MICROWAVE TECHNIQUES IN THE SYNTHESIS AND MODIFICATION OF ZEOLITE CATALYSTS. A REVIEW

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Microwave dielectric heating is a convenient and effective way of bringing about chemical reactions in suitable (usually polar) media. Microwave-mediated organic synthesis has been the subject of considerable research and microwave heating is being increasingly applied to the synthesis and modification of zeolites and related microporous and mesoporous catalysts. The observed rate enhancements are caused by a variety of thermal effects, including very high rates of temperature rise, bulk super-

heating and (in non-homogeneous systems) differential heating. Specific, non-thermal activation is unlikely and can usually be excluded. The microwave synthesis of zeolites, zeotypes and mesoporous materials is reviewed, with emphasis on those aspects which differ from conventional thermal methods. Such standard methods are not displaced by microwave techniques and may in some instances be preferable. However, microwave synthesis does offer a high probability of rapid (and in some cases selective) reaction to give a pure product of good crystal quality. Non-synthetic applications of microwave heating in zeolite catalysis are also briefly described. A review with 118 references.

Key words: Microwave; Synthesis; Zeolites; AlPO$_4$-n; MCM-41; Heterogeneous catalysis; Microporous and mesoporous materials.

1. INTRODUCTION

Zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimensions[1]. They are widely used in separation processes (ion exchange, selective sorption) and in their acid form are probably the most important heterogeneous acid catalysts used in industry. Most of the world's gasoline is produced by the fluidised catalytic cracking (FCC) of petroleum using zeolite catalysts. Their key properties are strong acidity together with size- and shape-selectivity. In recent years, many new zeolite-like materials (zeotypes) containing elements other than silicon and aluminium have been synthesised[2] and related structures with much larger pore sizes (up to around 100 Å) have also been discovered[3]. Such microporous and mesoporous catalysts form the subject of recent extensive reviews[4].

Aluminosilicate zeolites are usually synthesised[1,4] under hydrothermal conditions from reactive gels in alkaline media at temperatures between about 80 and 200 °C. An alternative course is to employ fluoride-containing compositions as mineralising media in which case the pH can be much lower. This latter approach has the advantages that (i) nucleation rates are reduced so that larger crystals are formed and (ii) in zeotype synthesis[2], the acid or neutral pH regime facilitates the structural incorporation of those heteroatoms where the precursor species would be precipitated (*e.g.* as hydroxides) at higher pH. Such zeotypes have considerably broadened the scope of zeolitic catalysis, which was formerly confined largely to strong acid reactions such as hydrocarbon cracking and rearrangement. The titanosilicate TS-1 is now used commercially as an oxidation catalyst, particularly in olefin epoxidation.

Many zeolites (and some zeotypes) can be made using only inorganic reactants and the classical synthetic zeolites A, X and Y are always made in this manner. However, in the 1960s, increasing use was made of organic compounds, particularly quaternary ammonium salts. These are often referred to as templates since the zeolite apppears to form around them, in some cases encapsulating them with a very close fit between the organic groups and the pore walls of the structure. Most high-silica zeolites (Si/Al > 10) are synthesised using organic templates, which usually have to be removed from the struc-

ture by calcination to produce the open-pore materials for use in sorption and catalysis. In general, crystal growth rates tend to decrease as the Si/Al ratio increases so that the relatively short preparation times of aluminous zeolites (min to hours) become more extended for the high-silica materials (hours to days) and the synthesis temperatures of the latter are usually considerably higher (100–200 °C rather than 80–120 °C).

Members of the aluminophosphate family of molecular sieves ($AlPO_4$-n series)[2] also almost invariably require the use of organic templates in their synthesis. However, with these neutral frameworks, amines are more often used than quaternary compounds. As with high silica zeolites, synthesis temperatures are in the 100–200 °C range and synthesis times are most often measured in hours or days.

In the latest development in the growing family of ordered porous materials, mesoporous materials with pore sizes of *ca* 20–100 Å (M41S family)[3] can be synthesised by using long-chain surfactant molecules as templates. Lamellar, hexagonal (*e.g.* MCM-41) and cubic (*e.g.* MCM-48) types are known. The materials are ordered, but not crystalline, since the pore walls are amorphous. Silicate, aluminosilicate and heterosubstituted varieties have been synthesised, usually at moderate temperatures (25–150 °C).

