

# The kinetics and mechanisms of the crystallisation of microporous materials

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The synthesis of microporous materials is one of the major activities in contemporary solid state chemistry. This perspective brings together the current thinking regarding the synthesis and growth mechanisms of these technologically important materials. Also reviewed are the latest experiments being utilised to probe the complex chemistry which occurs during the synthesis of these materials.

## 1 Introduction

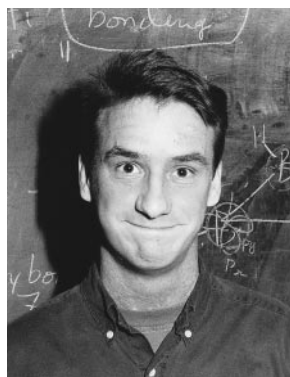
Microporous materials, often referred to as molecular sieves or open-framework materials, are a class of inorganic solids which possess regular pores or voids in the size range 5–20 Å (Fig. 1). Zeolites are the most well known family of such materials. Following the successful synthesis of the first artificial zeolite in 1948 (see below),<sup>1</sup> their utility as catalysts for the production of petrochemicals stimulated great interest in the synthesis of other zeolitic materials and this first report was quickly followed by many others. Today, there are hundreds of known microporous materials, and investigations on these compounds remain an extremely active area of research.<sup>2</sup> The continued effort to synthesise new materials in this class, and to gain a greater understanding of their crystallisation mechanisms, is driven by the broad range of useful and unique properties they possess. Microporous materials contain uniformly sized pores in the range 5–20 Å, and can thus display molecular recognition, discriminating and organisational properties with a resolution of less than 1 Å. They are therefore of great interest as materials for a range of molecular recognition applications,

as well as for the more familiar applications such as catalysts, absorption and ion exchange. For these reasons, the synthesis of new zeolitic materials and an understanding of their mode of formation continues to be of paramount importance.

The vast majority of microporous materials are constructed from linked TO<sub>4</sub> tetrahedra (where T = tetrahedral atom, e.g. Al, Si, P, etc.) in which each oxygen is shared between two adjacent tetrahedra to give frameworks with an O/T ratio of 2. The tetrahedra are linked in such a way as to form regularly sized pores, channels and cages within the materials such that a significant fraction (up to 50% in some cases) of the materials is literally 'empty space'. Zeolites are hydrated aluminosilicates constructed from linked AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra with the general formula M<sup>n+</sup><sub>x/m</sub>[(AlO<sub>2</sub>)<sub>x</sub>(SiO<sub>2</sub>)<sub>m</sub>]<sup>n-</sup>·zH<sub>2</sub>O.<sup>3</sup> Pure silica zeolites contain neutral frameworks, whereas aluminosilicates contain a negatively charged oxide framework (one negative charge per Al<sup>3+</sup>). This negative charge is balanced by extra-framework positive ions (M<sup>n+</sup>) which reside inside the channels and cages of the zeolite. Aluminophosphates (AlPO<sub>4</sub>s) constitute another large class of open-framework materials.<sup>4,5</sup> Their basic frameworks are built from linked tetrahedral Al<sup>3+</sup> and P<sup>5+</sup> units and have the general formula Al<sub>2</sub>O<sub>3</sub>·1 ± 0.2P<sub>2</sub>O<sub>5</sub>·xR·yH<sub>2</sub>O, where R is the amine or quaternary ammonium salt used in the original synthesis. Conceptually, a neutral AlPO<sub>4</sub> framework can be considered to be derived from a neutral pure silica zeolite by replacement of two Si<sup>4+</sup> cations with one Al<sup>3+</sup> and one P<sup>5+</sup> cation. Isomorphic substitution of framework Al<sup>3+</sup> and P<sup>5+</sup> ions by divalent metal cations or silicon produces the MeAPO (metal aluminophosphate) and SAPO (silicon aluminophosphate) family of materials respectively.<sup>6</sup> All of the above materials contain only tetrahedrally co-ordinated units. However, recently novel microporous materials have been

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*research, also performed under the supervision of Dr. O'Hare at Oxford, was concerned with the application of in situ diffraction techniques to elucidate the kinetics and mechanisms of the hydrothermal synthesis of microporous materials. He is currently engaged in postdoctoral research in materials chemistry under the supervision of Professors A. J. Jacobson and S. C. Moss at the University of Houston, Texas.*

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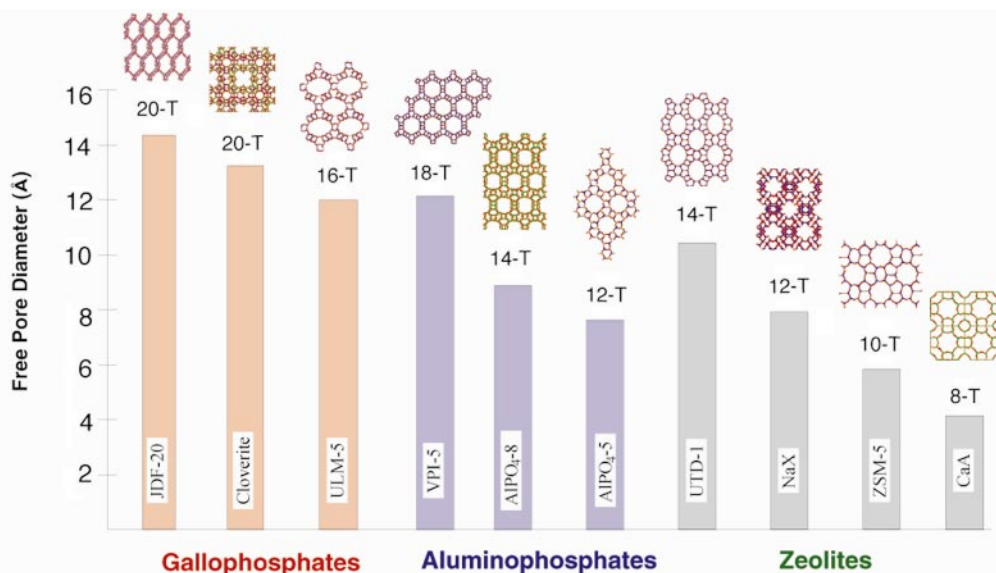


Fig. 1 The free pore diameters and structures of several well known microporous materials (after Davis and Lobo<sup>32</sup>).

synthesized in which the metal phosphate framework is constructed from units in which the metal atom resides in complexes of higher co-ordination than tetrahedral such as vanadium,<sup>7–11</sup> cobalt,<sup>12–15</sup> molybdenum,<sup>16,17</sup> iron,<sup>18</sup> gallium,<sup>19–26</sup> and indium<sup>27,28</sup> phosphates.

Nowadays, the synthesis and characterisation of new microporous materials is a huge field; over a thousand research papers a year are published on the subject, and new molecular sieve materials are regularly being discovered. This research effort is not only driven by pure academic interest but by the continued discovery and development of useful applications for these materials due to their unique chemical, physicochemical and catalytic properties. Unfortunately, the processes by which microporous materials form in hydrothermal crystallisations are very complex and poorly understood (see below). Lok *et al.*<sup>29</sup> have described understanding molecular sieve crystallisations as one of the most challenging chemical problems of today. The lack of mechanistic understanding of the formation of molecular sieves has meant that the discovery of new microporous materials, to date, has been a mainly heuristic exercise involving the systematic exploration of many reaction variables, and requiring a fair degree of serendipity for the successful synthesis of new materials. A more complete understanding of the fundamental processes occurring during hydrothermal crystallisations leading to more rational syntheses of new molecular sieve materials would therefore be of great value. In this short article we review the current state of the art relating to the kinetics, growth and mechanisms of formation of these materials, and the experimental techniques that are currently being applied to the study of their formation. This perspective is not intended to be a detailed review of the synthesis and structures of microporous materials, and for much more detailed information the reader is directed towards the many excellent books and reviews that have been written on the subject.<sup>3,5,6,30–33</sup>

## 2 Historical background

Although zeolites ‡ were first identified as a class of minerals in

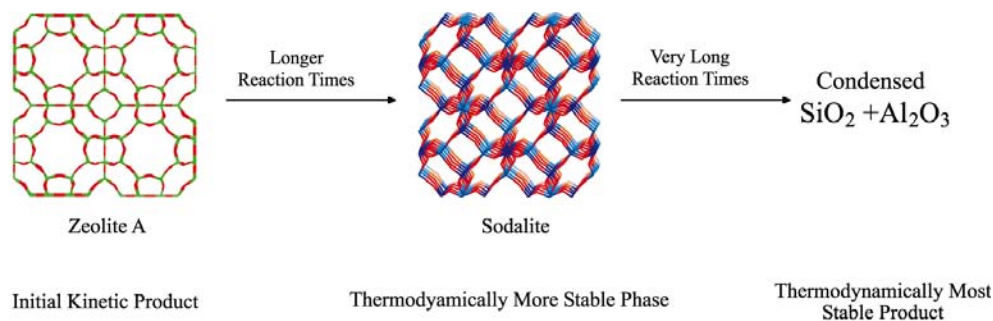
‡ Zeolitic materials were first recognised as a new class of compounds by the Swedish mineralogist A. F. Cronstedt in 1756. He observed that when an unidentified silicate material (since identified as stilbite) was heated in a blowpipe flame it fused with marked intumescence (swelling). This result led to all other minerals that showed this property to be called zeolites, which is derived from the Greek words *zeo* meaning 'to boil' and *lithos* meaning 'stone'. Since then approximately 40 natural zeolites have been discovered.

1756, attempts artificially to synthesize zeolitic materials did not begin until 1862. Early attempts concentrated on simulating the high temperatures and pressures ( $T > 200$  °C,  $P > 100$  bar; bar =  $10^5$  Pa) of geological conditions under which natural zeolites were believed to form. However, it was not until 1948 that the successful synthesis of a zeolitic material without a natural counterpart was reported by Barrer.<sup>1</sup> The first large scale synthetic methodologies for the synthesis of zeolites were pioneered by Milton and co-workers at the Union Carbide laboratories in the late 1940s, who developed hydrothermal zeolite syntheses at low temperature (*ca.* 100 °C) and low pressure (autogenous) using alkali metal aluminosilicate gels. The next major advance in zeolite synthesis occurred in 1961, when Barrer and Denny<sup>34</sup> reported the synthesis of zeolites using organic alkylammonium cations instead of alkali metal cations. The introduction of organic cations allowed the synthesis of zeolites with a much higher Si/Al ratio than is found in natural zeolites. The use of organic cations in zeolite synthesis increased rapidly after the work of Barrer and Denny, and the ready availability of a large range of organic cations allowed many new high silica zeolites to be prepared.

A further significant advance in molecular sieve synthesis occurred in 1982, when Wilson *et al.*<sup>4</sup> reported the synthesis of aluminophosphate (AlPO<sub>4</sub>) molecular sieves. These materials were synthesized under acidic or neutral conditions as opposed to the strongly basic conditions used in the synthesis of zeolites. Following this discovery other related classes of materials such as MeAlPOs and SAPOs were rapidly synthesized in which the addition of other elements into the reaction gels results in their incorporation into the framework.<sup>6</sup> Recently, the synthesis of microporous structures has begun to spread across all parts of the Periodic Table, and a number of new classes of microporous materials incorporating a large variety of main group and transition metal elements have been synthesized.

