The synthesis of molecular sieves from non-aqueous solvents

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Molecular sieves are important in many industrial processes and their synthesis has been the focus of much research. In addition to the traditional synthetic methods based on aqueous media there is a growing body of work describing preparations using non-aqueous solvents. This review will summarise some of the results of this work in the areas of zeolite, aluminophosphate and gallophosphate synthesis.

1 Introduction

Molecular sieves are an important class of materials that are widely used in a number of industries. Their large-scale applications as cracking catalysts in the oil industry and as water softening additives for detergents are well known, and they are becoming more important in bulk and fine chemical synthesis where they offer an environmentally benign alternative to corrosive liquid acids and oxidants. Separation technologies also make use of molecular sieves, and they are beginning to attract interest because of their molecular recognition and nanochemical host possibilities.

Molecular sieves can be split into three main groups of compounds, based on silicates (zeolites *etc.*), phosphates (aluminophosphates *etc.*) and the others, a class that includes a number of families such as the manganese oxide octahedral molecular sieves, all-carbon molecular sieves, pillared clays and the newly discovered aluminium methylphosphonates to name but a few (see Fig. 1). Materials containing silicate and phosphate, especially the zeolites and aluminophosphate based systems, are by far the most important materials currently available and the remainder of this review will concentrate on these families. The most noticeable, and perhaps most important feature of molecular sieves is their structural architecture; they contain pores, cavities and channels with dimensions comparable to those of small and medium sized molecules (from *ca.* 4–14 Å). This leads to materials that can be used to discriminate between molecules on the basis of their shape and/or size, a property that is important in many of the applications listed above. There are a number of excellent texts and papers which review both the structure and utility of molecular sieves and for more information the reader is directed to works by Dyer[1] and Barrer.[2] Section 2 of this review will, however, briefly introduce the essential features of molecular sieve structure.

During the last 50 years or so the study of molecular sieves has expanded to become an important part of chemistry and materials science, as indicated by the growing body of literature dealing with research in this exciting area. A large proportion of recent work has focused on elucidating the mechanism of formation of molecular sieves, with a view to being able to control their architecture, leading to new shape selective materials. There is a great incentive for work of this kind as many industries will directly benefit from an improvement in techniques aimed at improving our ability to tailor the properties of solids to meet the demands of today's technology. The vast majority of molecular sieves are synthesised hydrothermally (*i.e.* the solvent is water) and a number of research groups have taken large strides towards rationalising the processes involved. Section 3 will provide a short overview of the work that has been undertaken in this field, summarising some of the milestones that have been reached and introducing some important concepts.

In contrast to the large and wide ranging studies that have been undertaken on the hydrothermal synthesis of molecular sieves, the body of literature reporting preparations that involve non-aqueous solvents is still relatively small. Nevertheless, the work that has been done shows exciting possibilities for the preparation of hitherto unknown materials, for improved preparation of previously synthesised materials and for mechanistic studies. The major part of the work has, unsurprisingly,

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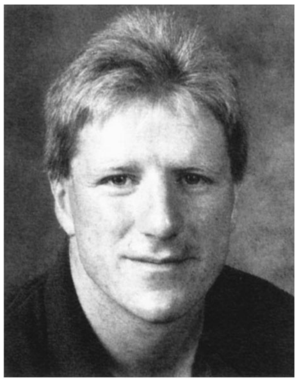

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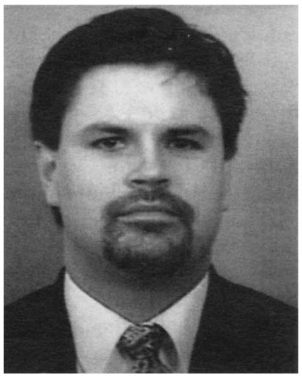

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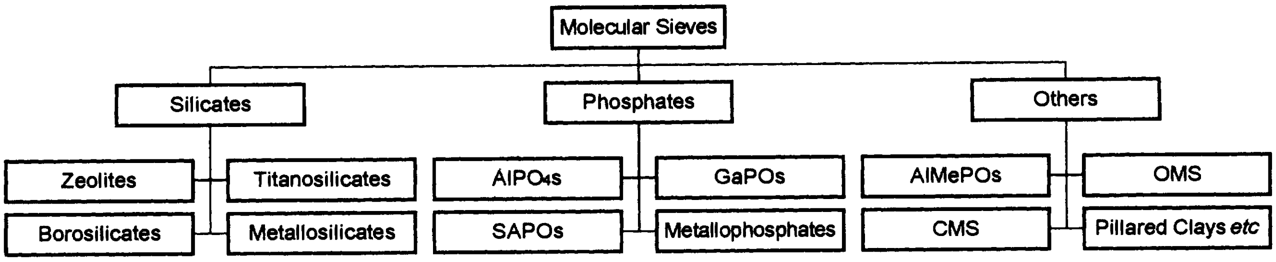

Fig. 1 Molecular sieves can be split into three main families, the silicates containing the zeolites and other metallosilicates, the phosphates containing the aluminophosphates ($AlPO_4$s), gallophosphates (GaPOs), silicoaluminophosphates (SAPOs) and other metallophosphates (such as zinc phosphates), and finally the other non-tetrahedral sieves such as aluminomethylphosphonates (AlMePOs), octahedral molecular sieves (OMS), carbon molecular sieves (CMS), pillared clays *etc*.

concentrated on zeolite, aluminophosphate and gallophosphate materials and we will look at each of these families in turn.

This review is intended to gather together information from non-aqueous molecular sieve synthesis, to identify any trends that appear and to discuss the effects that altering the solvent have on the chemistry involved when compared with aqueous synthetic methods. There is a marked incentive to design new molecular sieves, not only with new crystalline architectures but also with different chemical properties, as the possibilities for their use in many areas is extremely great. Unfortunately, the synthesis of molecular sieves is quite complex, and we have made only partial progress towards the goal of designing *a priori* a new material. We will discuss how knowledge of the chemistry involved in non-aqueous preparations is adding to the base of knowledge being gathered from aqueous-based syntheses, and how it will facilitate the design and synthesis of materials which, in the coming years, may lead to new technological advances.

