPO-5</td>
<td>58</td>
</tr>
<tr>
<td>MnAlPO-18</td>
<td>100</td>
</tr>
</tbody>
</table>
5.6) References


(36) Assenheim, H. M. *Introduction to electron spin resonance* 1966, Hilger & Watts Ltd.


(49) Raja, R.; Sankar, G.; Thomas, J. M. *Journal of the American Chemical Society 1999, 121*, 11926.
Chapter 6

A study of the crystallisation of cobalt aluminate from cobalt ion exchanged zeolite precursors

6.1) Chapter overview

Ion exchanged zeolites have previously been used as precursors for the production of condensed oxide phases. In this chapter some of the criteria for the preparation of cobalt aluminate (CoAl₂O₄) from cobalt ion exchanged zeolites have been investigated including the effect of the type of zeolite (A or B) used, its stability and the nature of the cobalt salt. The results obtained from EXAFS and XRD measurements suggested that both the zeolite type and the cobalt did have an affect on the extent of crystallisation of various cobalt containing phases. EXAFS however, did show that for zeolite A samples exchanged with cobalt acetate, very small XRD amorphous particles of CoAl₂O₄ had formed.

6.2) Introduction

Transition metal oxide spinels (TMOS) have been used in many industrial applications including semiconductors, magnetic storage media and in sensor technology. However, their thermal stability, high oxygen anion mobility and the ease in which other ions can be accommodated into the spinel framework have made them good candidates for heterogeneous catalysis. To date the most successful catalytic application of TMOS is in the high temperature water-gas shift reaction stage (to produce ‘Syn-gas’) of ammonia synthesis (equation 6.1).

\[
\text{CO} + \text{H}_2\text{O} \xrightarrow{\text{Fe}_3\text{O}_4, 400^\circ\text{C}} \text{CO}_2 + \text{H}_2 \quad \text{('Syn-gas')} \tag{6.1}
\]

Spinels have a general formula \text{AB}_2\text{O}_4 and a unit cell containing 32 oxygen anions with one-eighth of the 64 tetrahedral and half of the 32 octahedral sites occupied. If the A cations occupy the tetrahedral sites and the B cations the octahedral
a ‘normal’ spinel results, an example of which are the aluminates (figure 6.1) \( \text{MAI}_2\text{O}_4 \) (where \( M = \text{Co}^{2+}, \text{Zn}^{2+} \) or \( \text{Fe}^{2+} \)). However in certain other spinels the 8 tetrahedral sites are occupied by 8 of the B cations with the remaining B ions, together with the 8 A ions evenly distributed over the octahedral positions. In such a circumstance an ‘inverse’ spinel results with a formula \( \text{B(AB)}\text{O}_4 \) of which magnetite \( (\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4) \) and \( (\text{Co}^{3+}(\text{Co}^{2+}\text{Co}^{3+})\text{O}_4) \) are examples but it is also possible to find spinel structures (disordered spinels) where both A and B cations are randomly distributed over both sites. It is also easy to substitute foreign ions for either cation and this therefore offers a great deal of scope for the synthesis of multi-component, spinel-based systems with varying physical and chemical properties.\(^3\)\(^4\)

Although the use of TMOS as catalysts on an industrial scale is essentially limited to the production of Syn-gas, they have shown potential as heterogenous catalysts for the oxidation of both methane and carbon monoxide and for the alkylation of m-cresol to thymol and they are often used as catalytic supports.\(^5\)\(^-\)\(^10\)

![Figure 6.1 A fragment of the 'normal' spinel structure \( \text{ZnAl}_2\text{O}_4 \) with dark blue \( \text{Zn}^{2+} \) ions and red \( \text{O}^{2-} \) ions possessing tetrahedral coordination and green \( \text{Al}^{3+} \) ions occupying half of the octahedral sites.](image)