It is the aim of the present contribution to describe some recent advances in the synthesis and modification of zeolitic catalysts. Attention will be concentrated on one particular area of progress, namely the use of microwave dielectric heating in synthetic procedures. The microwave synthesis of zeolites, zeotypes and mesoporous materials will be reviewed, including both products which are actual catalysts and also those closely related to potentially active materials. Emphasis will be placed on those aspects of microwave synthesis which differ from traditional thermal methods. Some reference will also be made to non-synthetic applications of microwave heating in zeolite catalysis.

2. SOME FEATURES OF MICROWAVE HEATING

If microwave heating is regarded simply as an equivalent alternative to conventional oven heating, then its interest and potential in synthesis are limited. However, the input of microwave energy into a chemical reaction mixture is quite different from conventional (thermal oven) heating and it is the task of the synthetic chemist to exploit this special situation as fully as possible. Microwaves can heat a reaction mixture rapidly, uniformly and directly, without any problems of heat transfer through the walls of the container. There are also possibilities for selective effects but their limitations need to be understood. The comments which follow can provide only a brief introduction to the topic of microwave chemical synthesis. However, further information is available in a number of excellent reviews[5], some of which concentrate on particular areas such as organic synthesis, supported ("dry") organic synthesis and phase transfer catalysis[6].

2.1. The Nature of Microwave Heating

The heating effect of microwave radiation occurs through processes of dielectric loss[5]. The dielectric becomes polarised and also, if charges in the target medium can migrate, conduction results. A heating effect arises from the phase lag caused by the inability of the induced change to follow rapid reversals of the electric field and also, where conduction can occur, from ohmic heat generation. The dielectric polarisation may be related to dipoles in the bulk or to a build-up of charge at interfaces (the Maxwell–Wagner effect). Highly conductive solids or liquids, polar liquids and some suspensions or multiphase materials will therefore exhibit large dielectric losses, whilst hydrocarbons and low polarity solvents such as carbon tetrachloride will show little heating effect. The overall heating effect for a given medium depends on the dielectric constant (ε'), the dielectric loss (ε''), a conductivity term, the temperature and the frequency of the applied field.

2.2. Laboratory Equipment

Two types of microwave heating equipment (Fig. 1) have been used for studies on synthesis and some specialised equipment has been constructed by individual research groups[5,6]. Most commonly, a multimode oven (non-uniform electric field distribution) is employed – in some cases, a domestic oven, in others, a unit designed specifically for laboratory use. The former has the advantage of cheapness but lacks flexibility in control and reaction monitoring. The latter is more expensive but is purpose-built, has extensive facilities for programming and allows stirring of the reaction mixture and the continuous monitoring and control of temperature and pressure. Microwave ovens can accommodate large samples (*e.g.* 12×100 cm^3) and usually operate at 2.45 GHz. The second type of unit used in microwave synthesis is the single mode device in which microwave energy is piped (to some extent focused) into a reactor through waveguides.
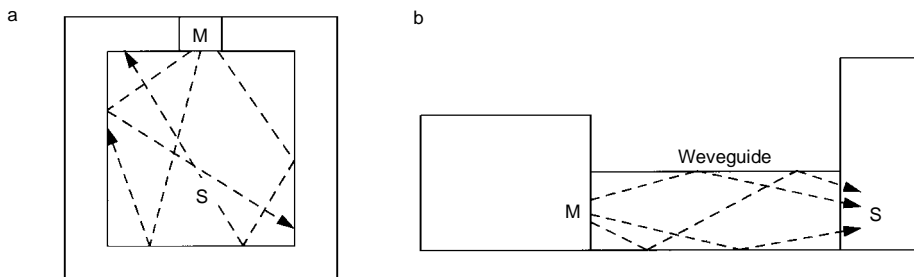

Fig. 1
Laboratory microwave heating equipment: a microwave oven (multimode), b monomode reactor (M magnetron, S sample) (after Loupy *et al.*[61])

Such a reactor is usually small (perhaps only 1–2 cm^3) but may be operable over a range of frequencies. Reaction vessels themselves are made of a material transparent (or largely transparent) to microwaves at the operating frequency, commonly borosilicate glass, PTFE or (for pressure vessels) a specialised polymer or composite. Temperature measurement is the biggest single problem in microwave synthesis. For microwave ovens, plated, earthed thermocouples or fibre-optic devices are used. For single-mode cavities, additional techniques include optical pyrometry and measurement of the temperature differential of a flowing gas.