## 3 Synthesis of microporous materials

Molecular sieves are almost exclusively synthesized under hydrothermal conditions at temperatures of between 100 and 250 °C under autogenous pressure, under either strongly basic conditions (for zeolites), or weakly acidic or neutral conditions (for metal phosphates or derivatives). The versatility of the hydrothermal technique derives from the extremely effective solvating ability of water under these conditions. This allows the dissolution and mixing of the solid reagents to form an inhomogeneous gel in the initial stages of the reaction. At



**Fig. 2** Schematic diagram illustrating Ostwald's law of successive reactions operating during the synthesis of zeolite A and sodalite. Zeolite A is the kinetically favoured product and at short reaction times it is the dominant product of the reaction. At longer reaction times a transformation to the more thermodynamically stable sodalite structure occurs. At very long reaction times conversion into the thermodynamically most stable product,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , will eventually occur.

later times nucleation centres are formed which subsequently grow as the reaction proceeds to form the final crystalline product.

The chief difficulty of the hydrothermal technique is the very large number of possible reaction variables, all of which affect the pathway and kinetics of the reactions in ways that are not generally understood.<sup>32</sup> Typical reaction variables include time, temperature, pressure, reactant source and type, pH, the inorganic or organic cation used, ageing time of the gel, reaction cell fill volume, and so on. Since, in general, variation of any one of these parameters can have an effect on several others, it is often difficult to evaluate the effect of varying one parameter in a straightforward way. Owing to this difficulty, the synthesis of new molecular sieves has generally proceeded by systematically exploring what the effect of changing each variable is on the synthesis. Since this effectively means exploring a vast  $n$ -dimensional reaction space (where  $n$  is the number of reaction variables), this process can be very time consuming and not very efficient. A greater understanding of the processes occurring during hydrothermal syntheses leading to a more rational approach to the synthesis of new molecular sieves would be very desirable. Nevertheless, despite these difficulties, certain guidelines for the effects of various reaction variables on hydrothermal syntheses can be given.

It is generally found that as the temperature of synthesis is raised there is a trend towards forming species with a lower intercrystalline void space and lower water content. For example, zeolites such as A and X which have porosities at the high end of the range for zeolites (up to 50% void space) are generally synthesized at temperatures close to 100 °C, whereas reactions at much higher temperatures (e.g. 350 °C) often yield dense phases. This can easily be rationalised by the exponential increase in the autogenous pressure of water with increasing temperature.

Of course, it is evident that changing the initial reaction composition will affect the nature of the final phase formed. However, it is unfortunately not simply the case that one can tailor the composition of the final product simply by using the desired ratios of the starting materials in the reaction. This is because molecular sieve syntheses are generally inhomogeneous reactions consisting of both liquid and solid components, and changing the qualities of any one component changes the chemical composition of *both* the solution and the solid phase. Hence, the chemical composition of the solid product does not reflect the overall composition of the mixture.

Molecular sieve materials are metastable phases which are thermodynamically unstable with respect to dense oxide phases. It is therefore clear that the formation of zeolitic materials cannot be rationalised on the basis of thermodynamics alone, and kinetics must also play a large part in determining which particular phases are formed. Time is therefore also an important factor governing the products formed in molecular sieve syntheses. The synthesis of zeolitic materials obeys Ostwald's law

of successive reactions. This law states that an initial metastable phase is successively converted into a thermodynamically more stable phase until the most stable phase is produced. Ostwald's law has been observed in a number of zeolite syntheses (Fig. 2). For example, zeolite A converts into the more stable sodalite after long reaction times. The successful commercial synthesis of the former phase relies on controlling the reaction time to produce optimum yields.

In molecular sieve syntheses it is found that the nature of the cation used in the synthesis is a critical factor in determining the composition and structure of the final product formed. In zeolite syntheses the use of alkali metal cations generally results in the synthesis of aluminium rich zeolites; if organic cations are used silicon rich zeolites are formed. Silicon rich zeolites can only be synthesized in the presence of organic cations. (The exception of ZSM-5, which is a high silica zeolite which can be synthesized in the absence of any organic cations over a very narrow range of  $\text{Na}^+$  and aluminium concentrations.)<sup>35</sup> This can be rationalised by a consideration of the much larger size of organic cations compared with alkali metal cations. This greater size means that fewer cations can be contained within the zeolite framework. Hence, for the material to be charge neutral the charge density of the host framework must be lower, *i.e.* the Si/Al ratio must be higher.

The large variety of sizes and shapes of organic cations when compared to spherical alkali metal cations means there is much more scope for the synthesis of new silicon rich zeolites compared with aluminium rich zeolites. The ability to control the steric and electronic nature of the organic cation adds a new dimension to the chemist's ability to control the interactions occurring during crystallisation, and consequently the structure of the final product. Implicit in this is the idea that the organic molecule is acting as much more than simply a charge balancing cation and is playing a structure directing or 'templating' role during the crystallisation of the zeolite. This idea is central to much molecular sieve synthesis and is discussed in much more detail in the next section.

The synthesis of metal phosphate molecular sieves and derivatives follows broadly the same principles as for zeolites, with the important difference that phosphate molecular sieves are always synthesized under either acidic, neutral or mildly basic conditions as opposed to the highly basic conditions used in the synthesis of zeolites.<sup>4,6</sup> The vast majority of phosphate molecular sieves are synthesized at a pH of between 4.0 and 6.5 and temperatures of between 130 and 200 °C. Phosphate based molecular sieves can only be synthesized in the presence of organic amines or alkylammonium ions. Thus, as with the synthesis of high silica zeolites, the organics appear to be acting in a structure directing template role. An interesting and notable exception to this rule is the synthesis of the extra-large pore aluminophosphate VPI-5. In the original synthesis reported by Davis *et al.*<sup>36</sup> a structure directing agent was used. However, subsequently, Duncan *et al.*<sup>37</sup> reported that under certain

conditions VPI-5 could be synthesized in the absence of any organic molecules. However, there is also some suggestion that the occluded water in as synthesized VPI-5 is ordered in a triple helix within the aluminophosphate framework.<sup>38-41</sup> Although the precise details are not fully understood it has been postulated that the water structure in VPI-5 in some way acts in the role usually played by the inorganic. In this report the synthesis of VPI-5 is unique. This kind of effect has not been observed in any other  $\text{AlPO}_4$  syntheses.

#### 4 The concept of templating

The concept that the organic molecules used in molecular sieve syntheses were not simply acting as charge balancing cations, and were in fact playing an active role in 'directing' the synthesis of a particular molecular sieve structure, was first suggested because of the close correlation that was often seen between the size and shape of the template and the size and shape of the cavities formed. For example, in the synthesis of sodalite using tetramethylammonium cations it is found that in the final product the  $\text{NMe}_4^+$  cations are located at the centre of the sodalite cages, from which the cation is too big to either enter or leave, suggesting that the sodalite framework must have formed around the cations.<sup>42</sup> Another well known example is the synthesis of high silica ZSM-5 using the tetrapropylammonium cation as the organic species. In this case it is found that the cation is located at the intersection of the two intersecting channel systems, with the four long alkyl chains lying along the four individual channels.<sup>43</sup> These and other observations led to the suggestion that the organic molecules were acting as 'templates' and 'building' the molecular sieve structure around themselves by directing the condensing oxide tetrahedra into a particular geometry.<sup>29,44</sup>

However, it is clear that the situation is very much more complex than originally suggested. For example, although it is true that  $\text{NPr}_4^+$  is an effective structure directing agent for the synthesis of ZSM-5, ZSM-5 can also be synthesized in the absence of any organic molecules.<sup>35</sup> There are also a plethora of examples of the same organic species forming a variety of different molecular sieve structures, or the same structure being formed by a variety of different organic molecules (there are at least 22 different organic molecules that can be used to synthesize ZSM-5 for example). Furthermore, the correlation between template shape and pore shape is often weak. In the synthesis of aluminophosphates the necessity of using organic molecules, and the specific requirement of using a particular organic agent in the synthesis of certain frameworks [e.g.  $\text{AlPO}_4\text{-20}$  (SOD) can only be synthesized using  $\text{NMe}_4\text{OH}$ ]<sup>4</sup> also suggested a templating effect. However, again, it is also true that some  $\text{AlPO}_4\text{s}$  can be synthesized using a number of templates [for example,  $\text{AlPO}_4\text{-5}$  (AFI) can be synthesized using over 20 different species],<sup>4</sup> and the same template can be used to synthesize a number of structures. A further interesting point is that the very-large pore phosphate based molecular sieves (e.g. VPI-5,<sup>36</sup> JDF-20,<sup>45</sup>  $\text{AlPO}_4\text{-8}$ ,<sup>46</sup> cloverite,<sup>21</sup> ULM-5<sup>23</sup> and ULM-16<sup>25</sup>) have all been synthesized using relatively small organic molecules. Although it is obvious that the organic molecules are playing some structure directing role in the synthesis of molecular sieve materials, it seems clear that in most cases they are not acting in a true templating manner; *i.e.* not directing the formation of a unique zeolitic structure which reflects the geometric and electronic structure of the template.

Some authors have sought to draw a distinction between 'templating' and 'structure direction'.<sup>47</sup> In this context, 'templating' refers to the process described above, in which a unique template leads to the formation of a unique structure which reflects the geometrical and electronic structure of the template, whereas 'structure direction' describes a more subtle effect in which the use of a particular organic moiety leads to a preference for the synthesis of a particular structure

*via* a combination of factors such as pH modification, solubility modification, and electrostatic interactions with the solubilised silica, aluminium and phosphate species in the reaction mixture. Davis and Lobo<sup>32</sup> in their review published in 1992 further extended this idea, and suggested that organic guest molecules can act in three distinct ways: (i) as space filling species, (ii) as structure directing agents, and (iii) true templates.

Space filling refers to the situation in which the role of the organic is simply to exclude water from the voids in the zeolite framework, decreasing unfavourable energetic interactions between the solvent water and the growing molecular sieve. It is clear that in the cases where an organic is simply acting as a space filler, the precise nature of the organic is not of great importance. Therefore the converse can also be implied, namely that in those cases where a great many different templates can be used to synthesize the same structure (such as ZSM-5 and  $\text{AlPO}_4\text{-5}$ ) the primary role of the organic in these cases must be simply as a space filling agent.

Actual structure direction by an organic molecule implies that the use of a particular template leads to a unique structure which cannot be synthesized by the use of any other templates. There are several examples of this kind of structure direction in the zeolite field. For example the synthesis of CIT-1 was achieved by using a very specific organic template.<sup>48</sup> There have been several studies published on structure direction in the synthesis of zeolites. One of the most detailed was Gies and Marler's work<sup>49</sup> on the structure directing effects of organic molecules during the crystallisation of porosils. By studying the synthesis of these materials using the simplified system  $\text{SiO}_2/\text{organic}/\text{H}_2\text{O}$  they were able to avoid the complicating effects of the mutual interactions that occur between the various components of the more complex zeolite syntheses studied by previous researchers. Gies and Marler found that there was a very high correlation between the size and shape of the organic used and the size and shape of the framework pore produced. They concluded that, since there are no ionic interactions between the guest molecules and the framework, the closeness of the geometrical fit between the host and guest must be due to an optimised arrangement for maximising the van der Waals contacts between host and guest. These results were supported by subsequent solid state NMR measurements by Burkett and Davis which suggested that weak non-covalent interactions between the organic molecules and the silicate species are important (see below). These results, together with work by Weibcke,<sup>51</sup> offer a fairly convincing argument for structure direction by organic molecules in the synthesis of high silica zeolites. However, it is not clear how true this is for other types of molecular sieves. Little work has been done on the mechanism of structure direction in the synthesis of phosphate molecular sieves. However, since the frameworks of  $\text{AlPO}_4\text{s}$  are neutral it seems clear that van der Waals interactions between the host framework and the organic guest must be the dominant factor in determining the structure formed. It has also been suggested that the amines also play a role in modifying the gel chemistry in  $\text{AlPO}_4$  syntheses. It is known that under the low pH conditions used in  $\text{AlPO}_4$  syntheses the tetrahedral  $\text{AlO}_4$  species that form the precursors to the crystalline products are unstable with respect to octahedral aluminium species.<sup>52,53</sup> It has therefore been suggested that the amine stabilises the  $\text{AlO}_4$  units by bonding to them and forming a hydrophobic shell which resists nucleophilic attack by the solvent water.<sup>54</sup>

Examples of templating in the truest sense of the word (*i.e.* corresponding to Davis' third definition) are much rarer. One notable example where true templating may be occurring is the formation of the zeolite ZSM-18. This was first synthesized in

§ Porosils are porous tectosilicates of the general formula  $x\text{M}\cdot\text{SiO}_2$  (where M is the organic guest and  $x$  can vary over a very wide range) and include clathrasils and pure silica zeolites such as ZSM-5, -11 and -48.