The active surface area of the material is important for these types of catalytic reaction since they occur at the phase boundary between the solid and the reactants. Normally in order for a catalyst to possess a high surface area it must consist of small
uniform homogenous particles but this is often difficult to achieve using conventional catalyst preparation procedures. Although it is possible to achieve spinels with surface areas of the order of 100 $\text{m}^2 \text{g}^{-1}$ via co-precipitation and calcination procedures (this method is preferred to the mixing of the solid oxides) these methods normally involve calcination temperatures in excess of 1000°C and are often plagued with problems such as the crystallisation of additional unwanted phases to which the large surface area is often attributed.\textsuperscript{11-13} As such new approaches have been developed for the preparation of such materials which make use of organic metal salts, sol-gel processes, polymerisation complexes, chemical vapour deposition and even hydrothermal methods and these have been successful in preparing a uniform product with a high surface area.\textsuperscript{13-20} The main drawback with using such procedures is that the reagents employed are often expensive and the techniques unsuitable for the production of large amounts of product such as might be needed for commercial catalyst production. However more recently an alternative and seemingly more viable synthetic route which avoids some of the aforementioned problems, has been investigated for the production of high surface area TMOS and involves their crystallisation from collapsed ion-exchanged zeolite precursors during heat treatment.\textsuperscript{21,22}

6.2.1) Zeolite structures and properties

As was mentioned in the Chapter 5 zeolites are microporous aluminosilicates consisting of channels and/or cages of a molecular dimension supported by a framework of Al(III)O$_4$ and Si(IV)O$_4$ tetrahedra.\textsuperscript{23} Since the formal charges for the respective constituents are 3+ (Al), 4+ (Si) and 2- (O) excess negative charge is imparted onto the framework, which is necessarily compensated by extraframework cations (often Na$^+$) located in the zeolite cages and channels. Since it is the aluminium site that is electronically deficient the charge balancing species often tend to locate closer to it. However since these extraframework moieties exhibit only an electrostatic attraction and are not attached by any formal chemical bond, it is normally possible to ‘exchange’ these cations particularly for divalent species (Ca$^{2+}$ and Mg$^{2+}$) in a more thermodynamically favoured process.\textsuperscript{22}
The thermal stability of zeolites is varied with structures such as stilbite collapsing at \textit{ca} 400°C whereas faujasite is able to retain its microporous structure at temperatures in excess of 800°C.\textsuperscript{24} Zeolites collapse to first form an amorphous material before at elevated temperatures crystallisation of other dense phases takes place. The abundance of silicon and oxygen in the zeolite framework means that the SiO\textsubscript{2} phases quartz and cristobalite are some of the first to crystallise. However in zeolites containing a high aluminium content and therefore a number of charge balancing ions, other phases have been observed to form. An example of this is the crystallisation of nepheline (NaAlSiO\textsubscript{4}) from Zeolite A containing Na\textsuperscript{+} ions.\textsuperscript{25} Interestingly these materials form from the collapsed zeolites at temperatures lower than that which is normally employed for their preparation using conventional synthetic procedures.

\subsection*{6.2.2) Zeolite collapse as a synthetic method}

As a synthetic approach for the production of ceramics this process was first employed by Subramanian et al. for the preparation of anorthite and cordierite from collapsed calcium and magnesium exchanged zeolites A, X and Y.\textsuperscript{26,27} Since then it has been demonstrated that a cordierite can be produced from a number of different of magnesium ion exchanged zeolites\textsuperscript{28} and that its crystallisation is even catalysed by the presence of other phases including ZnO.\textsuperscript{29} One of the main advantages of using such a synthetic approach is that in principle it can be utilised in order to make a whole variety of condensed, stoichiometric aluminate and/or silicate phases and as such it was soon discovered that other materials such as the spinel phases CoAl\textsubscript{2}O\textsubscript{4} and ZnAl\textsubscript{2}O\textsubscript{4} crystallised from collapsed Co\textsuperscript{2+} and Zn\textsuperscript{2+} exchanged zeolite A.\textsuperscript{25,30,31} More recently this work has been developed further resulting in a viable, reproducible and cheap method for the preparation of the transition metal alumimates CoAl\textsubscript{2}O\textsubscript{4}, NiAl\textsubscript{2}O\textsubscript{4} and ZnAl\textsubscript{2}O\textsubscript{4} with surface areas often in excess 100 m\textsuperscript{2}/g.\textsuperscript{21,22,32}

Crucial to the successful crystallisation of stoichiometric condensed phases from the collapsed structure is the atomic dispersion of the ion-exchangeable cations in the zeolite framework. This is possible since the element distribution of framework atoms and ion-exchangeable cations is very uniform since all the elements within the zeolite are fixed at regular crystallographically defined sites. Such a distribution is
maintained after collapse therefore enabling a uniform and homogenous nucleation of phases from the amorphous materials. Since zeolites are comprised mainly of Al-O-Si bonds\textsuperscript{24} when charge balancing Na\textsuperscript{+} ions are present in zeolite A the stoichiometry for nepheline (NaAlSiO\textsubscript{4}) is satisfied. Therefore when divalent species such as Co\textsuperscript{2+} are exchanged for two monovalent ions (Na\textsuperscript{+}) the divalent species must balance the charge for two separate framework aluminium ions and hence the stoichiometry of the cobalt aluminate phase results\textsuperscript{22,33}.