2.3. "Microwave Effects"

Much as been written about special (athermal) "microwave effects", particularly where it has been claimed that reactions proceeded faster in a microwave environment than under conventional conditions at the same temperature. However, it is now apparent that most of these early claims were the result of experimental artefacts, particularly in temperature measurement[5b,5f,6a,7]. In general, specific activation at a controlled temperature in homogeneous media is unlikely. Furthermore, the energy carried by microwaves at the usual output frequency (2.45 GHz) is too small (*ca* 1 J mol^{-1}) to bring about any significant direct molecular activation (such as occurs in photochemistry).

Nevertheless, real benefits for microwave energy input remain and can be summarised as follows:

1. Very high rates of temperature rise can be achieved, even in quite large samples (*e.g. ca* 1–2 °C s^{-1} for 100 g samples in laboratory microwave ovens; single mode devices may achieve ten times this rate for smaller masses).

2. Considerable bulk superheating can be achieved. In atmospheric pressure operation, the body of a boiling liquid may be at temperatures 10–30 °C in excess of the conventional boiling point (whereas the surface is at the boiling point and in equilibrium with the saturated vapour).

3. In non-homogeneous systems, there may be significant differential heating effects due to both the heterogeneity of the dielectric and the presence of interface regions. In this case, it is quite possible for some regions to be "hotter" than others on a macro or micro scale. On the larger scale, the situation is reminiscent of that in bulk superheating. Thus, in an experiment on the microwave heating of two immiscible liquids, the upper (water) layer could be maintained at *ca* 110 °C whilst the lower (chloroform) layer remained at around 50 °C (ref.[8]).

The first and second of these factors can account for many of the reported rate enhancements which had been attributed to "microwave effects", since a combination of rapid heating and up to 30 °C of superheating can provide reductions in reaction time of 10–50-fold based on purely conventional arguments[5c].

2.4. Selectivity

There are at least two mechanisms by which genuine selectivity effects may be produced in microwave-assisted reactions. In the first instance, the rapid heating rate achievable may allow one reaction pathway to be favoured over another. Stuerga *et al.*[9] report a selectivity effect in the sulphonation of naphthalene in which the ratio of 2 isomers can be changed from about 55 : 45 to 95 : 5 as a function of heating rate. The effect depends on the kinetics of two competing reversible reactions with one common reactant. Using an Arrhenius-type kinetic model, two situations are predicted, depending upon the choice of reaction parameters. The result found in practice corresponds closely with the first of these and is shown schematically in Fig. 2. As the heating rate is increased, the product ratio P_1/P_2 also increases. The second predicted pattern, in which the lines cross (inversion – not illustrated), so that P_1/P_2 is low at low heating rates and high at high heating rates, has not yet been observed experimentally. Such selectivity results directly from the temperature profile of the reaction and should not be dependent on the heating method. However, a sufficiently high temperature ramp rate cannot be achieved by conventional heating so that only the microwave experiment allows observation of the effect.

The second potential source of selectivity stems from the possibility of differential heating (see section 2.3, above). It is probable that some of the effects seen in zeolite synthesis (section 3), zeolite modification (section 7) and microwave-assisted organic reactions on supports (section 8) are attributable to this.

3. MICROWAVES IN ALUMINOSILICATE ZEOLITE SYNTHESIS

Although the heating of polymers with microwaves was described[10] in 1967, the first application of microwave dielectric heating to chemical transformations dates back to studies of aquation and dissociation in aqueous solution[11] in 1981. The authors selected the technique in view of the "almost complete absence of significant temperature gra-
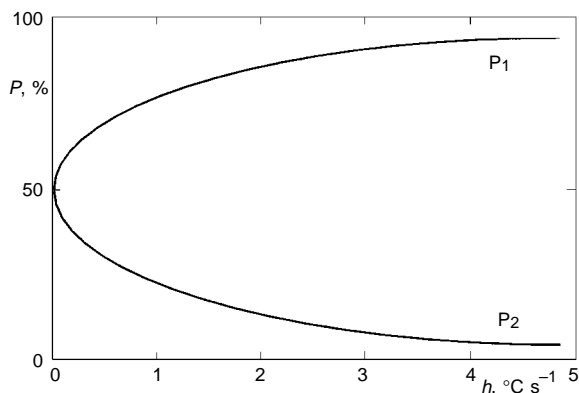
FIG. 2
Distribution of isomeric products (P_1 and P_2) as a function of heating rate h (schematic, after Stuerga *et al.*[9])