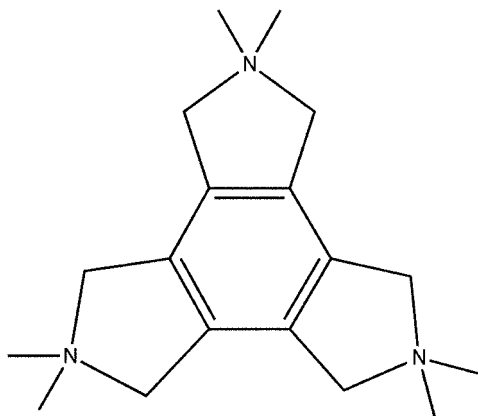


Fig. 3 The organic template, 'tri-quat', used to synthesize ZSM-18.

1970 using the triquaternary amine ( $C_{18}H_{30}N_3^{3+}$ ) shown in Fig. 3.<sup>55</sup> The extremely close registry between the shape of the organic molecule and the shape of the pore system in ZSM-18 suggested that true templating had indeed occurred. Energy minimisation calculations by Davis and Lobo<sup>32</sup> indicated that, in the lowest energy conformation, the template was held in a cage in the zeolite framework that has the same three-fold symmetry as the organic template, and that the organic molecule was not able to rotate in this cage which implies that true templating has taken place. Subsequent work by Stevens *et al.*,<sup>56</sup> who performed Monte Carlo simulated annealing calculations to predict the location and orientation of organic molecules inside zeolite hosts, supported these calculations. Their calculations showed that along the channels in ZSM-18 there is a perfect match between the shape of the organic and the shape of the zeolite pore. These results showed that the shape of the template plays a crucial role in determining the location of the  $TO_4$  groups around it, and hence the structure of the final product. It is these strong guest–host interactions that distinguish true templating from structure direction.

It should be obvious from the above discussion that the precise role that organic molecules play in molecular sieve synthesis is not entirely understood and the matter is still very much a subject of debate and discussion. Nevertheless, it is clear that the use of specific organics is frequently necessary for the successful synthesis of a particular molecular sieve structure. For this reason many authors (including us) often use the terms 'template' and 'structure directing agent' interchangeably and synonymously when referring to organic species.

## 5 Mechanisms of formation of molecular sieves

Conceptually, the crystallisation of a zeolitic material can be considered to follow an idealised process involving three states. Initial dissolution of the solid starting reagents by the solvent water to form a randomly distributed array of reaction components, followed by an ordering of some of these components on a microscopic level (*i.e.* formation of nucleation sites), and finally the growth of these nucleation sites to form the final material in which long range order is observed (*i.e.* the formation of crystals).

The difficulty in trying to understand the precise details of the mechanisms and processes occurring during the formation of a zeolitic material is due to the extreme complexity of hydrothermal crystallisations. The reactions occur in multi-component systems in which there are a plethora of interactions, chemical reactions, equilibria, and crystal nucleation and growth processes taking place throughout a heterogeneous reaction mixture. Further to complicate matters, many of these processes are interrelated and change with time over the course of the crystallisation.

Nevertheless, several authors have proposed mechanisms for

the synthesis of molecular sieve materials. In particular, there are two postulated mechanistic processes that comprise the two extremes of the range; (i) the solution-mediated transport mechanism, and (ii) the solid hydrogel transformation mechanism. The solution-mediated transport mechanism involves dissolution of the reagents in the solution phase followed by transport of the dissolved silicate/phosphate species *via* solution-mediated diffusion to the nucleation sites where crystal growth takes place. The solid hydrogel transformation mechanism involves the reorganisation of the solid phase from an initially amorphous state to one with long range order (*i.e.* the crystallised zeolite). It is clear that in any particular case the true mechanism could lie somewhere between these two extremes, or could proceed *via* a combination of both.

There are many examples of zeolitic crystallisations that appear to proceed *via* the solution transport mechanism, particularly in the synthesis of aluminium rich zeolites. Perhaps the most convincing examples are provided by Ueda *et al.*<sup>57</sup> who crystallised zeolites Y, S and P from *clear* solutions and Testa *et al.*<sup>58</sup> who crystallised zeolites ZSM-5 and ZSM-11 from similar *clear* solutions. In these cases the possibility of any solid–solid transformation appears to be ruled out. A good example of the solid hydrogel transformation mechanism is demonstrated by Xu *et al.*<sup>59</sup> They synthesized ZSM-5 and ZSM-35 by first dehydrating an amorphous aluminosilicate gel at 550 °C, and then treating this mixture with liquid triethylamine and ethylenediamine in the absence of water at 160 °C. They observed no silicate or aluminate species in the liquid phase during the crystallisation of the zeolite indicating that a solid phase transformation must be occurring. However, work by Iton *et al.*<sup>60</sup> and Bodart *et al.*<sup>61</sup> has shown that ZSM-5 can be synthesized *via* either of the two extreme reaction mechanisms depending on the reaction conditions. Aluminophosphates also appear to crystallise *via* both mechanisms depending on the reaction conditions. For example, Pang *et al.*<sup>62</sup> have synthesized element substituted  $AlPO_4$ s from *clear* solutions, while Davis *et al.*<sup>63</sup> have demonstrated that VPI-5 can be crystallised *via* a solid hydrogel mechanism (although as discussed previously the crystallisation of VPI-5 is unusual and may not be representative of the crystallisation of aluminophosphates in general).

Since different molecular sieves can crystallise *via* different mechanisms, and the same molecular sieve can crystallise *via* different mechanisms, or a combination of mechanisms, depending on the reaction conditions, no general conclusions can be drawn as to which of the postulated mechanisms is occurring in any particular system or class of molecular sieves. Also, neither of the proposed mechanisms addresses the question of exactly what are the detailed processes taking place during crystallisation. In particular, the issues that need to be clarified are: what controls which specific molecular sieve structure is formed?; what are the interactions between the various components in the system?; what species are formed in the solid and in solution as the reaction proceeds?; how is the mechanism of structure direction taking place? (*i.e.* how is the geometry and electronic structure of the template being transmitted to the silicate/phosphate species in solution in such a way as to translate in the structure of the final zeolitic product?); how does nucleation occur, and how does crystal growth take place once nucleation has occurred?

In an effort to gain a greater understanding of the processes occurring during the formation of a molecular sieve interest has focused on the formation and role in the nucleation process of small inorganic clusters present in molecular sieve synthesis gels. Many spectroscopic techniques have been used to try and identify particular silicate/phosphate molecular species which are postulated to condense initially to form nucleation centres which then grow to form the infinite framework structure. Spectroscopic techniques that have been used include NMR, MAS-NMR, IR and Raman. These studies have identified several fundamental structures found in molecular sieve

materials (such as single and double four membered rings), and yielded some interesting information about the interaction of species present in zeolitic precursor gels. For example, in the synthesis of zeolite A, Dutta and Shieh<sup>64</sup> observed the formation of 4 T-atom membered rings in the amorphous aluminosilicate solid, and observed that the solid reorganises *via* interaction with  $\text{Al}(\text{OH})_4^-$  ions in solution to form nuclei of zeolite A. However, it is also clear that in many cases species are observed spectroscopically that are never seen in the zeolitic products. Knight *et al.*<sup>65</sup> in their recent overview of NMR studies of zeolite crystallisations suggest that the silicate species observed by NMR are merely spectator species and do not condense to form the zeolite framework, and furthermore many of the previous assignments of the silicate species may be in error. Therefore, it is not clear exactly what the relationship is between the species observed spectroscopically and the final zeolitic products, and it seems unlikely that the very small species observable by spectroscopy react directly to form the final product. Davis and Lobo<sup>32</sup> have suggested that it seems more likely that these small species are not directly incorporated into the final lattice, but instead form more extended structures with medium range order that are not observable by short range spectroscopic techniques such as Raman/NMR. It is further suggested that it is these extended structures that participate in the formation of the nucleation centres and then, in turn, the long range structure of the material, whether it be by the solution transport or solid hydrogel transformation mechanism, or a combination of both. Therefore emphasis should be placed on understanding the formation of structures and nucleation centres on larger length scales than those probed by spectroscopy. Recently, a number of such longer length scale studies have been published. These experiments are described in detail in section 6.

There is evidence that at least in some cases molecular sieve structures are formed *via* a layer by layer growth mechanism and that extended sheet structures are important building units in their formation. In particular, this is suggested by the formation of layered intergrowth structures, for example ZSM-5/ZSM-11,<sup>66</sup> FAU/EMT,<sup>67,68</sup> and SSZ-26/SSZ-33/CIT-1<sup>48,69</sup> intergrowths, in which it is difficult to account for these structures by anything other than a layer by layer growth mechanism. The fact that the precise layer stacking sequence can be controlled by systematic manipulation of the organic templating agent adds weight to this view.<sup>48,67,70</sup> Finally, Vaughan<sup>71</sup> has provided evidence that the presence of sodium in an aluminosilicate gel promotes the formation of faujasite sheets.

One of the most detailed studies of the mechanism of formation of a molecular sieve was Burkett and Davis' study of the formation of pure silica ZSM-5 (Si-ZSM-5 or silicalite) using tetrapropylammonium.<sup>50,72,73</sup> The formation of ZSM-5 in the presence of  $\text{NPr}_4^+$  has long been considered to be a classical example of structure direction in the formation of zeolites, based on the close correspondence between the shape of the cation and the intersection of the channels in ZSM-5, and the tight enclathration of the  $\text{NPr}_4^+$  within the zeolite post synthesis.<sup>43</sup> In the original report of the synthesis of Si-ZSM-5 it was postulated that the mechanism of structure direction by  $\text{NPr}_4^+$  was *via* the preorganisation of silicate species around the organic cation prior to zeolite crystallisation.<sup>43</sup> Gies and Marler's work<sup>49</sup> suggested that this interaction was primarily *via* van der Waals contacts. Subsequent studies by, for example, <sup>29</sup>Si MAS NMR were hampered by the inappropriate length scales probed by such techniques, as discussed above.