2 Molecular sieve structure

The most well known family of molecular sieves are the aluminosilicate zeolites, a class of minerals first discovered in 1756 by A. Cronstedt. Zeolites are composed of tetrahedral AlO_4 and SiO_4 (the primary building units) linked through the sharing of corners to produce open frameworks with the chemical formula $[Al_xSi_{1-x}O_2]^{x-}$. The various zeolite structures can be classified in terms of their secondary building units (SBUs), which contain four or more tetrahedra. For example, in Fig. 2, all three zeolite structures shown can be built from 4- and 6-ring SBUs. Other SBUs include 5-rings, 8-rings and more complex units such as double 4-rings (cubes) and double 6-rings (hexagonal prisms). The negative charge which accompanies each aluminium atom in the framework must be balanced by an extra-framework cation. In naturally formed zeolites these cations are normally inorganic species such as Na^+, K^+, Mg^{2+} *etc.* while synthetic zeolites can be charge balanced by inorganic, organic or combinations of inorganic and organic cations.

Silica polymorphs (framework molecular formula is SiO_2) that have zeolitic structures can also be prepared. In this case there is no charge on the framework and thus there are no extra-framework cations. It is also possible to prepare isoelectronic group 13/15 analogues of these materials, for example, the aluminophosphates with the formula $AlPO_4$. Many of these have the same framework structures as zeolites, but still more have new structures entirely. In a similar way gallium can be substituted for aluminium to form gallophosphates. In both the silicate and phosphate families of molecular sieves it is possible to introduce small amounts of other elements (*e.g.* Cr, Fe, B *etc.*) into the framework, leading to metallosilicates and metallo-$AlPO_4$s. It is also possible to introduce silicon into a number of $AlPO_4$ materials to produce the SAPO group of solids, some of which make excellent catalysts for reactions such as the production of gasoline from methanol.

All of the zeolites and most aluminophosphates contain only tetrahedral silicon, aluminium or phosphorus. Gallophosphates on the other hand, show a wider range of coordination number and examples of four-, five- and six-coordinated species are known, and there are even cases of all three coordination numbers present in the same material.

An excellent and comprehensive reference source for information on molecular sieve architecture is the Atlas of zeolite structure types.[3]

3 Molecular sieve synthesis

Synthetic molecular sieves have been known since the 1940s, through the pioneering work of Barrer[4] and Milton.[5] During this period large-scale synthesis of zeolites was accomplished using alkali metal aluminosilicate gels at relatively low pressures and temperatures. Soon afterwards it was discovered that organic cations could replace the alkali metals in the gels to produce zeolites with either completely new structures or with Si/Al ratios that were previously unattainable.[6] The pH of the reaction mixture in these preparations is normally greater than 10.

In the 1980s Wilson *et al.*[7] reported the synthesis of aluminophosphate molecular sieves. These differ from zeolite syntheses in that they are normally performed in acidic conditions. Quaternary ammonium cations and amines are the most common additives to the reaction mixtures, although there are some cases of alkali metal cations being used especially when small amounts of other elements such as silicon are substituted into the materials. Since the discovery of the aluminophosphate family of molecular sieves many other elements have been incorporated into these structures to form microporous materials (*e.g.* zincophosphates, beryllophosphates *etc.*[8]) and the preparation of these types of solids continues to be the focus of a fairly large body of work. An especially interesting and wide ranging family of new molecular sieves are the gallofluorophosphates prepared by Ferey and coworkers.[9]

The mechanism of zeolite synthesis is still poorly understood, although progress is being made towards a fuller understanding. The synthesis of microporous materials usually involves the use of additives, alkali metals or organic guest molecules, added to the synthesis gels. The choice of additive often has a profound influence on the final structure of the microporous materials; the effects of the additive are generally split into three classes: 'true templating', structure directing and space-filling. Davis and Lobo, in an excellent general review of molecular sieve synthesis, have stated that 'templating' occurs only when a zeolite structure adopts the geometric and electronic configurations that are unique to the templating molecule and upon removal of the organic species retains the shape of that molecule.[10] Unfortunately, the specificity between the organic guest and the final solid host is not usually sufficient enough to be 'true templating' and there appears to be only one example in the literature to date.[11] Structure direction, on the other hand, refers to the formation of a specific zeolite structure *via* a single organic species. There are more examples of structure directing