dients within the sample, the possibility of varying the rate of temperature rise and the very short response time". Microwaves and zeolites received their first combined attention at about the same time but not in the field of synthesis. Microwave dehydration of zeolite 13X was reported[12] in 1981, followed by further papers[13,14] on 13X and an analysis of a mechanical cooling system based on water sorption by zeolites 4A and 13X with regeneration in a microwave field[15]. The first publication on zeolite synthesis came from the Mobil laboratories[16]. Using an industrial microwave oven, data are given for the synthesis of zeolites Na-A and ZSM-5. Comparative examples show that Na-A could be crystallised in 12 min at an indicated temperature of 100 °C whereas crystallisation of the same mixture required 2 h in a steam box. Under similar conditions (100 °C) the ZSM-5 (SiO_2/Al_2O_3 *ca* 300) crystallised in a seeded system in 100 min whilst conventional procedures required 6 h to reach a comparable level of crystallinity. No special effects were claimed, although the microwave Na-A product crystals were found to have more rounded edges than those in the conventional sample.

3.1. Microwave Synthesis of Aluminous Zeolites

Following the appearance of the Mobil patent[16], several other groups reported microwave syntheses of aluminous zeolites (Si/Al < 5). A study of the Na_2O–Al_2O_3–H_2O system[17] showed that the crystallisation fields for hydroxysodalite, Na-A and Na-X were essentially the same as those described in a standard reference work[1a] for conventional heating. However, a comparative study of Na-A formation showed that a conventional preparation took ten times as long as a microwave synthesis to achieve 100% crystallinity. The crystal size distribution in the microwave experiment was slightly narrower (0.5–1.4 µm) with a larger mean size (*ca* 1.0 µm) than in the thermal experiment (0.2–1.3 µm, 0.5 µm).

Using a 120 °C/100 °C 2-stage heating regime similar to that employed for the Na-A studies described above, zeolite-Y could be prepared by microwave heating in 10 min as uniformly sized crystal aggregates, Si/Al = 3.5 (as determined from the unit cell parameter). Products with very high Si/Al ratios (up to *ca* 5.0) could be made, although the crystallinity fell to *ca* 65% at these values and crystallisation times were not given[18]. Further studies on faujasite formation by microwave methods also showed short synthesis times. Pure zeolite Y could be obtained at temperatures (150 °C) where contamination by other phases would be regarded as inevitable using conventional heating[19].

Highly siliceous faujasites are of interest in the search for FCC catalysts of increased activity, stability and selectivity and it is possible to produce very siliceous variants of faujasite in a sodium cation system in the presence of crown ether templates[20]. The long synthesis times can be considerably shortened by the use of microwave energy input[19]. Hexagonal Y (EMT) (Si/Al ratio *ca* 4.2) is made using [18-crown-6] and is a difficult zeolite to synthesise, normally taking 4–12 days at 110 °C by conventional

heating[20]. However, it can be obtained in one day in a microwave synthesis at a higher temperature (130–150 °C). The silica-rich cubic equivalent of EMT can also be obtained by microwave synthesis on a similar timescale through the use of [15-crown-5] (ref.[21]). At 110 °C, a highly crystalline product having Si/Al = 4.0 can be made in 2.5 days (*cf.* 7 days by conventional heating[20]) and the time can be reduced to about 1.5 days at 125 °C.

Amongst other studies of aluminous zeolite synthesis, Na-A of 95% crystallinity was produced by microwave heating in 10–20 min (ref.[22]) and Na-A, faujasite, analcime and hydroxysodalite were prepared in a few minutes at an undisclosed temperature[23]. Selectivity effects in the microwave synthesis of faujasite[18,19] are discussed in section 9.2 whilst further work by the Delft group on the microwave synthesis of Na-A (ref.[24]) is described in section 9.1.