By applying the technique of solid state cross polarised magic angle spinning Burkett and Davis<sup>50</sup> could probe in detail, on the appropriate length scales, the interactions occurring before and during the crystallisation. By performing <sup>1</sup>H-<sup>29</sup>Si CP MAS NMR between the protons of the  $\text{NPr}_4^+$  and the silicon atoms of the zeolite precursors they were able to study the interaction between the organic and inorganic components. They found

that short range intermolecular interactions (*i.e.* of the order of van der Waals interactions) are established in the synthesis gel *before* the development of long range order indicative of a crystalline solid. Furthermore the NMR data suggested that the  $\text{NPr}_4^+$  adopt a conformation within the composite organic-inorganic zeolite precursor similar to that which they have in the final product. Burkett and Davis' work provides the first *direct* evidence of preorganised organic-inorganic composite structures during the synthesis of Si-ZSM-5, and is consistent with a mechanism of structure direction in which these organic-inorganic composite structures from the precursors to the formation of the ZSM-5 channel intersections.

Further, more detailed, work on the  $\text{NPr}_4^+$ /Si-ZSM-5 system allowed them to refine their proposed mechanism.<sup>72-74</sup> As shown in Fig. 4 they suggested that the formation of the organic-inorganic composite species is initiated by overlap of the hydrophobic hydration spheres around the  $\text{NPr}_4^+$  cation<sup>75</sup> and hydrophobically hydrated domains of soluble silicate species. (Hydrophobic hydration is the reorientation of water molecules in the vicinity of a hydrophobic solute species in order to accommodate them whilst still maintaining a fully hydrogen bonded network.)<sup>76</sup> This allows the establishment of favourable van der Waals contacts between the alkyl chains of the  $\text{NPr}_4^+$  and the hydrophobic silica species, whilst at the same time allowing the release of the water molecules from the ordered hydration spheres around the  $\text{NPr}_4^+$  and silica species. This process provides both an enthalpic and entropic driving force for the formation of the organic-inorganic species, which provide the precursor units for the formation of the final crystalline product. Furthermore, Burkett and Davis postulate that crystal growth occurs *via* diffusion of these composite species to the growing crystalline surface in a layer-by-layer growth fashion which is consistent with known layered intergrowth structures such as ZSM-5/ZSM-11<sup>66</sup> and SSZ-26/SSZ-33/CIT-1<sup>48,69</sup> intergrowths. Burkett and Davis' proposed mechanism which incorporates all these ideas is shown in Fig. 4.

Further insight was provided by studying the formation of Si-ZSM-5 and Si-ZSM-48 using hexanediamine as the organic structure directing agent. At lower temperatures (120 °C) ZSM-5 is formed, and interactions are again seen between the inorganic and organic components, suggesting that organic-inorganic composite units form prior to the formation of a long range ordered material. At higher temperatures ZSM-48 is formed and in this case no interactions are seen between the inorganic and organic components, suggesting that structure direction is not occurring in the same way in this case. Burkett and Davis suggest that the higher temperature could disrupt the hydrophobic hydration spheres around the hexanediamine molecules. This result is interesting in the light of the fact that Si-ZSM-48 can be synthesized in the presence of many amines suggesting that the amines are playing a space filling role, whereas Si-ZSM-5 can only be synthesized in the presence of  $\text{NPr}_4^+$  or hexanediamine suggesting that the amines are playing a specific structure directing role. This raises the question of whether the ability to form a hydrophobic hydration sphere is a pre-requisite for a species to serve as a structure directing agent, whether the formation of a hydrophobic hydration sphere is simply a reflection of other properties that make an organic molecule an effective structure directing agent, or the correlation is simply coincidental due to the relatively small number of syntheses studied so far (seven in the Burkett/Davis study). It also suggests that the synthesis of aluminosilicate ZSM-5, which is known to be effected by a large variety of organics, is formed by a different mechanism in which the aluminosilicate gel chemistry is the controlling factor rather than organic-inorganic interactions.

The mechanisms of formation of aluminophosphate and related classes of molecular sieves have been less thoroughly studied. It is generally considered that the first stage in the synthesis of aluminophosphate materials is the reaction of

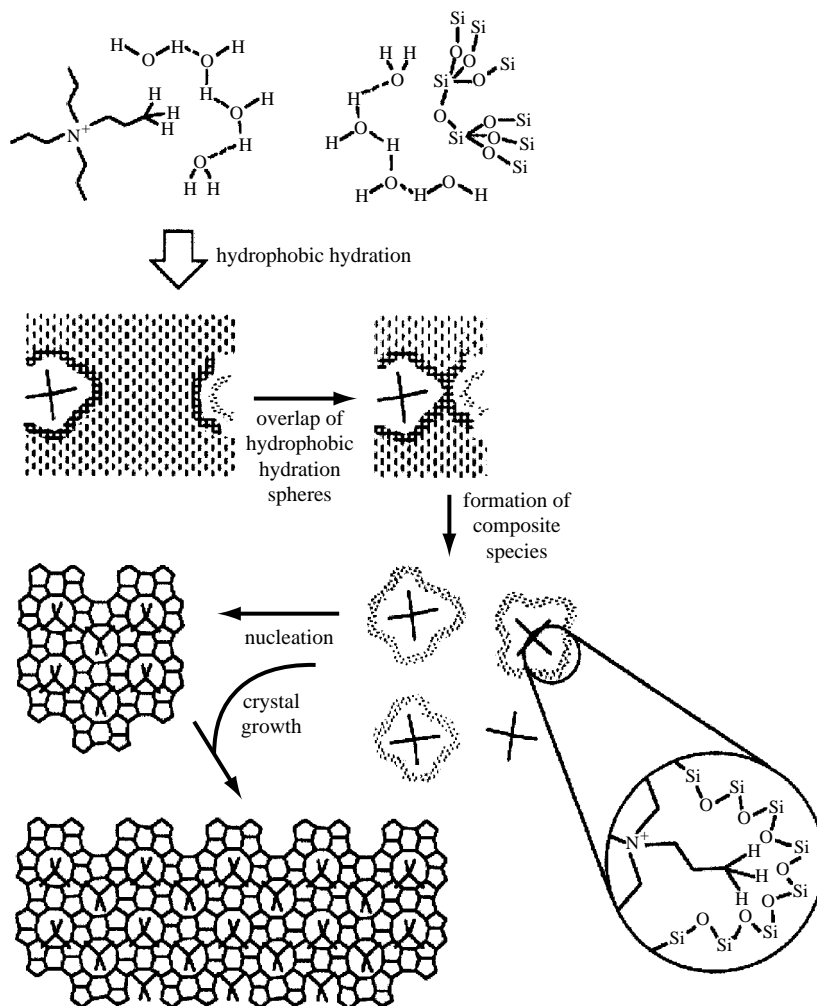


Fig. 4 Schematic diagram of Burkett and Davis' proposed mechanism for the formation of Si-ZSM-5 (adapted with permission from ref. 73).

the aluminium containing starting material (usually pseudo-boehmite or an aluminium alkoxide) with the phosphoric acid to form an amorphous aluminophosphate layer.<sup>77,78</sup> The next stage in the process is less clear, however. Some authors have argued that a direct solid-state transformation occurs to give the final crystalline product. Others have argued that complete dissolution of the aluminophosphate layer occurs to produce small solution phase building units, similar to those postulated to be involved in zeolite syntheses, which subsequently condense to form the final products.<sup>20</sup> However, as with the synthesis of zeolites, although there is some evidence for the existence of aluminophosphate entities in solution, there is little evidence that these species are the direct precursors of the final crystalline product. More recently, Ozin and co-workers<sup>79</sup> have proposed a model for the formation of aluminophosphates in which two- and three-dimensional structures are formed *via* hydrolysis and condensation of an initial chain structure which forms first in solution. However, whilst there is compelling evidence for the transformation of chain structures to layered structures in some systems studied,<sup>80</sup> it is far from clear at this time that this is a general pathway by which aluminophosphate molecular sieves are produced.

An alternative approach to the understanding of the formation mechanisms of microporous materials is to use computational techniques and molecular modelling as tools to probe the relationship between the templates used and the framework structures formed.<sup>81</sup> Some of the most successful approaches have used molecular mechanics methodologies to study the interactions between particular organic molecules and framework structures.<sup>56,82-86</sup> Such studies can lead to a more thorough understanding of how these interactions affect the efficiency of

a particular organic molecule to act as a template for a given host structure, and can therefore be used as a guide for selecting an effective template for a given target framework structure. The application of these techniques in relation to the synthesis of ZSM-18 has already been referred to.<sup>56</sup> More recently, work by Lewis and co-workers<sup>87,88</sup> has made the rational 'design' of a target microporous materials a much more realisable goal. They have developed 'de novo' molecular design methodology in which potential template molecules are 'grown' from an initial seed molecule. Potential templates grown in such a way are then ranked according to the binding energy within a given pore system, which gives a good guide to the likely effectiveness of a particular organic molecule as a template for that molecular sieve structure. A recent good example of the application of this technique was provided by the Lewis *et al.*<sup>89</sup> synthesis of DAF-5 (a CoAPO with the Chabazite structure). Using a computationally designed 4-piperidinopiperidine molecule as a template they were able to synthesize DAF-5 using short preparation times in the absence of any other microporous phases, a task impossible to achieve using the smaller organic templates known to result in the synthesis of Chabazitic cobalt aluminophosphates.

Whilst the experimental studies and computational approaches referred to above have shed light on the processes occurring during hydrothermal syntheses, and revealed details of the mechanisms of crystal nucleation and growth occurring for specific cases, it is clear that, in general, the mechanisms of hydrothermal syntheses are still not well understood. Although progress has been made, the rational *a priori* 'design' of a molecular sieve is in general still difficult to achieve because of a lack of mechanistic understanding of their synthesis. Given the

broad range of useful properties that molecular sieves possess a more complete mechanistic understanding of their formation leading to a more rational approach to their synthesis is still a highly sought after goal in materials science. The main difficulty is the lack of a universal crystallisation mechanism for molecular sieve materials, with the result that each individual synthesis must be studied using techniques such as those described above, which are often laborious, demanding, and sometimes ambiguous. For this reason, increasing use is being made of non-invasive '*in situ*' studies to probe the course of zeolitic crystallisations which are capable of delivering far more information. Cheetham and Mellot<sup>90</sup> have recently reviewed the application of *in situ* techniques to the study of a wide variety of materials synthesized from sol-gel precursors. Here we review in detail the specific application of *in situ* techniques to study the hydrothermal crystallisation of molecular sieve materials.

## 6 *In situ* measurements of crystallisation

The studies described above are all '*ex situ*' studies. That is, they were performed by periodically removing aliquots of the reaction mixture, quenching the reaction, working up the synthesized products, and finally analysing the products using conventional techniques such as X-ray diffraction (XRD), MAS NMR and SEM. Besides being labour intensive and providing relatively few data points, such techniques inevitably raise the question of whether the reaction is being affected by the analysis process, and if the species observed in these experiments are really representative of species present in the reaction medium at the time of quenching. *In situ* real time studies that probe the processes occurring during crystallisation, without the need for quenching, not only allow the continuous monitoring of the reaction (thus vastly increasing the amount of data that can be obtained), but also allow the reactions to be studied under *normal reaction conditions*. Thus the question of the method of analysis causing unknown structural changes does not arise.

The advantages of *in situ* experiments over *ex situ* experiments can be summarised as follows. (i) *In situ* experiments eliminate the need for sample quenching and work-up, during which the sample may undergo significant and indeterminable structural changes. (ii) Since the reaction is monitored continuously the information gained per reaction is vastly higher. In particular, the time resolution that can be routinely achieved in most experiments is much higher than with conventional techniques; which is important for kinetic and mechanistic studies. (iii) *In situ* studies allow the direct observation of intermediate phases and their subsequent conversion into the final crystalline product. (iv) *In situ* experiments provide a ready method for easily probing the effect of changing synthesis parameters such as temperature, pressure, reagents used, and the gel composition, and allow one to monitor the interconversion of phases as the conditions are varied.