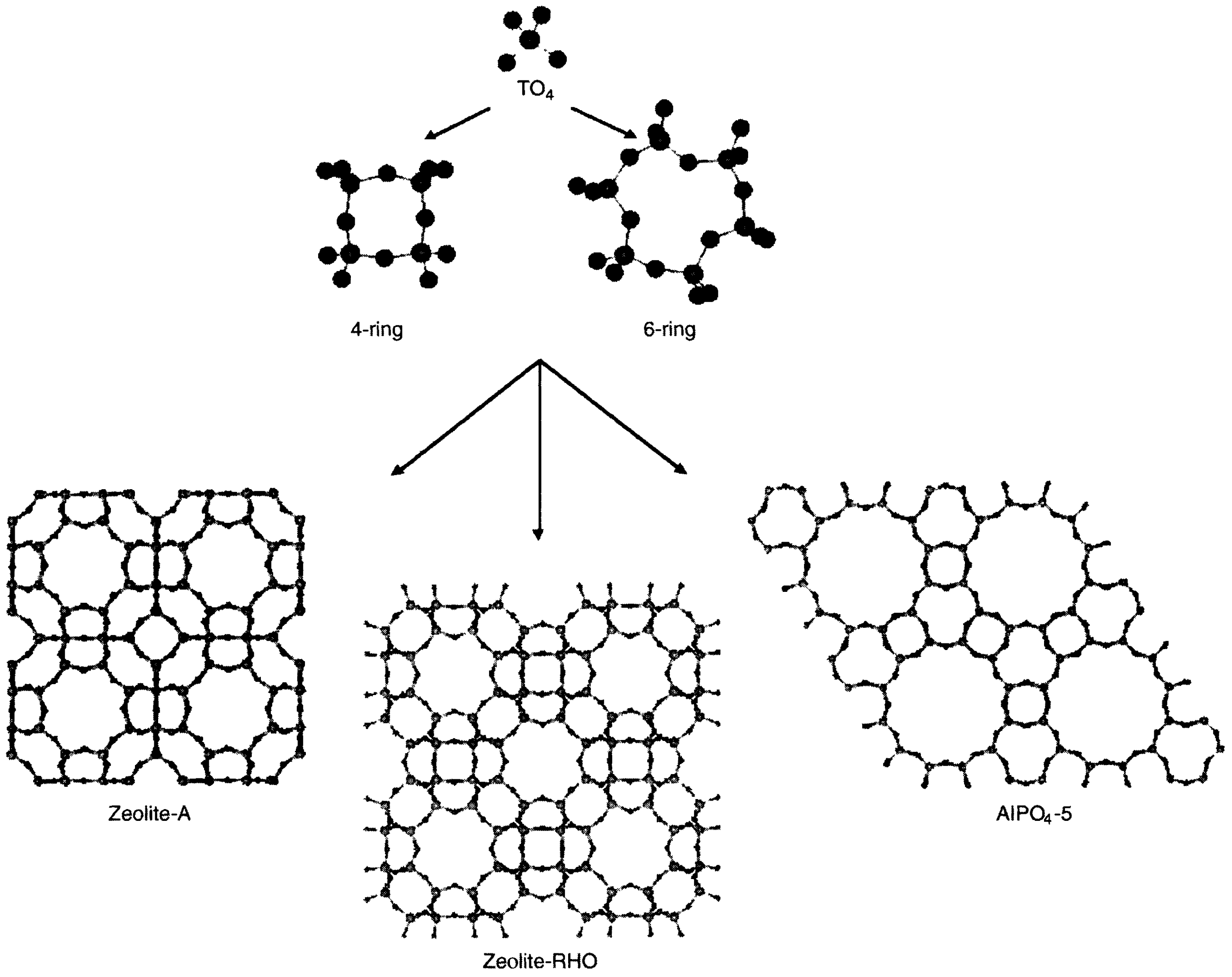

Fig. 2 Assembly of a molecular sieve structure. The tetrahedral primary building units are linked through oxygen atoms to form the secondary building units, in this case 4- and 6-rings. These secondary building units can be linked in a number of different ways to form solid frameworks.

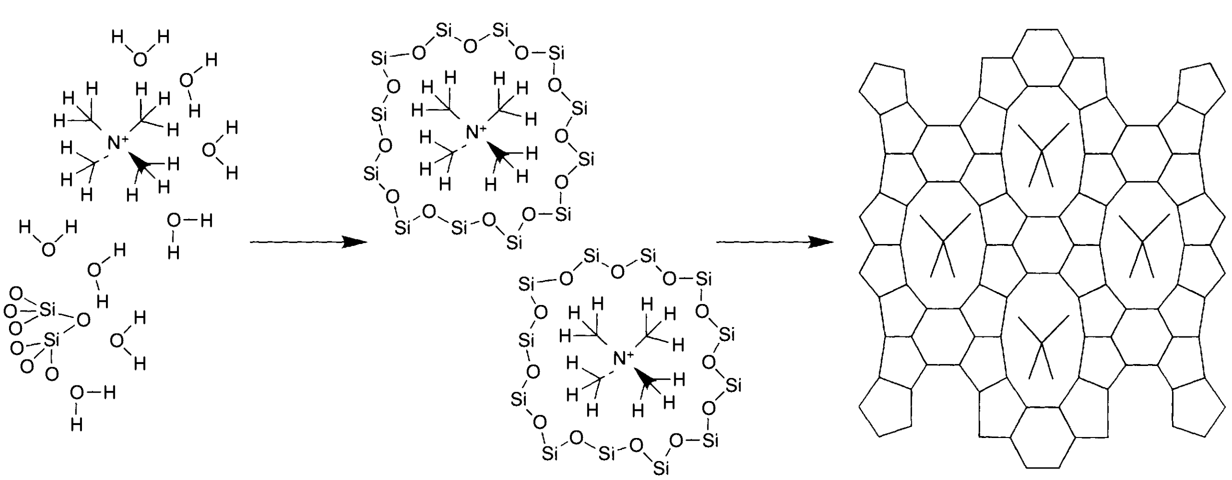

Fig. 3 Schematic illustration of siliceous zeolite formation. The hydration sphere of the template (in this case tetramethylammonium cations) is partially or fully replaced by silicate species. It is these inorganic–organic interactions that form the basis of the geometric relationship between the template and the zeolite pores once nucleation and crystal growth have occurred. A similar mechanism can be proposed for microporous aluminophosphate synthesis.

agents, including some elegant work done by Zones and co-workers using heterocyclic organic additives.[12] Space filling, the most common process in which organic additives are involved, implies an increase of thermodynamic stability of the organic–framework composite, as compared to the framework alone, simply due to the van der Waals' interaction between the organic and the inorganic regions of the structure.

Although the complete mechanism of a zeolites synthesis is not available to us yet, a reasonable proposal is shown in schematic form in Fig. 3.[13,14] The reaction involves the 'organisation' of silicate anions around the additive (in this case a tetramethylammonium cation, TMA) to form solution 'complexes' that form the basis of the nucleation centres from which the zeolite crystallites form. The van der Waals' interactions between the framework species (the silicate anions) and the templates provide the enthalpic driving force for the reaction, while the release of ordered solvent back into the bulk provides the entropic driving force.

There are two extremes by which this reaction can take place, from a clear solution where all the starting materials are fully dissolved (the solution-mediated transport mechanism), or from the dissolution and recrystallisation of an amorphous gel which is in contact with the liquid phase (solid phase transformation mechanism). Examples of both types of process are known, and some zeolites have been shown to be formed from either mechanism depending on the reaction conditions.

All of the above information has been collected through extensive work by many research groups over the years, all of which use hydrothermal synthesis. Further discussion is outside the scope of this article, but for more information on the synthesis of molecular sieves from aqueous media, including discussions on the templating *versus* space-filling issue, the reader is directed to the excellent review by Davis and Lobo[10] and the references contained therein.

The basic principles of templating and the types of mechanism found in hydrothermal synthesis can also be applied to non-aqueous solvent systems and in the remainder of this review we will concentrate on the chemistry involved in the synthesis of molecular sieves from primarily non-aqueous synthesis.