6.2.3) Aims and objectives

The aim of this work was to establish some criteria for the crystallisation of the cobalt aluminate spinel CoAl\textsubscript{2}O\textsubscript{4} phase from amorphised zeolites. In particular the effects of the cobalt salt (cobalt acetate and cobalt nitrate) used in the ion exchange process and zeolite type (sodium forms of zeolites A and B prepared containing a Si:Al = 1) on the crystallisation of this phase were investigated. Furthermore in previous studies XRD had been the principle method used to characterise the crystallised phases but this technique is limited to the detection of solids possessing some degree of long-range order. Therefore the EXAFS technique was also employed in order to determine if very small CoAl\textsubscript{2}O\textsubscript{4} particles had formed within the collapsed XRD amorphous zeolite matrix.

6.3) Experimental

6.3.1) Zeolite synthesis

6.3.1.1) Synthesis of zeolite A

The zeolite A pre-cursor gel with the composition Al\textsubscript{2}O\textsubscript{3}:2SiO\textsubscript{2}:Na\textsubscript{2}O was prepared as follows, using a standard synthetic method.\textsuperscript{34} 2.67 g of sodium hydroxide pellets (Aldrich) were dissolved in 10.50 ml of distilled water (Fluka) and to this was added 2.60 g of Aluminium Hydroxide (Aldrich) before the resultant mixture was thoroughly stirred. To this mix 2.00 g of fumed silica (Cab-O-Sil) (Riedel de Haën)
was added during vigorous mixing before finally the resultant translucent precursor gel was sealed in a polypropylene screw-top bottle and placed in an oven at ca 100°C for 4 hours. The resultant white solid was filtered, washed and dried in an oven overnight at 100°C.

6.3.1.2) Synthesis of zeolite B

The zeolite B precursor gel with the composition Al₂O₃:2SiO₂:Na₂O was prepared as follows, using a synthetic method reported previously.³⁵ 130 g of sodium silicate solution (10% NaOH/27% SiO₂) (Riedel de Haën) was added to a 1 litre round bottomed flask containing 100 ml of distilled water (Fluka) and the contents were thoroughly mixed. In a separate container a solution of sodium aluminate was made by the dissolution of 30 g sodium aluminate solid (Aldrich) and 80 ml of distilled water. This was then added to the round-bottomed flask and the contents were left to react whilst stirring at ca 120°C for 45 hours. The resultant white solid was filtered, washed and dried in an oven overnight at 100°C.

6.3.2) Preparation of Co²⁺ ion-exchanged zeolites A and B.

Ion-exchanged zeolites A and B were obtained according to the method previously used for such studies.²² 5 g of zeolite was added to 250 ml of distilled water (Fluka) containing 0.1 M of either cobalt acetate tetrahydrate (Aldrich) at pH ≈ 7.0 or cobalt nitrate hexahydrate (Aldrich) at pH ≈ 6.5. The origin of the slight acidity of these exchange solutions has been attributed to the hydrolysis of the Co²⁺ cation.³⁶ Ion-exchange was carried out at 70°C for 30 minutes before the solid materials (pink in colour) were filtered, washed and dried overnight at 100°C.

6.3.3) Collapse of ion exchanged zeolites

2 x 20 mm pellets were pressed from 0.3 g portions of both the as prepared and Co²⁺ ion-exchanged zeolites and these were placed in a ceramic crucible before firing began at a heating rate of 5°C/minute up to 950°C. Samples were withdrawn and the reaction quenched at 850°C and 950°C (it has been shown previously that
these temperatures bring about first the collapse of cobalt ion-exchanged zeolite A followed by the crystallisation of CoAl₂O₄)²²,³¹ respectively before they were subjected to XRD and XAS measurements.