Unfortunately, the nature of molecular sieve crystallisations means that *in situ* studies of hydrothermal reactions are a far from routine procedure. The chief difficulty is the necessity of constructing reaction cells that are able to withstand the relatively high temperatures and pressures required for the synthesis of molecular sieve materials, whilst also conforming to the constraints imposed by the environment in which the measurements will be performed, for example a diffractometer or an NMR machine. However, despite these difficulties, a number of *in situ* studies on the formation of molecular sieves have been published over the last few years. A variety of techniques have been successfully applied, including NMR, IR/Raman, EXAFS, optical microscopy, light and neutron scattering, X-ray diffraction, neutron diffraction and small angle diffraction. These experiments have shed light on the species involved in nucleation, the mechanisms of nucleation and growth, the kinetics and energetics of growth, the influence of

reaction conditions on the course of the reactions, and the observation and identification of intermediate phases.

### 6.1 *In situ* spectroscopic and optical techniques

The range of spectroscopic and optical techniques that have been used to study molecular sieve synthesis *in situ* includes NMR,<sup>91</sup> IR/Raman,<sup>92</sup> EXAFS,<sup>93-96</sup> optical and electron microscopy,<sup>97</sup> and light scattering.<sup>98</sup>

*In situ* NMR studies are relatively uncommon despite the large number of good NMR nuclei present in molecular sieve materials, e.g. <sup>27</sup>Al, <sup>29</sup>Si, <sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N. This is probably a reflection of the difficulty of designing suitable reaction cells and heating systems for studying crystallisations at high temperatures that are compatible with being contained within an NMR chamber. There have been a number of NMR studies of the unheated gel prior to reaction but, as was discussed above, the relationship of the species observed in these studies and the final zeolitic product have proved difficult to determine, and hence the value of such studies is limited.

An example of a true *in situ* NMR measurement of a zeolite crystallisation is provided by Shi *et al.*<sup>91</sup> who studied the synthesis of zeolite A at 65 °C, by constructing a rotor which could be sealed and held at relatively high temperatures whilst recording MAS NMR spectra. They studied the time variation of the <sup>27</sup>Al and <sup>29</sup>Si spectra during the crystallisation. Unfortunately, during the nucleation period both spectra remained unchanged reflecting the fact that the NMR technique is insensitive to the length scales at which changes are occurring during this period of the reaction. However, they were able to observe that during the growth of the zeolite the NMR lines narrowed (see Fig. 5) indicating that NMR can be used to probe the onset of long range ordering within a growing zeolitic structure. Taulelle and co-workers<sup>99,100</sup> have also developed apparatus capable of studying hydrothermal syntheses *in situ* using NMR spectroscopy. Using specially designed NMR tubes capable of withstanding high temperatures and pressures<sup>99,101</sup> they have been able to extend the range of conditions that can be studied, and have used the technique to observe the formation of solution phase species during the synthesis of zeolites under true hydrothermal conditions. They have demonstrated that it is possible to achieve sufficient time resolution using this experimental technique to perform kinetic studies and observe transient intermediate phases that are formed during the syntheses.

There have been very few *in situ* studies of hydrothermal syntheses by IR or Raman techniques, although there have been numerous *in situ* IR studies of catalysis by molecular sieves. In part, this again reflects the difficulty of constructing suitable cells, but also the presence of unwanted scattering from typical zeolitic gels that hampers observation. The principal work of interest in this area was performed by Twu *et al.*<sup>92</sup> who studied the synthesis of faujasite zeolites, and the effects of changing the silica source on the reaction. They were able to identify the species forming in solution, as well as the solid zeolite product as it crystallised from the aluminosilicate gel. The main point of interest was that they were able to detect the crystallisation of the zeolite well before it could be detected in powder X-ray diffraction patterns. The work of Twu *et al.* was not really *in situ* as such, since the measurements were performed on gels that had been separated from solution by centrifugation, but they are illustrative of the kind of information that could be obtained by *in situ* IR and Raman spectroscopies.

*In situ* light scattering studies are a potentially valuable technique for studying hydrothermal syntheses. This is because they provide information about the very small particles (<200 Å) present in molecular sieve gels that are believed to play an important role in the initial nucleation stage of a zeolitic crystallisation, a process about which very little is understood. A recent example of the application of *in situ* light scattering techniques was a study of the synthesis of NPr<sub>4</sub><sup>+</sup>-silicalite



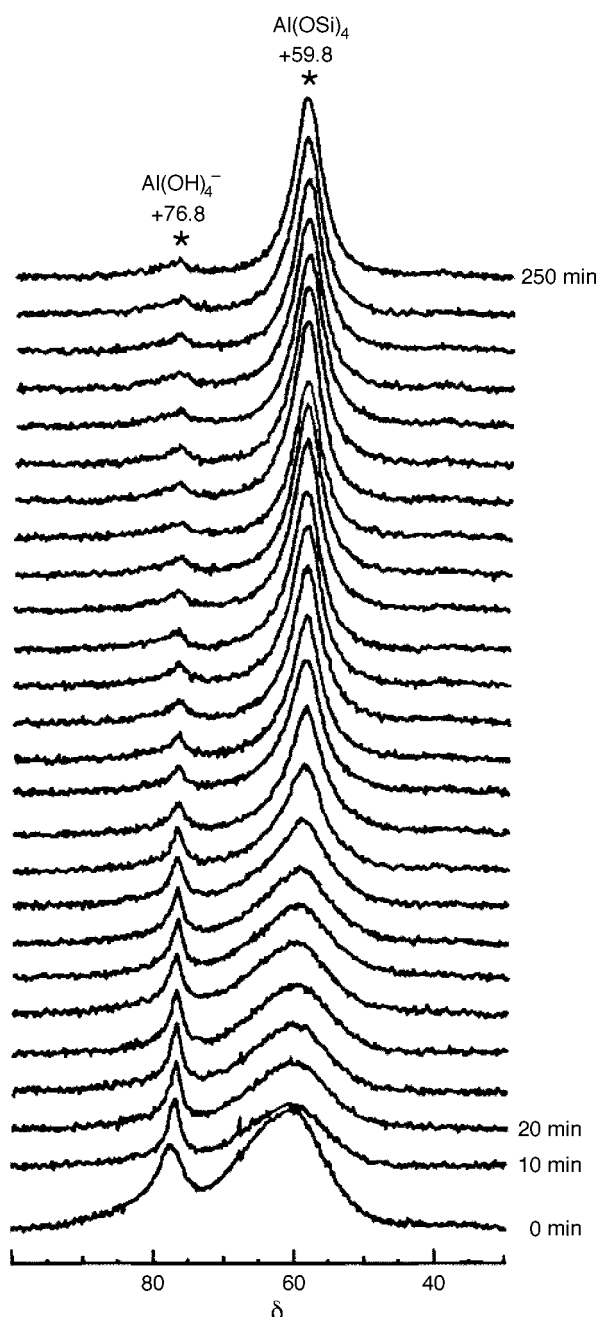


Fig. 5 *In situ*  $^{27}\text{Al}$  MAS NMR spectra of a zeolite A synthesis from a gel at  $65\text{ }^\circ\text{C}$  showing the narrowing of linewidths as long range order is established (Figure reproduced with permission from ref. 91).

reported by Schoeman.<sup>98</sup> In contrast to an earlier *ex situ* study by the same author,<sup>102</sup> by using a laser as the light source he was able to study the synthesis in a non-invasive manner. He found that there were two distinct populations of particles present in the reaction gel; subcolloidal silicate particles with a diameter of *ca.* 33 Å which remained present throughout the crystallisation and remained essentially unchanged in size, and a second population of larger crystallites which were detected at later times in the reaction. These larger particles were found to grow in size as the reaction proceeded, and correspond to growing silicalite crystals. Evidence was obtained that the larger crystals may grow from the subcolloidal particles, and that the subcolloidal particles may possess short range order, *i.e.* they may be considered to be zeolite nuclei. A similar earlier study was reported by Twomey *et al.*<sup>103</sup> who studied the influence of various synthetic parameters on the silicalite system and were able to distinguish between the nucleation and growth stages of the synthesis.

Useful information can also be gained about the kinetics and energetics of crystal growth by using optical microscopy. For example, Iwasaki *et al.*<sup>97</sup> described methods for monitoring the growth of zeolites by *in situ* optical microscopy from both clear solutions and gels, and illustrated these by studying the growth of ZSM-5 and silicalite. The disadvantage of this technique is the limited resolution obtainable using optical techniques. This disadvantage could be overcome by performing electron microscopy, but such experiments are hampered by the difficulty of constructing suitable reaction cells. This obstacle has proved to be insurmountable to date.

*In situ* EXAFS studies are discussed at the end of the following section due to their frequent combination with *in situ* diffraction studies.

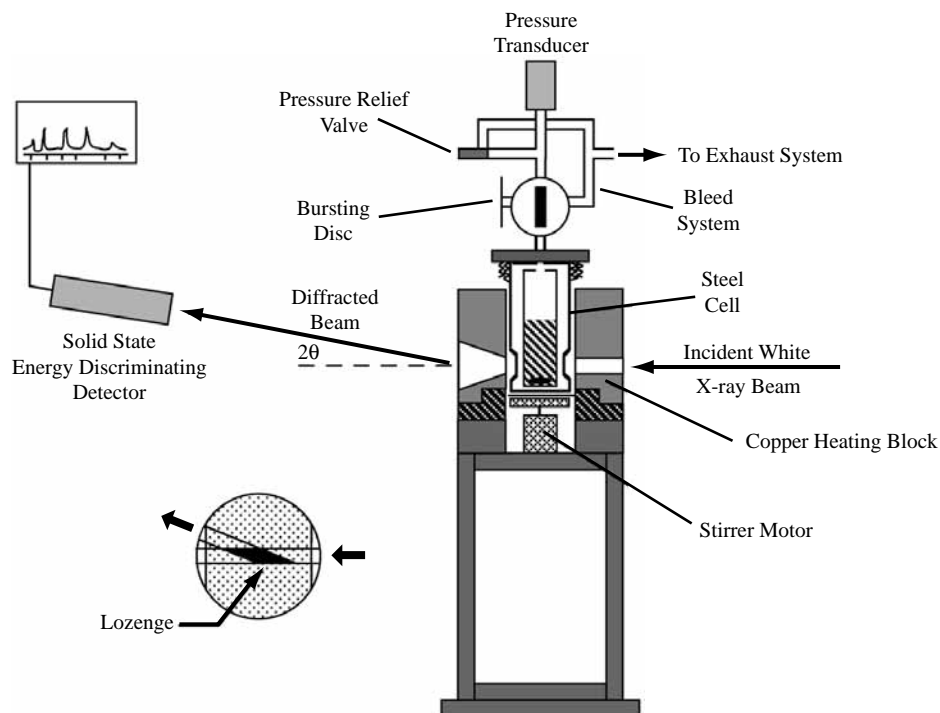
## 6.2 *In situ* diffraction and scattering studies

Most *in situ* studies performed over recent years have been diffraction or scattering studies using X-rays or neutrons. This reflects both the increased availability of high flux X-ray and neutron sources which are generally necessary for this work (see below), and also that many of the questions relating to the synthesis of molecular sieve materials, such as the kinetics and mechanisms of nucleation and growth, the existence of intermediate phases, and the effects of changing reaction variables, are readily amenable to investigation by diffraction and scattering techniques. Barnes and co-workers first described the potential advantages of *in situ* diffraction studies over conventional studies in a series of seminal papers in the early 1990s.<sup>104–107</sup> Since then a number of such studies have been published, which have begun to shed light on some of the issues relating to the kinetics and mechanisms of molecular sieve crystallisations.