In an unusual approach, zeolites and other mineral phases were synthesised from fly ash by conventional and microwave-assisted hydrothermal treatments in alkaline solution[25]. In a sodium system, the zeolites obtained were Na-P1, hydroxysodalite, hydroxycancrinite and analcime. Using KOH solution, zeolite F (Linde) and phillipsite-KM were found. Yields and products were very similar for microwave and conventional experiments but reaction times were much reduced in the microwave case (24–48 h to 30 min).

3.2. High-Silica Zeolites

Zeolites having Si/Al ratios of around 10 and over are referred to as high-silica zeolites[26]. Some structures can be made as nominally aluminium-free silica polymorphs. Such highly siliceous materials are essentially cation-free and are hydrophobic.

Zeolite Beta is most frequently synthesised in its Na,TEA-form (TEA = tetraethylammonium). A typical composition has been investigated at 140 °C and is found to crystallise in 14 h in a microwave heating environment[19]. This represents about 25–33% of the time taken by conventional oven heating. The product had a Si/Al ratio of 14 as measured by ^{29}Si NMR spectroscopy.

3.3. ZSM-5

Extensive work has been carried out on that most studied of high-silica zeolites, ZSM-5. The comparative examples in the original Mobil microwave patent[16] are mentioned above. Further examples in the patent show that ZSM-5 can be synthesised with microwave heating when some or most of the water in the reaction mixture has been replaced by ethylene glycol. Elsewhere, in a highly alkaline system (OH$^-$/SiO$_2$ = 6.6, OH$^-$/H$_2$O = 0.04), Na,TPA-ZSM-5 (TPA = tetrapropylammonium) was crystallised in 30 min at 140 °C (ref.[18]).

3.3.1. Fluoride Route

The hydroxide-based synthesis of ZSM-5 has been compared with the fluoride route[19]. The composition 5 Na_2O–0.2 Al_2O_3–60 SiO_2–4 TPABr–900 H_2O can be crystallised in 5.5 h at 175 °C by oven heating and in half that time when microwave heating is used at a similar temperature[27,28]. For a synthesis based on ammonium fluoride, the crystal growth step takes about 1.5 h for both microwave and oven heating at 170 °C. However, the induction period in the microwave case (6–7 h) is about 40% of the equivalent time in the traditional synthesis. This shows that nucleation is the major factor controlling the overall synthesis time in the fluoride synthesis and that it is on this period that the microwave technique provides the greatest reduction. By substitution of $TiCl_3$ for $AlCl_3$ in the NH_4F-based synthesis mixture, the titano-silicalite oxidation catalyst TS-1 can be synthesised in a manner very similar to that used for Al-ZSM-5 (ref.[19]).

3.3.2. Inorganic ZSM-5 (No Organic Template)

Within a certain range of Si/Al ratios, Na-ZSM-5 can be crystallised in the absence of organic templates[29]. The standard synthesis using the composition 10 Na_2O–Al_2O_3–60 SiO_2–3 000 H_2O takes 1–3 days in a stirred autoclave at 150 °C. Using conventional heating at 175 °C, only a trace of product was detectable by XRD after 7 h in a static system, whilst no crystalline product was evident after microwave heating for 3 h. However, using a nanocrystal seeding technique (see section 3.3.3), an oven-heated sample crystallised in 5 h at 175 °C whereas the equivalent microwave reaction was complete in 30 min (ref.[28]).

3.3.3. Nanocrystal Seeding

The original report on microwave ZSM-5 synthesis[16] involved the inclusion of "ZSM-5 seeds" in the reaction mixture. This is assumed to refer to crystalline material formed in a previous, and probably similar, synthesis. Recent work[27,28] has explored the use of well-defined nanometre-sized seed crystals. The effects observed are illustrated in Fig. 3 where it can be seen that the crystallisation of Na,TPA-ZSM-5 at 175 °C in the presence of 70 nm seed crystals was almost complete by the time that the reaction mixture had reached working temperature (3 min). Comparative microwave unseeded and thermal (seeded and unseeded) reactions were all considerably slower. The corresponding preparation with a reaction composition requiring no organic template showed a similarly large acceleration for the seeded microwave reaction (not shown) which was only a little slower than the TPA-templated synthesis. There thus appears to be strong synergy between microwave energy input and the use of nanosized seed crystals.