6.3.4) Characterisation

The phase purity of the as-synthesised materials (dried at 100°C) were verified by X-ray diffraction measurements recorded using a Siemens D500 diffractometer (of Bragg-Brentano geometry) utilizing Cu-Kα₁ radiation. Co K-edge XAS measurements were carried out on stations 7.1 at the SRS (which operates at 2 GeV with a typical current of 150 to 250 mA) and on the Swiss-Norwegian beamline at the ESRF (which operates at 6 GeV with a typical current of 200 to 250 mA). Both stations were equipped with a Si(111) double crystal monochromator and ion chambers for measuring incident and transmitted beam intensities. In a typical experiment about 20 mg of zeolite sample was mixed with a 20 mg of support material (MCM-41) and pressed in to a disc of 20 mm diameter. XAS spectra were recorded on the as prepared ion-exchanged samples and on ex-situ samples heated to 850°C and 950°C respectively.

XAS data were processed using the suite of programs available at Daresbury laboratory, namely EXCALIB (for converting the raw data to energy vs. absorption coefficient), EXBROOK (to obtain normalised XANES part of the spectra and for background subtraction to extract EXAFS) and EXCURV98 (to obtain information on the cobalt local coordination environments).

6.4) Results and discussion.

6.4.1) As prepared and ion exchanged zeolites

In figure 6.2 are shown the X-ray diffraction patterns of both the as prepared zeolites. These were similar to those previously reported for both zeolites A and B.²⁹,³⁷ In figure 6.3 are shown the XRD patterns for the cobalt acetate and cobalt nitrate ion-exchanged zeolites A and B respectively. It is clear that although the
zeolite structures have remained intact the ion-exchange process has altered the XRD patterns slightly. For zeolite A the peaks at 10.20 and 12.50 degrees 2θ have in both cobalt acetate and nitrate exchanged samples, decreased in intensity whilst at the same what seemed to be an additional broad reflection appeared at ca 11.50°. For the zeolite B samples whilst there was no obvious decrease in intensity after ion exchange the reflections did appear slightly broader and additional peaks appeared at 19.90, 26.80 and 29.70 degrees 2θ in both samples. Although the peak at 26.80 degrees 2θ might be attributable to the 002 reflection of SiO₂ low quartz the origin of the other two is not obvious. It is possible that some (or all) of these additional reflections are due to the replacement of sodium with cobalt after ion exchange.\textsuperscript{35} However, previous studies have also noted that the ion exchange process in slightly acidic solutions affects the crystallinity of the zeolites and that this damage has previously been attributed to the hydrolysis of Si-O-Al linkages and removal of aluminium.\textsuperscript{32}

\textbf{Figure 6.2} XRD patterns of the as prepared sodium forms of zeolites A (top) and B (bottom).
Figure 6.3 XRD patterns of the cobalt acetate and cobalt nitrate ion exchanged zeolites A (top) and zeolite B (bottom). The ion exchange process carried out at 70°C for 30 minutes has resulted in the growth of one additional reflection (marked with an open circle) in the zeolite A patterns and three new reflections in both zeolite B patterns (asterisked).
In order to determine the nature of the cobalt species in all of the ion-exchanged zeolites (including the oxidation state and the co-ordination geometry) we employed XAS. In figure 6.4 (a-h) is shown the EXAFS data and the associated Fourier transforms of the ion-exchanged zeolites A and B along with the best fit (the dotted line represents the calculated EXAFS and the solid curves the experimental data) to the data. The analysis was performed taking a simple average local structural arrangement consisting of oxygen atoms around cobalt as the first neighbours and the results of the analysis are shown in Table 6.1. The best data fit was obtained for an average first neighbour distance in all four samples of 2.08 Å and a coordination number close to six. This is consistent with previous measurements for ion-exchanged cobalt in zeolites in which it has been proposed that high-spin octahedral Co^{2+} ions are present as the hexa-aqua species [Co(H_{2}O)_{6}]^{2+}.^{38,39} It has also been possible to fit a second shell of silicon and/or aluminium* atoms in both zeolites at a distance of about 3.30 Å and this is likely to be a contribution from the zeolite framework.^{39,40} For the two zeolite A samples a coordination number of ca two is observed but for the zeolite B samples the second shell is much more intense and a coordination number close to five is obtained. This may be because the zeolite B sample does not appear to contain particularly large pores/spaces (ie. first reflection occurs at 12.60 degrees 2θ corresponding to a plane separation of ca 7 Å in comparison to zeolite A (which has two reflections at ca 7.24 and 10.20 degrees 2θ corresponding to lattice plane separations of ca 12.20 and 8.63 Å) and as a result the cobalt species in this zeolite might be more restricted and are therefore likely to be closer to the zeolite framework.