**6.2.1 *In situ* X-ray diffraction studies.** Although some *in situ* X-ray diffraction studies have been performed using conventional laboratory equipment, the vast majority of studies have made use of high flux X-ray and neutron sources, in particular synchrotron X-ray sources. The extremely high flux at high energies of such sources allows the X-rays to penetrate the thick walls of typical reaction cells without significant attenuation, and enables the collection of high quality diffraction data using very short acquisition times, even when the cells are constructed of, for example, several millimetres of steel. There have been two very distinct ways in which *in situ* X-ray diffraction experiments have been performed; in the energy dispersive diffraction mode using 'white' polychromatic radiation,<sup>104–111</sup> and angular dispersive diffraction mode using a monochromatic beam.<sup>112–123</sup>

In energy dispersive X-ray diffraction (EDXRD) full spectrum polychromatic ('white') radiation emanating from the synchrotron source is allowed to impinge on the reaction cell, and an energy discriminating detector is employed which is held at a fixed angle of  $2\theta$ . Thus, diffraction from different Bragg reflections is separated by energy coordinate, instead of  $2\theta$  spatial coordinate as in conventional X-ray diffraction. Diffraction occurs from a lozenge-shaped diffraction volume which is defined by the collimation geometry and the scattering angle  $2\theta$  as shown as an inset in Fig. 6.

The principal advantages of the EDXRD technique are twofold. First, by employing the entire spectral range of the radiation produced by the synchrotron source, the total flux used in the experiment is extremely high. This allows the use of very short acquisition times (of the order of seconds in some cases) whilst still obtaining very high quality data. Secondly, the fixed angle geometry of the EDXRD technique simplifies reaction cell design because only very small windows are required for the incident and diffracted beams. This allows the construction of reaction cells with sophisticated environmental control systems in which a large volume of sample can be kept at a controlled temperature and pressure. This is important because it allows



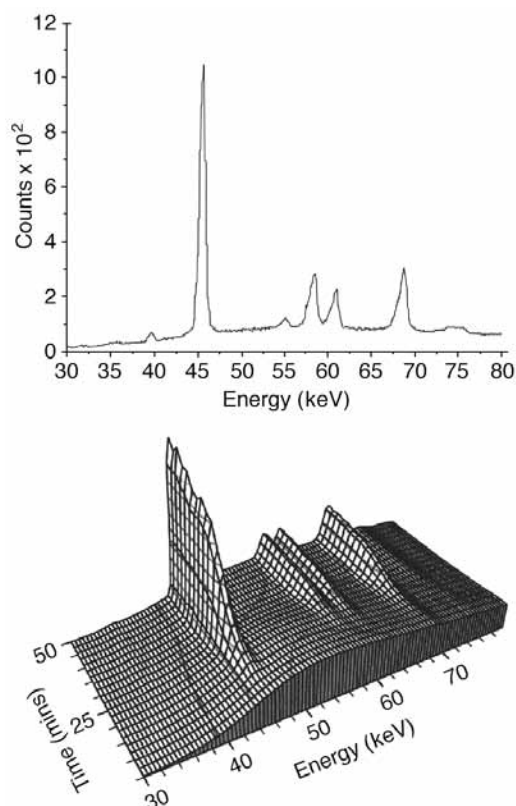
**Fig. 6** Schematic diagram of the experimental apparatus used for *in situ* EDXRD studies of hydrothermal reactions. The apparatus is designed for use on station 16.4 of the UK SRS at Daresbury Laboratory.

one to perform reproducible experiments under conditions very similar to those employed in conventional zeolite syntheses. The chief disadvantage to the EDXRD technique is the rather low resolution of the data obtained, which is caused by the poor energy resolution obtainable using presently available solid state detectors, and the unrefinability of the data obtained. This can particularly cause problems if the materials being studied are low symmetry, or if structural refinement of the data is desirable.

The first study of a zeolite crystallisation using *in situ* EDXRD was performed by Barnes and co-workers<sup>106</sup> in 1992. By adapting an environmental cell which they had previously used for studying the hydration of cement,<sup>105</sup> they were able to study the crystallisation of zeolite A and sodalite from an amorphous aluminosilicate gel and kaolinite respectively. Their cell could operate in both open and closed modes, and temperature regulation was achieved by circulating either water (for temperatures up to 95 °C), or silicone oil (for temperatures up to 110 °C). The inner lining of the cell was coated to provide an inert lining to contain the corrosive alkaline solutions, and the cell could be spun to try to prevent sample settling.

Despite the ground-breaking nature of this work, there were a number of limitations to the cell design. Primarily, these related to the fairly unsophisticated nature of the sample environment control system and sample containment system. Most importantly, the maximum temperature at which syntheses could be studied was fairly low (they did not study any syntheses at temperatures greater than 110 °C). Most zeolitic syntheses are performed at between 130 and 200 °C, with some being carried out at up to 250 °C. In addition the question of sample settling and accurate sampling of the reaction mixture by the synchrotron beam was not really addressed.

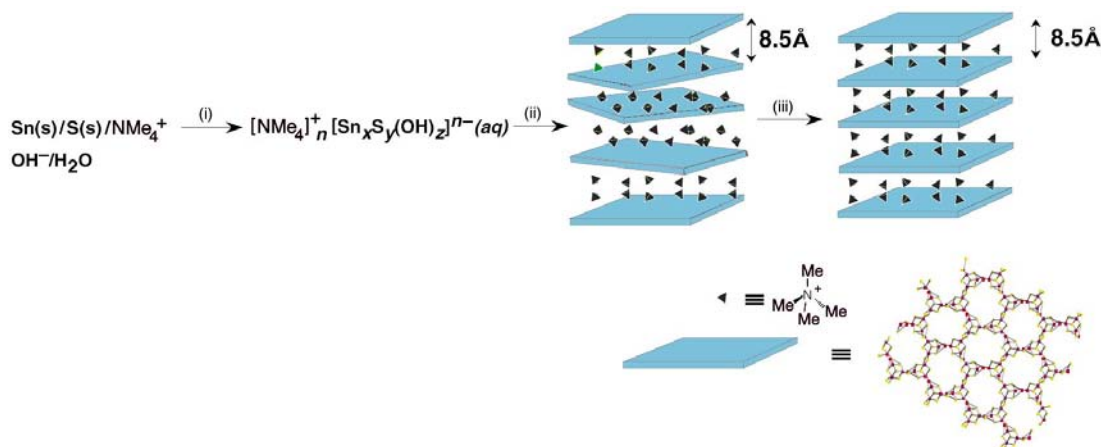
Over the past few years we have developed a large volume (*ca.* 30 ml) hydrothermal reaction cell suitable for collecting *in situ*, time-resolved EDXRD data under autogenous pressures of up to *ca.* 30 bar and temperatures of up to 250 °C. The high time resolution and high quality of data that can be achieved using this system allow one to follow the structural changes that occur during hydrothermal crystallisations in real time. A schematic illustration of the cell and the experimental set-up is



**Fig. 7** Three-dimensional plot showing the EDXRD spectra as a function of time during the synthesis of a pyridine templated aluminophosphate. Each spectrum was acquired in 300 s. Also shown inset is a single 300 s EDXRD spectrum of the final observed product.

shown in Fig. 6; a full description of the experiment has been published previously.<sup>108</sup>

We have used this facility to study a number of hydrothermal syntheses. Fig. 7 shows a three-dimensional plot of the crystallisation of the pyridine templated aluminophosphate  $[\text{Al}_2\text{P}_3\text{O}_{12}\text{H}_2(\text{Hpy})]^{124}$  at 180 °C and is illustrative of the type



**Fig. 8** Schematic representation of the proposed mechanism of formation of TMA-SnS-1. (i) Dissolution of the solid reagents to form solution phase ions such as  $[\text{Sn}_2\text{S}_6]^{4-}$ . (ii) Condensation of these ions under the influence of the template to form a disordered layered material. (iii) Ordering between adjacent tin sulfide sheets to give a material with crystallographic registry in all three spatial dimensions. Stages (i) and (ii) are rapid and take place on a timescale of minutes to hours, whereas stage (iii) is much slower and takes place on a timescale of days (Figure reproduced with permission from ref. 10).

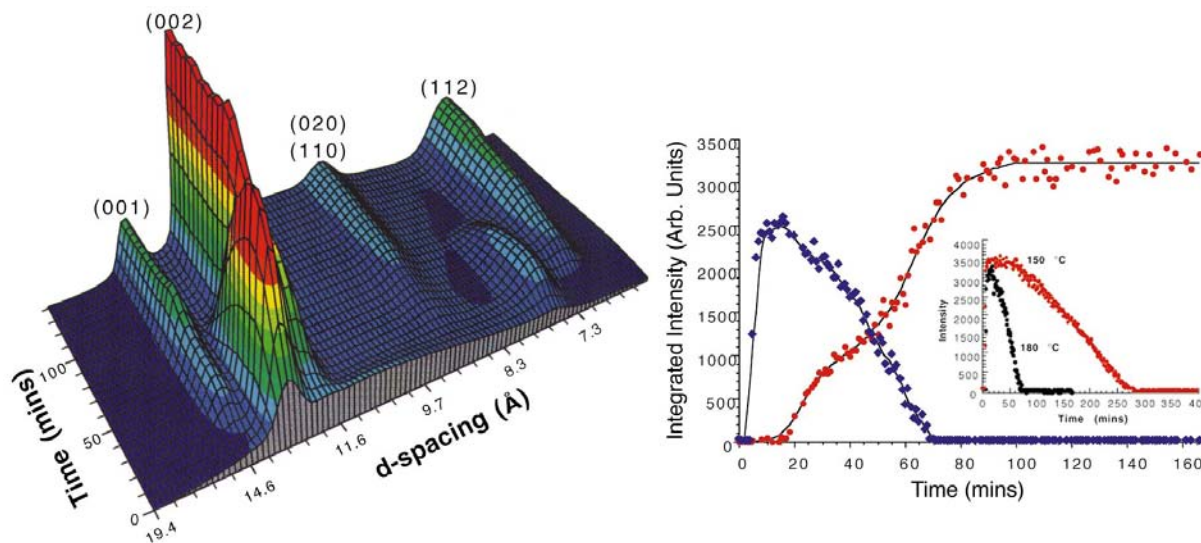
and quality of data that can be obtained. Each spectrum was collected in 300 s and an individual spectrum is shown inset in Fig. 7. After an induction time of 10 min when only a broad amorphous background is observed, the aluminophosphate product crystallises smoothly from the reaction as shown by the steady growth of the Bragg diffraction peaks. No intermediate crystalline products are seen. Integration of the intensities of each of the observed Bragg reflections using a Gaussian fitting routine shows that each reflection grows at the same rate, and obeys second order Avrami kinetics of order 2, *i.e.* the intensities can be fitted to the expression  $\alpha = 1 - \exp[-k(t - t_0)]^2$ , where  $\alpha$  = fraction of crystallised material,  $k$  = rate constant,  $t$  = time, and  $t_0$  = time of onset of crystallisation. Of particular note is the unexpected rapidity of the reaction. In the original reported synthesis the reagents are heated for between 36 and 48 h, whereas our experiments indicate that the crystallisation is complete after only *ca.* 1 h. This unexpected rapidity is a common feature of the systems we have studied to date.