3.1 The effect of the solvent

The properties of the solvent are, of course, vital to the success or failure of attempted preparations and it is instructive to examine the effect that changing a solvent will have on the chemistry of the reaction mixtures. The nature of the interaction between the solvent and the reacting species is critical to the outcome of the molecular sieve synthesis. Organic solvents can be grouped into four categories based on their tendency to form hydrogen bonds; high, high-medium, low-medium and non hydrogen-bonding. It is clear from the proposed scheme of formation (Fig. 3) that the structure directing agents need to be intermediate in their ability to interact with the solvent; they must remain as isolated molecules in solution, but the interaction with the solvent must not be so strong as to prevent the framework species from forming interactions with them. In this way high hydrogen-bonding organic solvents effectively shield the framework particles (silica/phosphate *etc.*) and the templates from interaction with each other, preventing nucleation. In the case of high-medium and low-medium hydrogen bonding organic solvents, interactions between the framework and template species are more likely, and it is these solvents which tend to be the most successful in molecular sieve synthesis. It is the balance of interactions between solvent, additive and the framework species that is important in determining whether the organic molecule is a successful template. A major goal for synthetic chemists is the rational design of molecular sieves with new architectures. One method of achieving this goal would be to develop the use of organic additives so that 'true' templating occurs, leading to a solid with a 1 : 1 correlation between the template and the framework. The solvent–templating balance described above can be tipped against the templating reaction if either the template or the framework species become more hydrophilic, when either no templating will occur, or it will be the hydrated template which acts to direct the structure of the resulting framework.

Control over the crystal size, and also crystal morphology, is also an important goal for synthetic chemists and materials scientists. The emerging field of nanochemistry, where molecular sieves may act as hosts, may need single crystals of the sieve to be large enough that, for instance, electrical contacts can be made. Many non-aqueous solvents have higher viscosity than water and this may well act to reduce convection currents, especially in gel syntheses. This means that mass transfer only occurs by diffusion, reducing the chances of secondary nucleation and preventing crystallisation by sedimentation. Of course, increasing the viscosity of a solvent sufficiently will reduce the rate of diffusion of the reactant particles sufficiently that eventually there is no crystal growth, so solvents of both intermediate viscosity and intermediate hydrogen bonding ability should be the favoured media for the formation of large single crystals of molecular sieves.

As will be seen in the following sections, some progress towards the twin goals of control over crystal structure and crystal size is being made through the use of non-aqueous media. The following sections describe recent work done in the areas of zeolite, aluminophosphate and gallophosphate synthesis from non-aqueous solvents. Some emphasis is placed on the use of the chemical properties of non-aqueous solvents to control the final product of the reactions.

4 Zeolites and silica polymorphs

The instances of zeolites being synthesised from organic solvents are still relatively rare. In 1985, Bibby and Dale published the first example, where they prepared the sodalite structure type with a large range of Si/Al ratios (including pure silica sodalite) from ethylene glycol and propanol solvents.[15] Similar alcoholic solvents have now been used to make a number of different zeolite structures. Ruren Xu and co-workers used ethylene glycol, glycerol and butyl alcohol to prepare the pure silica polymorph of sodalite.[16] They also prepared silicalite-1 in a similar fashion but with tetrapropylammonium bromide as the template, and two pentasil zeolites, ZSM-39 and ZSM-48, using mixed glycerol–butyl alcohol and ethylene glycol–butyl alcohol solvents, respectively.[17] Xu and co-workers have also shown that isomorphous substitution of metals into the framework of zeolites such as ZSM-48, which is well established in hydrothermal synthesis, can also be accomplished in non-aqueous systems. For example, Fe-ZSM-48 was prepared from a mixed amine (ethylenediamine–triethylamine) solution.[18] The mechanism of this synthesis is a solid-phase transformation and the presence of Fe^{3+} in the zeolite framework was confirmed by IR and ESR spectroscopy. Xu also reported the synthesis of a zeolite isostructural with ZSM-22 using methanol as the solvent and pentaerythritol as the templating agent.[19]

The discovery that fluoride ions, in aqueous solution, act as efficient mineralisers in the preparation of a number of microporous materials, has had a profound effect on the synthesis of molecular sieves.[20] Many new phases have been prepared in this way and it has also been shown that fluoride ions facilitate the formation of large single crystals.[21] Ozin and co-workers extended this to show that HF–pyridine and HF–alkylamine solvents can be used to prepare large single crystals of zeolites such as ferrierite, silicalite and the clathrasil dodecasil-3C (MTN).[22,23] Large single crystals of zeolites do occur in nature, but the conditions needed to grow large crystals in the laboratory hydrothermally are difficult to obtain, and many important zeolite materials could only be synthesised as microcrystalline powders. The extremely large size of the crystals produced in this work—Ozin referred to them as 'giant', and although they are still only a few mm in length they are significantly larger than crystals prepared using any other method—may have some impact in the field of nanochemistry.

An especially interesting feature of these HF–amine syntheses is the need for a small amount of water to be present in the reaction mixture to help with the dissolution of the silicate species. The amount of water present in the mixture has a marked effect on the crystal size of the product, probably by reducing the viscosity of the solvent, but has little effect on the phases produced. The water also acts as a transport agent for soluble species and aids in the hydrolysis of the silicon fluoride and oxyfluoride species in solution.

For the synthesis of dodecasil-3C, the solvents used were pyridine, triethylamine, tetrahydrofuran, dimethylformamide and diethylene glycol. The hydrogen fluoride was added to the reaction as a complex with either pyridine or triethylamine, where the HF is predominantly present as a polymeric chain with only a small amount present as free HF. All preparations were successful in producing dodecasil-3C but with different crystal sizes, by far the largest when pyridine was used as the solvent (crystals *ca.* 2 mm long). The solvents themselves acted as the templates in all of these preparations, except for the triethylamine-based systems, which required the addition of cyclopentylamine. This fact may prove useful in other preparations where it is desirable to have only the additive acting to template the structure rather than both the additive and the solvent.

The structure of dodecacasil-3C (MTN) comprises two types of cage; a pentagonal dodecahedron and a hexadecahedron, fused through their five-ring faces. When synthesised using pyridine as the solvent, it shows an excellent example of space filling as a way to increase the thermodynamic stability of the product; the pyridine fits quite snugly into the larger hexadecahedron cages but is too large to fit into smaller cages. The large size of the MTN crystals prepared in this system has allowed an *in situ* single crystal X-ray diffraction experiment to be performed during a synthesis reaction.[24] Single-crystal X-ray diffraction data, collected using a synchrotron source and image plate detection systems, allowed the crystallisation kinetics to be analysed. As far as the authors are aware, this is the only example to date of an *in situ* single crystal diffraction experiment performed during the preparation of zeolites. It is clear that this type of experiment holds great promise for the elucidation of crystallisation kinetics, and possibly crystallisation mechanisms. The experimental set-up allows both temperature and pressure to be varied between experiments, and from such data more information on the energetics of the crystallisation processes can be obtained. Further experiments of this kind will be especially enlightening with respect to the MTN–FER synthesis (see below), where variations in the chemical compositions of the gel are also expected to alter the nucleation and crystallisation processes.