* Since both aluminium and silicon possess similar scattering factors it has not been possible to discriminate between them. Very little difference in the overall goodness of fit is observed when fitting a second shell consisting of entirely one or the other or a mixture of both.
Figure 6.4 Best fit between experimental Co K-edge EXAFS and the calculated EXAFS data and associated FT’s for cobalt acetate exchanged zeolite A (a and b), zeolite B (e and f) and cobalt nitrate exchanged zeolite A (c and d) and zeolite B (g and h). The results from this analysis are shown in Table 6.1.
Table 6.1 Structural parameters determined from Co K-edge EXAFS of ion exchanged zeolites A and B.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Salt</th>
<th>Co-O distance (Å)</th>
<th>N</th>
<th>2σ² (Å²)</th>
<th>Co-Si/Al distance (Å)</th>
<th>N</th>
<th>2σ² (Å²)</th>
<th>R-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cobalt acetate</td>
<td>2.08</td>
<td>5.9</td>
<td>0.016</td>
<td>3.33</td>
<td>1.4</td>
<td>0.013</td>
<td>15.1</td>
</tr>
<tr>
<td>A</td>
<td>Cobalt nitrate</td>
<td>2.08</td>
<td>5.7</td>
<td>0.016</td>
<td>3.35</td>
<td>2.0</td>
<td>0.024</td>
<td>14.5</td>
</tr>
<tr>
<td>B</td>
<td>Cobalt acetate</td>
<td>2.07</td>
<td>5.7</td>
<td>0.017</td>
<td>3.33</td>
<td>5.0</td>
<td>0.012</td>
<td>25.7</td>
</tr>
<tr>
<td>B</td>
<td>Cobalt nitrate</td>
<td>2.07</td>
<td>5.7</td>
<td>0.018</td>
<td>3.33</td>
<td>5.1</td>
<td>0.013</td>
<td>26.9</td>
</tr>
</tbody>
</table>

6.4.2) Zeolite collapse

6.4.2.1) Zeolite A

In figures 6.5 (a and b) are shown the XRD plots from the ex-situ heating studies performed at 850°C and 950°C for the zeolite A samples. It is clear that both the colour of the samples and the XRD patterns recorded after ion exchange underwent considerable alteration after heat treatment. On heating at 850°C a colour change from pink to blue/green was observed and this was accompanied by the disappearance of the reflections that corresponded to zeolite A. This suggested that the zeolites has collapsed to form an amorphous phase although in the cobalt nitrate exchanged samples it is possible to make out some broad reflections at 33.50 and 45.60 degrees 2θ which appeared to be evidence of the crystallisation of a spinel phase. These reflections were present in both samples after heating at 950°C although they were now both more intense and sharper than in the cobalt nitrate exchanged samples at 850°C. However it was not possible to identify whether these reflections corresponded to the CoAl₂O₄ or Co₃O₄ phases (or both) since their diffraction patterns are very similar (see figure 6.6) and the reflections in the collapsed samples were broad and difficult to make out from the amorphous background. However since both samples were now blue in colour it is most likely that the predominant spinel phase
present is CoAl₂O₄ since it is navy blue in colour whereas Co₃O₄ is black. No other phases were detected.

Figure 6.5 XRD patterns of cobalt acetate exchanged (a) and cobalt nitrate exchanged (b) zeolite A calcined at 850°C and 950°C respectively. The broad hump on the left hand side of the patterns in (b) is due to scatter from the XRD sample plate.
Figure 6.6 XRD patterns of cobalt aluminate (top) and cobalt oxide (bottom). The two patterns are almost identical save for a small extra reflection at 38.70 degrees 2θ in the cobalt oxide pattern.