Another system we have investigated is the synthesis of the open-framework tin sulfide TMA-SnS-1 [empirical formula  $(\text{NMe}_4)_2\text{Sn}_3\text{S}_7 \cdot x\text{H}_2\text{O}$ ] under basic hydrothermal conditions.<sup>110</sup> In this case the time-resolved X-ray data revealed highly anisotropic growth of the TMA-SnS-1 product. This is a layered material in which the tin sulfide microporous layers lie in the 001 plane. It was found that the 002 Bragg reflection corresponding to the interlamellar separation appeared first and grew very rapidly in the initial stages of the reaction. Other  $hk0$  and  $hkl$  reflections appeared later and grew much more slowly. In particular, the 111 reflection corresponding to interlamellar ordering was still increasing in intensity after 62 h of reaction, well after the 002 reflection had reached maximum intensity. This suggests that ordering along the direction perpendicular to the layers occurs at a much faster rate than the ordering either within the layers or between adjacent layers. Combined with kinetic data on the initial growth of the 002 reflection which show that the rate of crystallisation is dependent on the initial pH of the reaction mixture, these data can be used to provide an overall picture of the mechanism of formation of TMA-SnS-1 involving three stages: (1) initial dissolution of the starting materials by  $\text{OH}^-$  to give solution phase ions such as  $[\text{Sn}_2\text{S}_6]^{4-}$ , which has been suggested as the dominant solution phase ion present in these syntheses,<sup>125,126</sup> (2) rapid condensation/polymerisation of these ions under the influence of the template to form a layered but poorly ordered material in the initial stages of the reaction, and (3) a much slower process in which registration between tin sulfide sheets occurs to give a crystalline product with crystallographic order in all three

spatial directions. A schematic diagram of this process is shown in Fig. 8.

More recently we have been studying the synthesis of members of the ULM-*n* family of materials,<sup>20</sup> in particular one member, ULM-5, a microporous oxy-fluorinated gallophosphate containing very large 16 T-atom pores.<sup>23,127</sup> It is synthesized hydrothermally *via* the reaction of gallium oxide, a phosphorus source, hydrofluoric acid and the templating agent 1,6-diaminohexane. These studies have highlighted the critical importance of the form of the phosphorus source on the reaction pathway and the kinetics of crystal growth.<sup>111</sup> Using phosphoric acid ULM-5 is found to crystallise smoothly from the amorphous starting materials at an extremely rapid rate (half-life *ca.* 1 min) after a short induction time. No other crystalline materials are observed at any stage, and the reaction is complete in *ca.* 40 min. Kinetic analysis of the growth of diffraction peaks indicates that the crystallisation of ULM-5 under these conditions is an essentially diffusion controlled process, and that the rate of crystallisation is independent of temperature over the range 130–200 °C.<sup>128</sup> In marked contrast, when phosphorus pentaoxide is used as the phosphorus source the crystallisation of ULM-5 proceeds at a much slower rate *via* a previously unobserved crystalline intermediate phase which subsequently reacts to form ULM-5.<sup>111</sup> The course of the reaction at 180 °C is shown as a three-dimensional plot in Fig. 9, together with a plot of the integrated intensity of the 13.1 Å reflection and the ULM-5 final product 002 reflection. The growth and decay of the intermediate Bragg reflections and the product Bragg reflections are highly correlated which, although not conclusive, strongly suggests that the two phases are related and the intermediate phase converts directly into the final product. Recent *in situ* results have revealed that there are in fact two different intermediate phases, and that in any particular reaction ULM-5 may form *via* either one or other of the two intermediate phases exclusively, or a mixture of both phases.<sup>129</sup> The relative proportion of each intermediate phase formed is found to be critically dependent on the precise quantity of phosphorus pentaoxide, hydrofluoric acid and 1,6-diaminohexane used in the reaction.<sup>128</sup> The rate of conversion of the intermediate to product is strongly dependent on the temperature of reaction, with the transformation taking place at a much slower rate as the temperature is lowered.

The determination of the composition and structure of the intermediate phases is clearly of great interest with regard to the mechanism of formation of ULM-5, and efforts are continuing in this regard. Very recent *in situ* experiments have revealed that under certain conditions the syntheses of ULM-3,



**Fig. 9** Three-dimensional plot showing the evolution of the EDXRD spectra as a function of time during the synthesis of ULM-5 using phosphorus pentoxide as a starting material. The peak labels correspond to the indices of the Bragg reflections of ULM-5. Each spectrum was acquired in 60 s at a diffraction angle of  $2\theta = 1.22^\circ$ . Also shown is a plot of the intensity of the (100) Bragg reflection of the intermediate ( $\blacklozenge$ ) and the (002) Bragg reflection ( $\bullet$ ) of ULM-5 as a function of time at 180 °C. Inset: plot of intensity of the (100) reflection of the intermediate at 180 and 150 °C.

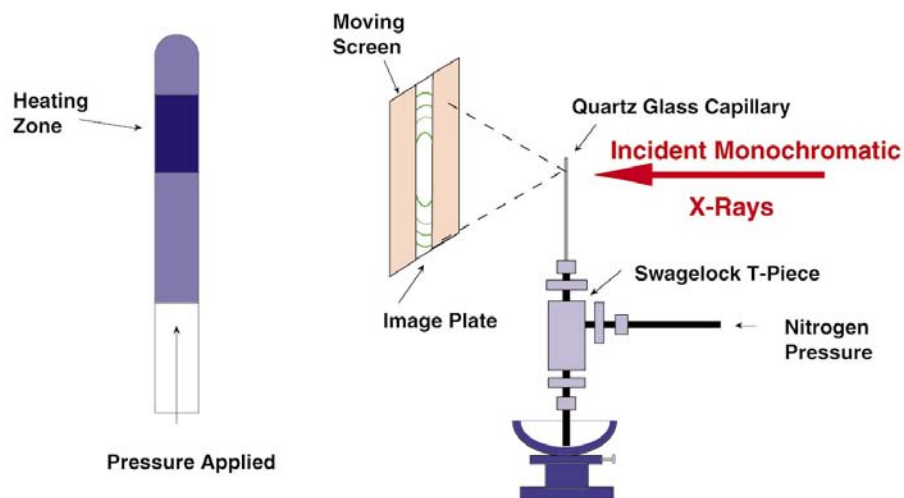
-4 and -16 also proceed *via* crystalline intermediate phases.<sup>130</sup> Given the known structural relationships between these phases,<sup>20</sup> this raises the fascinating prospect that the syntheses of these materials may proceed *via* structurally related phases, allowing one to build a coherent picture of their formation mechanisms. These experiments also dramatically illustrate the complexity of hydrothermal syntheses, and how subtle changes in the reaction conditions, such as the use of slightly different starting materials or reactant ratios, can greatly affect the kinetics and mechanisms of these reactions. It also demonstrates the power of *in situ* EDXRD techniques quickly and efficiently to gain unique information about these reactions and the factors affecting them.

Rey *et al.*<sup>131,132</sup> and Davies *et al.*<sup>133</sup> have also made use of the same experimental set-up to study hydrothermal crystallisations *in situ*. To date, they have focused on the synthesis of metal substituted aluminophosphates (MeAlPOs). Rey *et al.* studied the template-mediated formation of AIPO-5 and its cobalt substituted derivative CoAIPO-5. They found that whilst AIPO-5 crystallised directly from the reaction mixture, in the CoAIPO-5 case competitive formation of a metastable chabazite type phase occurred.<sup>131,132</sup> Further work by Davies *et al.* showed that the competitive formation of chabazite only occurs for reactions with a Co/P ratio of above *ca.* 0.04. Turning their attention to kinetics, they found that the rate of crystallisation of CoAIPO-5 increased with increasing cobalt content up to the critical Co/P ratio of 0.04, possibly due to the competitive formation of the chabazite phase, and both AIPO-5 and CoAIPO-5 crystallised at an increasing rate with increasing temperature. Relative to AIPO-5 it was found that cobalt and manganese substituted AIPO-5 (Co/P = 0.04 and Mn/P = 0.04) crystallised faster than unsubstituted AIPO-5, whilst silicon substituted AIPO-5 (SAPO-5, Si/Al = 0.04) crystallised at a slower rate. Davies *et al.* attributed this somewhat surprising result to the fact that metals substitute exclusively for  $\text{Al}^{3+}$ , whereas silicon has been found to substitute for both  $\text{Al}^{3+}$  and  $\text{P}^{5+}$  resulting in silicon island formation.<sup>133</sup>

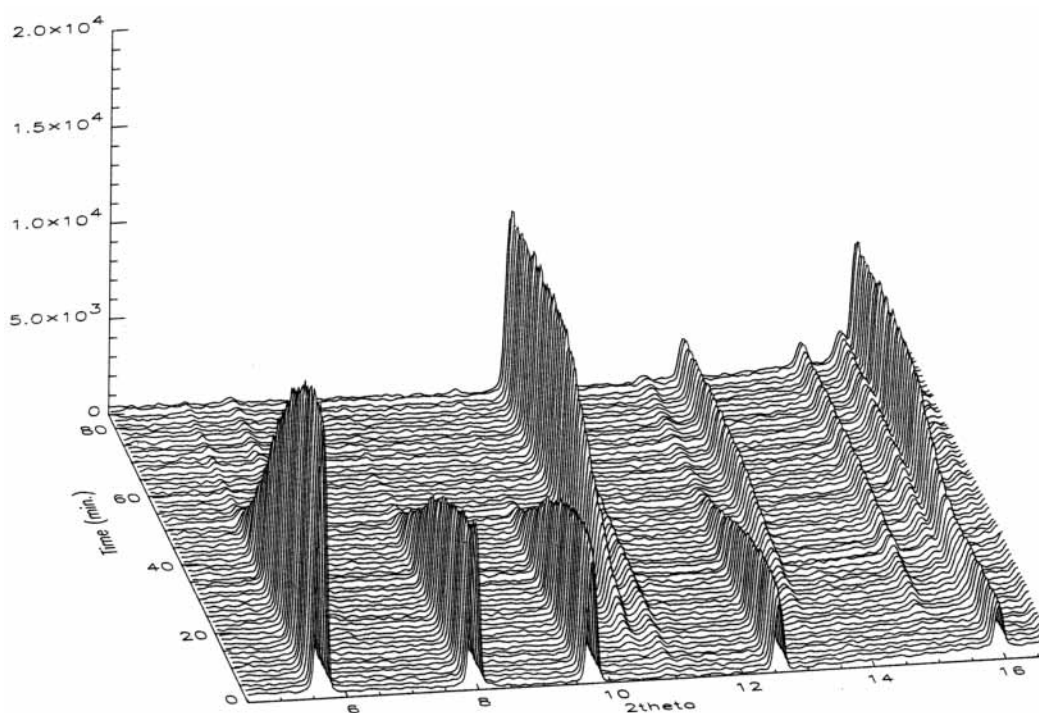
In contrast to the energy dispersive diffraction experiments reported above, the angular dispersive diffraction technique makes use of monochromated X-ray radiation, and the different Bragg reflections are split by spatial coordinate rather than energy coordinate. The chief advantage of using constant wavelength monochromatic radiation is that the resolution obtained can be much higher, and the data obtained are suitable

for structure refinement. The possibility of performing time-resolved Rietveld refinement thus becomes available.<sup>134-136</sup> The chief disadvantage of the angular dispersive technique is that the much lower flux of a monochromatic beam does not allow the construction of large volume cells with bulky sample environment control systems. Generally, angular dispersive *in situ* X-ray diffraction experiments have employed a system in which an external pressure is applying to a capillary containing the sample, and the reaction occurs by heating a small zone of the sample. This inevitably raises questions about whether such a system is operating under true hydrothermal conditions, and about the reproducibility of such experiments.