Large single crystals of silica ferrierite and aluminosilicate ferrierite can be prepared using similar methods, but only from the pyridine-based systems, and only when propylamine has been added as a template.[22] The interest in ferrierite currently stems from its use as a catalyst in the isomerisation of butenes to isobutene. This is important because the latter is a major feedstock in the production of methyl *tert*-butyl ether, an oxygenate additive that is increasingly added to motor fuel.

The synthesis of ferrierite competes with that of dodecasil-3C, a small change in conditions leading to a different product distribution. Calculations indicate that dodecasil-3C is the more thermodynamically stable of the two compounds, and that the ferrierite is preferentially formed under kinetic control at lower temperatures or shorter reaction times.

The relatively large size of the single crystals formed allowed Weigel *et al.* to perform single crystal X-ray diffraction studies and to locate the pyridine solvent inside the channels (Fig. 4).[25,26] During the synthesis of ferrierite the propylamine template acts as both a pH buffer, preventing the pyridine from protonating, and as a template, preorganising the silicate species in solution before they are laid down in layers; the layers are then stabilised thermodynamically by interaction with the pyridine molecules. When MTN is the major product, formed normally in the absence of propylamine, it is postulated that pyridinium ions are important in the nucleation stages of crystal growth. Fig. 5 is a schematic of how the proposed synthesis of ferrierite occurs.

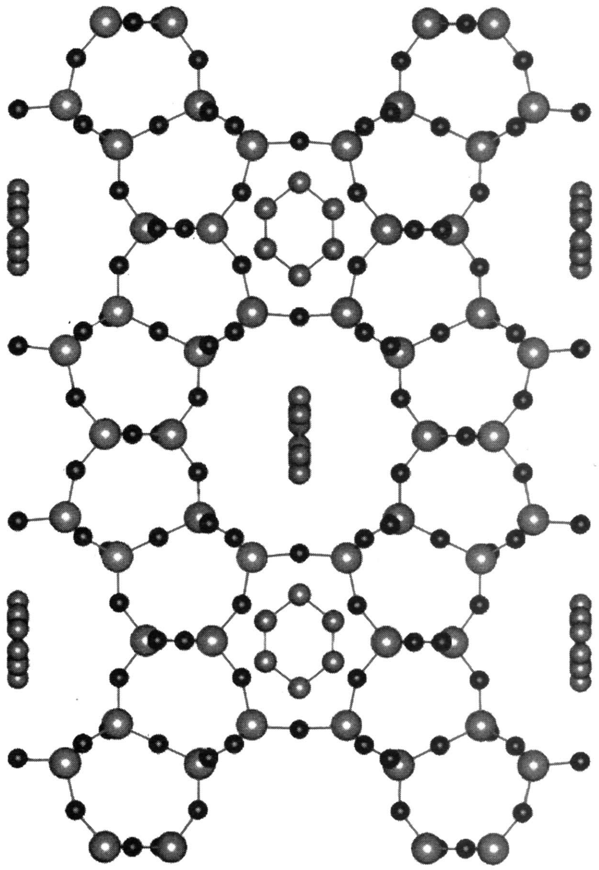

Fig. 4 The structure of ferrierite viewed parallel to the 10-ring channels showing the crystallographic positions of the pyridine template molecules.

Ferrierite can also be prepared using glycerol as the solvent. Again, by altering the conditions of synthesis, various zeolites, including ZSM-5 and ZSM-48 are alternative products, illustrating the subtle effects that control the major phases of a preparation.[27]

In comparing the materials cited in this review with those prepared previously using aqueous methods the most obvious advantage is the large size of the crystals that are formed. There are almost no examples of hitherto unknown structures being prepared using non-aqueous solvents, although even in aqueous based synthesis new and exciting structures are still being discovered (such as the new 14 ring zeolite discovered by Davis and co-workers[28]). It would seem likely that given time non-aqueous synthetic procedures will produce equally exciting and novel phases. So far there has been relatively little discussion of the properties of the zeolites prepared from non-aqueous solvents and it is as yet unclear whether these methods produce materials with any advantages over the usual preparations.

5 Aluminophosphates

Among the first reports of aluminophosphate molecular sieves prepared using non-aqueous solvents were from the groups of Ruren Xu at the University of Jilin, China and John Meurig Thomas from the Royal Institution in London. The solvent for most of these experiments was ethylene glycol, and depending on the organic templates used aluminophosphates with the $AlPO_4$-5, $AlPO_4$-11 and $AlPO_4$-21 structures could be synthesised.[29] These syntheses are unusual amongst non-aqueous molecular sieve preparations in that they seem to be truly anhydrous; any water which was added to the reaction system with the phosphoric acid starting material could be distilled off with no effect on the products of the reaction.