6.4.2.2) Zeolite B

A slightly more complex picture emerged for the zeolite B samples during heat treatment. In both cobalt acetate and nitrate exchanged samples after heat treatment at ca 850°C the reflections that corresponded to the zeolite B pattern had completely vanished. Instead, along with a broad hump around 25° 2θ, a number of new weak reflections had appeared. In the cobalt nitrate exchanged sample these new reflections corresponded to the formation of the phase Co₃SiO₄ (JCPDS database entry no. 33-0048) (figure 6.7). This was also identified as the predominant phase in the cobalt acetate exchanged sample although reflections corresponding to a spinel phase also appeared to be present. In both cases the loss of crystallinity was accompanied by a colour change from pale pink to black for both samples.

The XRD patterns for both samples heated at 950°C were very similar to those recorded for both samples at 850°C except that some of the reflections were slightly more intense and sharper suggesting that the particles of the crystallised phases were larger. However, for the cobalt acetate exchanged sample there appeared to be more of the Co₃SiO₄ phase relative to the amount of spinel than at 850°C.
Figure 6.7 XRD patterns of cobalt acetate exchanged (a) and cobalt nitrate exchanged (b) zeolite B calcined at 850°C and 950°C respectively. The vertical lines marking the calculated 2θ positions in (b) correspond to the phase Co$_2$SiO$_4$ (JCPDS database entry no. 33-0048). The broad hump on the left hand side of some of the patterns is due to scatter from the XRD sample plate.

Table 6.2 contains a summary of the most likely identities of the condensed phases which were observed to have crystallised from the collapsed zeolites as well as an estimate (where applicable) of the average particle size determined using the Scherrer equation (equation 3.5). Also included was a calculation for the average
particle size from figure 6.6 for the CoAl₂O₄ reference material. The peak shapes were modelled using the XFIT programme in order to obtain FWHM values. Measurements were not made on either the XRD amorphous or multiphasic materials since it was not possible to model the peak shape accurately. This was because the peaks were either too broad or else tended to overlap.

Table 6.2 A list of dominant phases observed in the XRD patterns of the collapsed zeolites and an estimate of particle size obtained using the Scherrer equation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Salt</th>
<th>Phases formed at 850°C</th>
<th>Estimated Particle size at 850°C (nm)</th>
<th>Phases formed at 950°C</th>
<th>Estimated Particle size at 950°C (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>Cobalt acetate</td>
<td>CoAl₂O₄</td>
<td>N/A</td>
<td>CoAl₂O₄</td>
<td>29</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Cobalt nitrate</td>
<td>CoAl₂O₄</td>
<td>15</td>
<td>CoAl₂O₄</td>
<td>24</td>
</tr>
<tr>
<td>Zeolite B</td>
<td>Cobalt acetate</td>
<td>Co₂SiO₄ + Spinel</td>
<td>N/A</td>
<td>Co₂SiO₄ + Spinel</td>
<td>N/A</td>
</tr>
<tr>
<td>Zeolite B</td>
<td>Cobalt nitrate</td>
<td>Co₂SiO₄</td>
<td>N/A</td>
<td>Co₂SiO₄</td>
<td>N/A</td>
</tr>
<tr>
<td>CoAl₂O₄</td>
<td>-</td>
<td></td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Since it was not possible to formally identify which cobalt spinel form had crystallised from the amorphised zeolite, EXAFS was employed since this information could be elucidated by comparison of the average Co-O distances. Furthermore it would be possible in the case of the cobalt acetate exchanged zeolite A material to determine whether any XRD amorphous spinel phase was present in the sample after heating at 850°C.

In figure 6.8 (a and b) is shown the EXAFS data for CoAl₂O₄, Co₃O₄ and for both zeolite samples recorded after heat treatment at 850°C and 950°C. Although the experimental EXAFS data for the model spinel phases shown in figure 6.8 are similar, there are noticeable differences by which it is possible to discriminate between them. It is clear therefore from a comparison of the 950°C data recorded for the exchanged zeolite A materials that the EXAFS oscillations are very similar to that recorded for CoAl₂O₄ and as such it is concluded from this similarity that this is the dominant phase formed from the collapsed zeolites. For the zeolite B samples the oscillations do
not match that of either CoAl$_2$O$_4$ or Co$_3$O$_4$ although this is not totally unexpected since Co$_2$SiO$_4$ was the principle phase detected by XRD.