Norby and co-workers<sup>116,119-121</sup> have developed a facility to study hydrothermal reactions *in situ* using angular dispersive X-ray diffraction for use on beamline X7B at the NSLS at Brookhaven, USA. Samples are contained in 0.7 mm capillaries mounted in a Swagelock fitting with a Vespel ferrule. Pressure is then applied to the capillary from an external source (usually a nitrogen cylinder), and a hot air stream is used to heat a part of the sample approximately 5 mm wide (much smaller than the height of the beam). A schematic diagram of the experimental set-up is shown in Fig. 10. Norby *et al.*<sup>119</sup> have used this experimental set-up to study a number of hydrothermal syntheses. In a study of the synthesis of CoAPO-5 they studied the temperature dependence of the crystallisation rate. By fitting the crystallisation curves by using the Avrami equation,  $\alpha = 1 - \exp[-k(t - t_0)^n]$  ( $n$  = the order of the reaction, all other symbols as above), they were able to show that the reaction obeys first order kinetics, *i.e.* the nucleation rate has very little influence on the reaction. The formation of magnesium aluminophosphate was also studied and the influence of the templates on the final products formed investigated.<sup>115</sup> Another study investigated the hydrothermal conversion of zeolite LTA into zeolite Li-A(BW) and  $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$  using LiCl, with a view to determining the mechanism of transformation.<sup>121</sup> Fig. 11 shows a three-dimensional plot of the evolution of the X-ray pattern as a function of time and shows the decay of the Bragg reflections of zeolite LTA and the corresponding growth of Bragg reflections of zeolite Li-A(BW). It was found that the conversion is a solution mediated process, but that only very small amounts of aluminosilicate are in the solution phase. There was no evidence for the formation of any amorphous phases during the course of the reaction. Using the same experimental apparatus Morris *et al.*<sup>118</sup> studied the formation of single crystals of



**Fig. 10** Schematic diagram of the experimental apparatus developed by Norby and co-workers for studying hydrothermal reaction *in situ* using time resolved angular dispersive X-ray diffraction.



**Fig. 11** Three-dimensional plot of the evolution of the *in situ* angular dispersive X-ray powder diffraction profiles with time during the hydrothermal conversion of zeolite LTA into zeolite Li-A(BW). Data recorded at a wavelength of 1.1727(2) Å and a temperature of 200 °C (reproduced with permission from ref. 121).

the clathrasil dodecasil-3C under solvothermal conditions. The high time resolution that they were able to achieve using this system allowed the accurate fitting of rate expressions to the experimental data, and thus to study the crystallisation kinetics of dodecasil-3C in detail.

Although not strictly examples of hydrothermal crystallisations, *in situ* angular dispersive techniques have also been used to study the structural changes that occur during the dehydration of molecular sieve materials. A good example is a study of the dehydration of the natural zeolite laumontite performed by Stahl *et al.*<sup>122,137</sup> Powder diffraction profiles were collected at time intervals of 5 min as the temperature was raised in steps of 5 K from 310 to 584 K. Rietveld refinements of each of the profiles proved possible and thus a dynamic picture of the dehydration process and the host structure's response to the dehydration was obtained. More recently Norby *et al.*<sup>138</sup> have reported a study of the migration of Na<sup>+</sup> and Cs<sup>+</sup> cations within the cavities of zeolite Cs(Na)-Y during dehydration. Time-resolved Rietveld refinement of the *in situ*

data allowed the cation populations of the various sites within the zeolite framework to be determined with excellent precision throughout the entire dehydration process.

**6.2.2 *In situ* neutron diffraction studies.** There have been very few *in situ* neutron diffraction studies of hydrothermal syntheses. This is despite the fact that neutrons have low absorption cross-sections relative to X-rays and thus they appear suited for studying reactions carried out in special environmental cells. Of course, neutrons also have the advantage that they can be used to probe the behaviour of light atoms in the presence of heavy atoms. Unfortunately, the successful application of *in situ* neutron diffraction techniques is severely limited by the low fluxes obtainable at neutron sources when compared to synchrotron X-ray sources. Consequently the collection of high quality spectra requires acquisition times that are inappropriately long for *in situ* time-resolved studies. Therefore, in spite of the potential advantages, there has only been one report of an *in situ* neutron diffraction study of a hydrothermal synthesis of

a molecular sieve material (zeolite A).<sup>139</sup> Nevertheless, future advances in instrument design may reduce the time needed for the collection of powder neutron data,<sup>90</sup> and thus make the collection of time-resolved neutron diffraction data a more technically realisable goal, especially for syntheses that take place over a period of hours to days rather than minutes.

**6.2.3 *In situ* X-ray and neutron scattering studies.** Despite the power of *in situ* diffraction methods as a tool for understanding hydrothermal syntheses, they are, of course, probes of long range order. They are therefore insensitive to the structures of nucleation centres that are formed in the initial stages of the reaction and which are too small to be observed by diffraction. Small angle X-ray and neutron scattering studies (SAXS and SANS) provide information about the size, shape and fractal dimension of aggregates of particles in the size range 1–1000 Å.<sup>140</sup> They therefore complement diffraction experiments by probing much shorter length scales, and obtain information about the critical nucleation step of crystallisations, before long-range order has been established. In addition, it is possible to use isotopic substitution to modify the scattering length densities of the various components (inorganic, template and solvent) of the reaction mixture. Of particular importance is the ability to label the organic template with deuterium and thus be able to differentiate between purely inorganic particles and those incorporating template molecules.

Two groups have made extensive use of *in situ* SAXS/SANS experiments to study the formation of ZSM-5 and its pure silica analogue silicalite. White and co-workers<sup>60,141–143</sup> investigated the room temperature ageing and crystallisation of both ZSM-5 and silicalite. The SANS experiments revealed that on mixing of  $\text{NPr}_4^+$  and soluble silicate species the cations are rapidly incorporated into amorphous  $\text{NPr}_4^+$ /silicate structures.<sup>60</sup> Such a process is consistent with the formation of composite  $\text{NPr}_4^+$ /silicate species in the mechanism of silicalite formation proposed by Burkett and Davis.<sup>50</sup> Further studies focussed on the changes that occur during the ageing process (the elapsed time from mixing of the reagents before the onset of heating).<sup>141</sup> They found that particles in the size range 10–50 Å formed in the first 60 h and their numbers grew until an equilibrium state was reached. Interestingly, in the absence of aluminium no such process occurred suggesting that the aluminium acts as a cross linking agent and drives the formation of loose networks of aluminosilicate species. The SANS measurements showed that these particles did not contain template molecules, and they could not therefore be considered to be crystal nuclei. However, in recent subsequent studies of the high temperature crystallisation of silicalite<sup>142,143</sup> the same group have detected the growth of particles of 50–100 Å in size during the induction period of the crystallisation. The SANS measurements indicated that these particles have a composition close to that of silicalite and contain  $\text{NPr}_4^+$ , which strongly suggests that these are the nuclei for the growth of silicalite crystals. They propose that the crystallisation occurs by a process whereby these nuclei assemble preferentially along the *c* axis to form 330 Å cylindrically shaped ‘primary crystallites’, which subsequently aggregate to form polycrystalline particles of approximate length 6000 Å.

Van Santen and co-workers<sup>144–147</sup> have also performed extensive SAXS/WAXS and SANS experiments on the silicalite/ZSM-5 system. They also observed the formation of amorphous particles in the 50–70 Å range both prior to and during the formation of crystallites with long range crystallographic order.<sup>144,145</sup> However, additionally, they obtained evidence that a structural reorganisation of the gel occurs prior to crystallisation, and proposed a mechanism of formation of silicalite involving additional aggregation and densification steps.<sup>146</sup> Their proposed mechanism can be summarised as follows: (1) the formation of small  $\text{NPr}_4^+$ -silicate clusters less than 16 Å in size, (2) aggregation of these clusters into amorphous particles

ca. 60–70 Å in size, (3) densification of these 60–70 Å particles, and (4) combination of these to densified aggregates into crystallites containing long range order. Initially a secondary aggregation step prior to the formation of the final crystalline product was proposed,<sup>146</sup> but recent studies indicate that this step does not in fact occur.<sup>147</sup> It was also shown that the formation of the aggregate particles is dependent on the Si/OH ratio used in the synthesis. No aggregate particles were observed when the reactions were performed under conditions of high alkalinity (Si/OH = 2.4).

**6.2.4 *In situ* EXAFS/XRD studies.** Extended X-ray absorption fine structure (EXAFS) is a potentially very powerful method of studying zeolitic syntheses because it enables the determination of the environment around an atom (co-ordination number, bond lengths and angles) even when that particular element is only present in small quantities and is part of an amorphous or highly disordered phase. Thus, it is highly suited to the study of zeolitic gels prior to crystallisation. The use of a synchrotron as the X-ray source is highly desirable because it provides a tuneable, broad-band source of X-rays over a wide spectral range making it possible to study several different elements within the same reaction system.

It is especially advantageous to record a combination of *in situ* EXAFS and *in situ* XRD measurements on the same reaction simultaneously, because this allows one to correlate the changes in both the short and long range order which occur as the system undergoes nucleation and crystallisation. Couves *et al.*<sup>96</sup> first demonstrated the power of such a combined EXAFS/XRD approach with a detailed study of the synthesis of an active Cu/ZnO catalyst from a powdered precursor phase. A disadvantage of this original design was that it was performed in energy dispersive mode which makes collection and analysis of high quality EXAFS spectra difficult. Clausen *et al.*<sup>93</sup> first developed a combined EXAFS/XRD experimental method in the quick scanning mode (QuEXAFS) which does not have these drawbacks. They used this system to study the calcination and reduction of Cu based methanol catalysts. These studies provided information about the presence of possible intermediate phases during the calcination and reduction processes. More recently Sankar *et al.*<sup>94</sup> also reported the construction of a combined QuEXAFS/XRD cell. They demonstrated the application of the technique with a study of the crystallisation of CoAlPO-5 in which they observed a change in the co-ordination of the  $\text{Co}^{2+}$  ion from octahedral to tetrahedral immediately prior to crystallisation.<sup>148</sup>

## 7 Conclusion

This review brings together the current thinking regarding the kinetics and mechanisms of the formation of microporous materials. It is clear that, despite the complexity of these reactions, great strides are being made towards understanding the processes by which molecular sieves are synthesized. In particular, the range of *in situ* experiments that are currently being developed are beginning to demonstrate their power for elucidating in detail the processes occurring during hydrothermal syntheses. *In situ* techniques now span the full range of atomic length scales from short range probes (NMR and EXAFS), to medium range probes (SAXS/SANS), up to probes of long range order (X-ray and neutron diffraction). Continuing experimental developments are likely to bring further insights. In particular, combined multitechnique *in situ* experiments will also be of great importance since they allow a range of length scales to be probed simultaneously. Thus, although to date no new microporous structure type has been designed and synthesized *ab initio*, the developments described above suggest that such a breakthrough will be achieved in the near future.

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