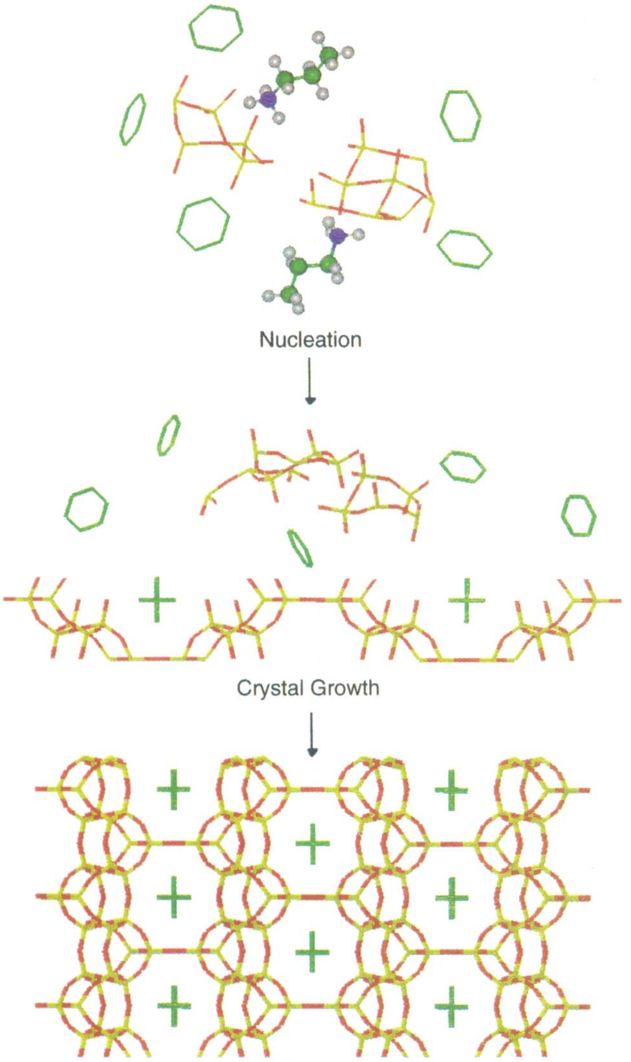

Fig. 5 Proposed mechanism for the synthesis of ferrierite from a pyridine solution in the presence of propylamine. The propylamine is only important in the nucleation stages of crystallisation, crystal growth then occurs through layer by layer deposition of pyridine-stabilised silicate sheets.

The same groups have also reported the synthesis of a very large pore aluminophosphate, which they gave the name JDF-20.[30,31] The structure, shown in Fig. 6, has a pore opening that is defined by 20 tetrahedral atoms. This is the same window size as that of cloverite,[32] the largest pore size material so far prepared. Both cloverite and JDF-20 are so-called interrupted structures, with -OH groups lining the pores and JDF-20 differs from other $AlPO_4$s in that the ratio of Al : P is 5 : 6 rather than the normal 1 : 1, which is rare in three-dimensional materials but is seen more often in layered materials. JDF-20 is prepared in a similar manner to the $AlPO_4$s described above, with either triethylene glycol, diethylene glycol, tetraethylene glycol or butane-1,4-diol as solvents with triethylamine as the template. At higher temperatures or with longer crystallisation times, $AlPO_4$-5 is the favoured product from the same starting gel compositions. The two interesting features of JDF-20, the interrupted structure and the different Al : P ratios found in this solid may be important in the synthesis of other very large pore molecular sieves, and the search for such materials is ongoing.

In contrast to the aluminophosphate materials so far described in this section, Ozin and co-workers have prepared a large number of materials where the presence of water in the synthesis mixture has a profound effect upon the types of

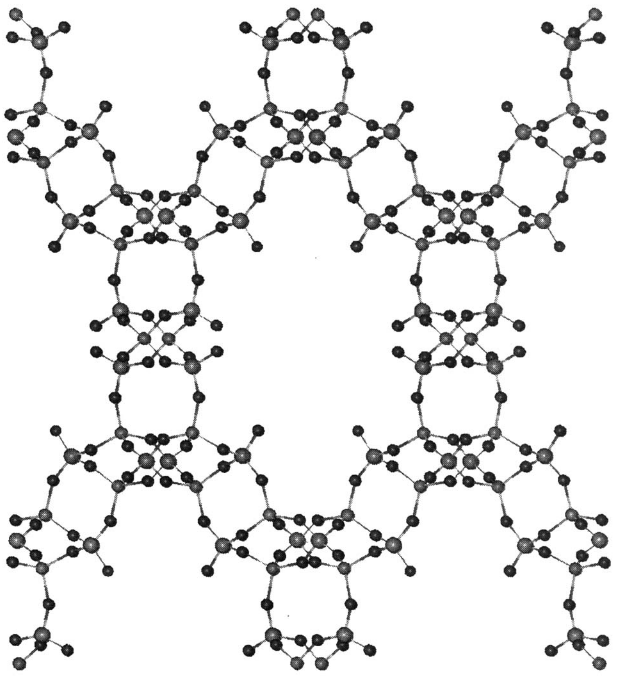

Fig. 6 The structure of JDF-20 viewed parallel to the 20-ring channels. The hanging-OH groups lining the inner surface of the pores are clearly seen.

material produced.[33] Using tetraethylene glycol as the solvent, pseudoboehmite alumina and phosphoric acid as the aluminium and phosphorus sources respectively, and then preparing reaction mixtures with varying amounts of water from trace up to a sixfold excess (relative to the tetraethylene glycol), produced a range of aluminophosphate materials. With only a small amount of water, the recovered product had a chain motif, closely related to the JDF-20 structure. As more water is added the major product of the preparations becomes JDF-20, then an $AlPO_4$-5-like sheet structure. As the relative amount of water increases to approximately 50% by volume of the solvent $AlPO_4$-5, $AlPO_4$-cristobalite and $AlPO_4$-15 become the favoured products, and as the system becomes more aqueous $AlPO_4$-5 and $AlPO_4$-cristobalite become the only phases produced. This pronounced effect that added water has on the final products of the experiment can be explained both in terms of its influence on the solubility of the alumina source material and on the hydrolysis of the species in solution. The major species after dissolution of psuedoboehmite alumina and reaction with phosphoric acid in the glycol solvent are $[AlP_2O_8H_2]^-$ chains, which when only trace water from the phosphoric acid is present crystallise out of solution together with the Et_3NH^+ counter cations to form the chain compound reported above. When there is more water present in the reaction mixture the $[AlP_2O_8H_2]^-$ chains are hydrolysed, releasing phosphoric acid and neutral template molecules, thus forming a variety of new species, a number of which are shown in Fig. 7. Each of the product solids can then be described in terms of the condensation of these solution species. For example, the addition of a small amount of water will produce some of the ladder chain [Fig. 7(*b*)] together with some of the original $[AlP_2O_8H_2]^-$ chains. The JDF-20 structure can then be formed by the condensation of these two species. In primarily aqueous solutions the crankshaft structure is predominant because it requires the highest degree of hydrolysis to be formed, and these crankshaft chains are the precursors for the $AlPO_4$-5 and cristobalite structures. Ozin has proposed a hydrolysis and condensation scheme that can account for all the products in this system, and relate them back to the amount of water present in the reaction mixture. It is apparent that studies of mixed solvent systems of this kind can yield a large amount of information that can be used to identify the solution species present in a reaction mixture and their relationship to the final products, perhaps