![Graphical representation of EXAFS data](image)

**Figure 6.8** EXAFS data of Co$_3$O$_4$, CoAl$_2$O$_4$ and the heat-treated zeolite A samples (a) and zeolite B samples (b). It is clear that the EXAFS for the 950°C zeolite A samples in (a) and the cobalt acetate zeolite B sample also treated at this temperature resemble CoAl$_2$O$_4$.

In order to verify the observations made from a comparison of the EXAFS a more detailed analysis was performed. The results of the EXAFS data analysis are shown for CoAl$_2$O$_4$, Co$_3$O$_4$ and both the zeolite A and zeolite B samples calcined at 850°C and 950°C in Table 6.3 along with the associated Fourier transforms and the
best fit for the first peak in the data (shown in figures 6.9 and 6.10) for a single oxygen shell around cobalt as the first neighbours. A coordination number close to four was obtained in all but one of the zeolite A samples with an average first neighbour (Co-O) distance of between 1.95-1.96 Å. These EXAFS results are similar to those, which have previously been reported for high-spin tetrahedral Co\(^{2+}\) ions in CoAl\(_2\)O\(_4\), and this suggests that this is the predominant phase formed in all of the calcined samples.\(^{41}\) However, the slightly larger coordination number and Co-O distance observed for the cobalt acetate exchanged zeolite A sample calcined at 850°C suggested that, in addition to the cobalt aluminate phase, minor amounts of XRD amorphous phase(s) may also be present or that the formation of the spinel is incomplete. The values of the Debye-Waller factors are slightly higher at 850°C than at 950°C suggesting that the cobalt environment in these lower temperature samples is also more disordered. The large R-factors observed were due to the fact that only one of the coordination shells had been fitted.

Although it was not possible to obtain information on particle size from the fitting of the higher coordination shells in the EXAFS, particularly for the XRD amorphous samples, it is clear that there is a correlation between the magnitude of the second peak in the Fourier transform and the particle size as estimated from XRD (see Table 6.2). The order for this magnitude of the second peak follows: CoAl\(_2\)O\(_4\) > cobalt acetate 950°C = cobalt nitrate 950°C > cobalt nitrate 850°C > cobalt acetate 850°C much like the XRD particle size estimation. Judging from this comparative analysis it was possible to propose that the spinel particles in the cobalt acetate 850°C sample were smaller than the 15 nm particles observed in the corresponding cobalt nitrate exchanged samples.
Table 6.3 Results of the Co K-edge EXAFS first Co-O shell analysis for the two spinels standards and the collapsed zeolites.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ion exchange salt</th>
<th>Calcination temperature (°C)</th>
<th>Co-O distance (Å)</th>
<th>N</th>
<th>2σ² (Å²)</th>
<th>R-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoAl₂O₄</td>
<td>-</td>
<td>-</td>
<td>1.95</td>
<td>4.0</td>
<td>0.008</td>
<td>81.49</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>-</td>
<td>-</td>
<td>1.91</td>
<td>4.6</td>
<td>0.008</td>
<td>80.58</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Cobalt acetate</td>
<td>850</td>
<td>1.96</td>
<td>4.6</td>
<td>0.016</td>
<td>31.38</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Cobalt acetate</td>
<td>950</td>
<td>1.95</td>
<td>4.2</td>
<td>0.012</td>
<td>61.04</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Cobalt nitrate</td>
<td>850</td>
<td>1.96</td>
<td>4.2</td>
<td>0.017</td>
<td>28.80</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Cobalt nitrate</td>
<td>950</td>
<td>1.95</td>
<td>4.0</td>
<td>0.018</td>
<td>64.40</td>
</tr>
<tr>
<td>Zeolite B</td>
<td>Cobalt acetate</td>
<td>850</td>
<td>2.01</td>
<td>5.2</td>
<td>0.033</td>
<td>61.38</td>
</tr>
<tr>
<td>Zeolite B</td>
<td>Cobalt acetate</td>
<td>950</td>
<td>2.03</td>
<td>5.7</td>
<td>0.022</td>
<td>61.11</td>
</tr>
<tr>
<td>Zeolite B</td>
<td>Cobalt nitrate</td>
<td>850</td>
<td>2.04</td>
<td>5.8</td>
<td>0.029</td>
<td>62.70</td>
</tr>
<tr>
<td>Zeolite B</td>
<td>Cobalt nitrate</td>
<td>950</td>
<td>2.06</td>
<td>6.4</td>
<td>0.026</td>
<td>61.08</td>
</tr>
</tbody>
</table>

Figure 6.9 FT’s of the Co K-edge EXAFS (solid line) and the calculated best fit (dotted line) for the first Co-O shell for (a) CoAl₂O₄, (b) Co₃O₄, cobalt acetate exchanged zeolite A calcined at 850°C (c) and 950°C (d), and cobalt nitrate exchanged zeolite A calcined at 850°C (e) and 950°C (f). The results from this analysis are shown in Table 6.3.
For the zeolite B samples a variety of coordination numbers and first
neighbour Co-O bond lengths were observed ranging from 5.2 and a distance of 2.01
Å for the cobalt acetate exchanged sample treated at 850°C to ca 6.0 and 2.06 Å for
both cobalt nitrate treated samples. These results seemed to reflect the XRD
observations in which the samples contained a varying mixture of the high spin six
coordinate Co$^{2+}$ containing Co$_2$SiO$_4$\textsuperscript{42} phase and a cobalt spinel. From these results it
is possible to conclude that the cobalt nitrate sample calcined at 950°C contains
predominantly Co$_2$SiO$_4$ and very little cobalt spinel whereas in comparison the cobalt
acetate exchanged sample treated at 850°C contains relatively more spinel. The
multiphasic nature of these materials meant that it was difficult to determine which
spinel phase had formed.

![Figure 6.10](image)

**Figure 6.10** FT’s of the Co K-edge EXAFS (solid line) and the calculated best fit (dotted line) for the
first Co-O shell for cobalt acetate exchanged zeolite B calcined at 850°C (a) and 950°C (b) and cobalt
nitrate exchanged zeolite B calcined at 850°C (c) and 950°C (d). The results from this analysis are
shown in Table 6.3.
6.5) Summary and conclusions

The crystallisation of condensed phases at elevated temperatures from collapsed cobalt acetate and cobalt nitrate ion-exchanged zeolites A and B containing similar Si:Al synthesis ratios, has been investigated. For the zeolite A samples it appeared that small particles of phase pure CoAl₂O₄ crystallised from the amorphised zeolites (as identified from both XRD and XAS) although for the cobalt acetate exchanged sample treated at 850°C these particles were so small that they lacked the necessary long-range order to be seen by XRD. It was therefore estimated from a comparison of the magnitude of the second peak in the EXAFS Fourier transform that these particles were less than 15 nm wide. In contrast, for the zeolite B samples, the formation of a cobalt silicate (Co₂SiO₄) and a spinel phase was observed, although the amount of each phase appeared to depend upon both the cobalt salt used in the exchange process and the calcination temperature.

It is difficult to rationalise exactly why both the zeolite structure type and the ion exchange salt used in the synthesis process have had an affect upon phase crystallisation in the zeolite B samples. What is clear is that there were differences between the types of ionic species in the ion exchange solutions, the pH of these solutions, the nature of the cobalt environment in the ion exchanged forms of the two zeolites and the zeolites’ thermal stability. Since it had not been possible to obtain detailed enough structural information on the cobalt exchanged forms of the zeolites it was difficult to determine whether the last of the two differences might provide some clues as to why the crystallisation behaviour of the two zeolite structures differed. However, since the extent of Co₂SiO₄ and spinel formation varied between the two zeolite B samples, it seems possible that the type of cobalt salt used during ion-exchange at least has an affect upon the cobalt phases that crystallised from zeolite B.

Previous work has ascribed a decrease in zeolite crystallinity to the effects of dealumination of the zeolites during ion-exchange in an acidic environment, leaving a structurally weakened, silicon rich zeolite. For the zeolite B samples this may explain why firstly there were modifications in the XRD patterns after exchange and why predominantly it is cobalt silicate that crystallises from the more acidic cobalt nitrate solution (pH 6.5) whereas cobalt aluminate is the majority phase in the cobalt acetate exchanged samples (pH 7.0). Since zeolite A is a more stable zeolite this may explain why similar effects of the cobalt salt on phase crystallisation were not observed.
In summary, whilst this method does seem to be both a cheap and viable alternative to the conventional methods used to prepare aluminate phases it appeared that careful selection and control of zeolite, ion-exchange salt and calcination conditions was important for the crystallisation of very small spinel particles possessing high surface area.
6.6) References