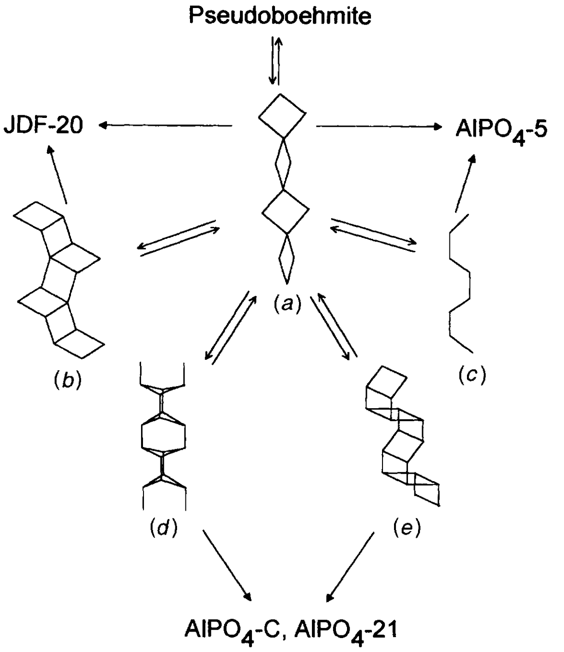

Fig. 7 The species present in glycol solution during the synthesis of aluminophosphate molecular sieves. The relative amounts of the chains depend on the degree of hydrolysis, and so on the amount of water in the reaction mixture. The dissolution of the pseudoboehmite starting material initially produces the $AlP_2O_8H_2^-$ (*a*), which then further hydrolyses to the ladder chain (*b*), the crankshaft chain (*c*), the UDUD chain (*d*) and the UUDD or double crankshaft chain (*e*). The UD representation of chains refers to linking of double 4-rings which can be either up (U) or down (D). The chain species can be viewed as direct precursors to the aluminophosphate precursors indicated.[33]

allowing a detailed description of the mode of formation of these important materials to be made.

Once again a major feature of the non-aqueous $AlPO_4$ synthesis as compared to the aqueous methods is the relatively large size of the crystals produced. Unlike the zeolites, $AlPO_4$ materials with new structures have been prepared, and the extra degrees of freedom, such as the interrupted nature of the large pore solids such as JDF-20 should mean that there is scope for other new phases to be discovered in the near future.

6 Gallophosphates

Until 1993, there had been no reports of gallophosphates being prepared from non-aqueous solvents. Then Xu *et al.* prepared two materials using ethylene glycol as the solvent and varying amounts of methylamine as the template.[34] Low methylamine to phosphorus ratios produce one structure type which when heated to more than 300 °C leads to a phase with the GaPO-25 structure. At high methylamine to phosphorus ratios another microporous gallophosphate is produced, although this one is unstable with respect to heating and loses framework crystallinity when heated above 270 °C.

Since the discovery that fluoride anions are effective mineralisers and the subsequent synthesis of cloverite there has been a large amount of interest in the synthesis of gallophosphates. Gallium differs from aluminium in that it is somewhat less likely to have tetrahedral coordination in solids, and the wider range of coordination polyhedra has led to a large number of compounds, again most of them synthesised hydrothermally, with a wide range of structural architectures. An especially interesting set of compounds recently prepared are the ULM-*n* materials prepared by Ferey and co-workers at the Universite du Maine, Le Mans, in which some of the materials have fluorine directly bonded to the gallium.[9] In view of the interest generated by the success of non-aqueous synthesis of zeolites (see section 3) using HF mineralisers it seemed likely that similar preparative methods should be successful for gallophosphates.

One striking feature of zeolite and aluminophosphate synthesis in particular is that the template molecules are highly disordered and difficult to locate using diffraction techniques. True templating such as that described in section 3 would seem to require that there should be only one orientation of the template possible within the framework cavities. Although this situation might be possible with only van der Waals' interactions between organic additive and framework, it seems more likely that this would occur when stronger hydrogen bonds are involved, where the template might be 'locked' into one position through these strong interactions. Presumably, the interactions between template and framework are minimised when, for example, the available nitrogen atoms of the template molecule are capable of hydrogen bonding as effectively to the framework oxygen atoms as they are to the solvent molecules, *i.e.* inorganic structure direction *versus* solvent ordering. Changing the solvent to one which has less 'solvating power,' *i.e.* one which forms less strong interactions with the template, is one method of increasing the relative strength of the template–framework interactions. Another method would be to change the framework species in solution by, for example, adding a mineralising agent such as HF. The combination of oxofluorogallium species present in solution, capable of forming strong interactions, with protonated amine templates leads to stronger template–framework interactions in many of the ULM-*n* gallofluorophosphates than is normally seen in zeolites and aluminophosphates. Combining this with the use of a less strongly hydrogen bonding solvent, or a mixed non-aqueous/aqueous system, leads to an even greater degree of strong template–framework interactions. Recent work completed at the University of California Santa Barbara (UCSB) has indeed shown this to be the case. The use of two seemingly completely different organic additives, 4,4′-bipyridine and 1,6-diaminohexane in the Ga_2O_3–P_2O_5–HF system using mixed solvents, produced single crystals of the same framework structure which were solved using X-ray diffraction.[35] The hydrogen-bonding interactions between the amine nitrogen atoms of the template (which are on almost identical crystallographic sites) and the framework oxygens are essentially the same in both structures, indicating that it is these interactions rather than simply size and shape of the templates, which are quite different, that are important in determining the architecture of the framework (see Fig. 8) rather than any simple space-filling stabilisation. There are subtle differences in the framework structures, most notably that the elliptical cavity in the 1,6-diaminohexane templated material is slightly longer and thinner than in the 4,4′-bipyridine structure. This is because the two templates are not exactly the same length, and to position the nitrogen atoms in the correct place for hydrogen bonding some distortion of the framework is necessary. Apart from the intriguing templating occurring in these materials, they are interesting because they are the first directly synthesised 14-ring phosphate materials.

The positioning of amine nitrogen atoms to form H-bonds with the framework is also important in a number of the other structures prepared similarly. Some templates, however, have no amine nitrogens available for H-bonding, for example tetramethylammonium cations, and these molecules necessarily act simply as space-filling templates, the only link with the framework being van der Waals' interactions through the external shell of hydrogen atoms on the methyl groups. This is much more like the type of templating seen in the synthesis of zeolites and aluminophosphates.

The substitution of framework atoms by other metal atoms is well known in zeolite and aluminophosphate chemistry, but seems less well explored for gallophosphates. The first metal substituted gallophosphate synthesised from non-aqueous systems was prepared by Chippindale who prepared a series of cobalt–gallium phosphates, some of which are analogous to

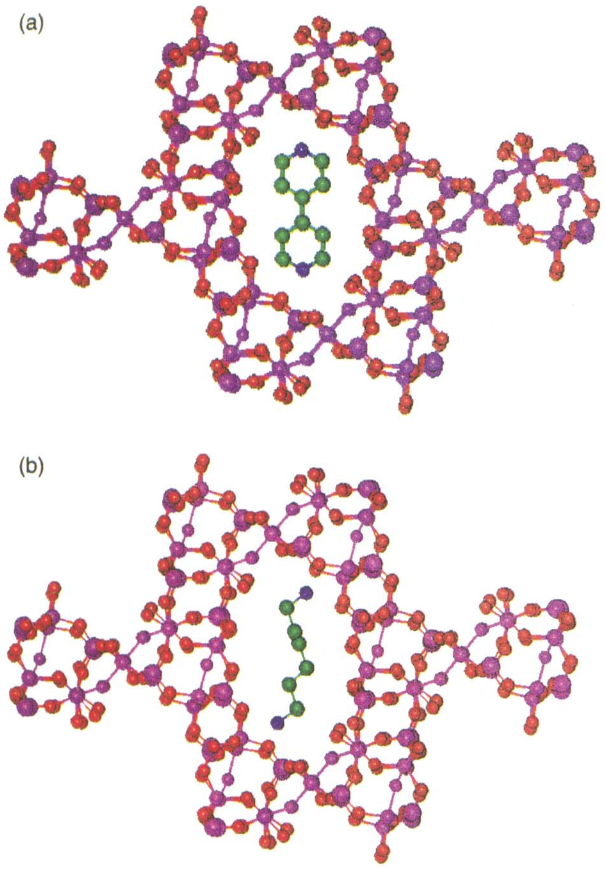

Fig. 8 Two microporous gallium phosphate materials of the same framework composition. The templates are 4,4′-bipyridine (a) and 1,6-diaminohexane (b). The nitrogen positions of the two template molecules are on almost exactly identical crystallographic sites. Pyridine is also present in the channels but is not shown.

known zeolite structures while others have new structures entirely.[36,37]

The gallophosphates are the least studied of the three families discussed in this review. Even in aqueous based preparations, the majority of the literature is taken up with reports of the synthesis of new materials rather than any study of their properties. The non-aqueous synthesis of gallophosphates has many parallels with this work, especially with excellent research of Ferey at Le Mans, where for example, fluoride mineralisers have been used to prepare many new gallophosphate and gallofluorophosphate phases. There seems much scope for synthetic chemists to explore this area of molecular sieve science to produce new and potentially interesting solids. However, as with the zeolites and aluminophosphates, there has been very little characterisation of the physical and chemical properties of these new materials, and only time will tell whether they will constitute a commercially interesting family of materials rather than simply an interesting one.

7 Conclusions

When comparing the results reported in this review with those found in hydrothermal synthesis, we see there are many parallels between the two methods. However, there are a number of qualitative features that set non-aqueous preparations apart from their hydrothermal counterparts. The large crystal sizes that are often possible in non-aqueous synthetic procedures are important, both in terms of their amenability to accurate crystal structure determination using diffraction techniques and their possible uses in advanced applications. The combination of the viscosity of the solvent decreasing mass transfer by convection, the decrease of secondary nucleation and the use of an effective mineraliser, such as HF, is successful in preparing large crystals of zeolites, aluminophosphate and gallophosphate. This increase in size of the crystals produced, albeit based on a rather small body of work, seems to be general and may well be of significance if devices which use larger crystals of, for example, zeolites are developed. The use of *in situ* X-ray diffraction already demonstrated on these types of materials will also facilitate the understanding of the processes involved in the synthesis, allowing identification of any intermediate phases that are important.

The use of non-aqueous solvents also adds a significant new variable to the armoury of the synthetic chemist; the ability to control the amount of water present in a synthesis, and so to control the degree of hydrolysis of the species in solution. The majority of preparations cited in this review need water in reactant quantities to be successful, and control of the species present in solution is important if new materials with novel structures are to be synthesised. Further work identifying each of the species present is required before we gain a full understanding of the effect of water concentration on the final products.

The synthesis of molecular sieves is complex, and as such, it is difficult to make generalisations regarding the rationale required for *a priori* design of new materials. Nonetheless, the increasing amount of work being reported is making headway towards this goal and it is well worth keeping in mind some of the major points brought forward in this review.

The synthesis of gallophosphates (section 6) illustrates the possibility of using hydrogen bonding, rather than the weaker and less directional van der Waals' interactions, between the additive and the framework in order to achieve a true templating situation, where the final product adopts exactly the template's geometry, and where the template has no freedom to translate or rotate inside the channels of the molecular sieve. The balance between the hydrogen bonding ability of the solvent and that of the template is a fine one, as one must ensure that the competition between the two types of organic for the interaction with the framework is not tipped too much either way, which will either lead to no reaction at all or the wrong species being the most important in directing the structure of the product. It must also be remembered that there are a number of other factors that need to be taken into account, such as the relative basicities of the species in solution, especially in the acidic HF media used in a number of systems. Molecular sieves are the kinetic, rather than thermodynamic, products of these reactions and the time which the synthesis gel is aged, as well as the temperature and time for which the gel is heated, are also important variables.

Strictly speaking, a material is only a molecular sieve when the templates can be removed from the channels leaving room for the adsorption of other molecules. Many of the materials cited in this review, such as the zeolites, fit this definition as the organic additives can be removed by heating in suitable atmospheres or by chemical means. Unfortunately, it is unclear from the literature whether many of the gallophosphate and aluminophosphate materials can be calcined to remove the templates, and it seems likely that as the strength of the interaction between template and framework increases this might become ever more difficult, eventually needing conditions too harsh for the framework itself to survive.

In summary, the synthesis of molecular sieves using reactions in non-aqueous solvents is an exciting and promising field which can both add to and complement the large amount of work that has already been, and continues to be, done in aqueous systems. The results illustrate the need to continue this work, and we expect many new materials with potentially interesting properties to be prepared and new insights into the mechanism of synthesis to be found. We are still some way from being able to design and synthesise molecular sieves by demand. The knowledge of reaction mechanisms is still incomplete, and our ability to tailor-make new solids is limited, but the evidence from both non-aqueous and aqueous systems seems to suggest that rational design of zeolites is possible and as the amount of knowledge increases over the next few years we expect significant progress in this area to be achieved

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