3.3.4. Template Degradation

In view of the established use of microwave heating in degrading organic materials for subsequent analysis[30], it might be anticipated that the tendency of quaternary am-

monium templates R_4N^+ (R = alkyl chain > methyl) to undergo Hofmann degradation in solutions of high pH could pose a particular difficulty in microwave synthesis. It has been reported[17,18] that this is indeed the case for TPA^+ although the problem was more severe for fresh rather than aged solutions. However, it may be noted that in the preparation of zeolite Beta mentioned earlier (section 3.2) no unusual difficulty was experienced, although the tetraethylammonium template is particularly prone to decomposition.

3.3.5. Dry Synthesis

Useful results have been obtained in microwave organic synthesis by the use of "dry" methods in which the reagents are absorbed upon a solid support (see section 8). Although the reactions involved are quite different, a related "solventless" approach has been applied to zeolite synthesis in order to provide preparations with a very high batch yield (*i.e.* high mass of zeolite product per unit volume of reactor)[27]. For the reaction composition 5 Na_2O–0.2 Al_2O_3–60 SiO_2–4 TPABr–n H_2O with nanocrystal seeding (section 3.3.3), it is found that the water content can be reduced from $n = 900$ to $n = 400$ without seriously affecting the final crystallinity or completion time (5 min). With $n = 100$ and a slightly higher alumina content (0.4 Al_2O_3), synthesis mixtures having the appearance of dry powders were heated by both microwave and conventional methods. It was found that in this case normal oven heating gave the best result (75% crystallinity after 4 h at 180 °C). Only a very small amount of ZSM-5 could be found by XRD after 5 h microwave heating at 175 °C, suggesting that such a "dry" mixture is unsuitable for microwave synthesis. The reason for this behaviour was found to lie in the nature of the reaction mixture, which was more heterogeneous than a conventional fluid gel. Alkali-rich, water-deficient local areas were believed to have absorbed too much microwave energy (by a conduction mechanism) and melted to glassy products under the action of the microwave heating. Small beads of Na-rich glassy materials
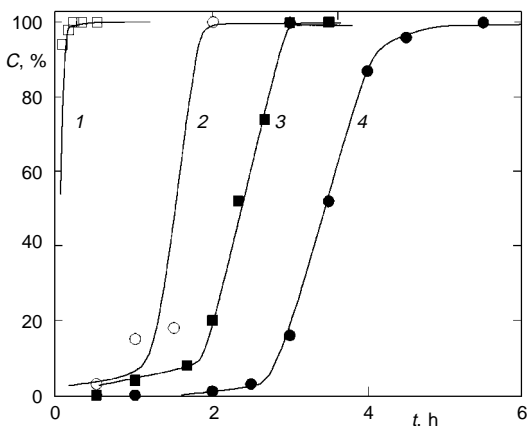
FIG. 3
Growth curves for Na,TPA-ZSM-5: *1* seeded, microwave; *2* seeded, thermal; *3* unseeded, microwave; *4* unseeded, thermal (*t* reaction time, *c* crystallinity, TPA = tetrapropylammonium)

were found in the reaction residue. These sparingly soluble products have the effect of sequestering active components of the reaction mixture which are then no longer available for zeolite synthesis. Conventional heating will be free from this differential heating effect and will therefore (in this instance) be a more effective form of energy input.

3.3.6. Growth on Surfaces – Membranes

Microwave heating provides an improved degree of control over the temperature–time profile of a synthesis reaction. One of the ways in which this has been exploited is in the growth of surface films of microporous crystals. In one case[17], crystals of Na-A were grown under microwave conditions at 120/95 °C on the surfaces of (i) activated copper metal and (ii) cordierite. From differences in the crystal form in the two instances, it was concluded that microwaves stimulated the interaction between the growing zeolite crystal and the conductor (copper) more strongly than that with the non-conductor (cordierite). However, no details were provided of temperature checks, crystal growth rates or control experiments. In an extension of this work[31], thin (<0.15–1.10 µm) films of silicalite-1 were grown upon silicon wafers using rapid heating and cooling. XRD studies on a selected sample showed only 0k0 reflections, indicating good crystal orientation, whilst overall surface coverage varied between samples from zero to 40%.

Table I summarises published work on microwave zeolite synthesis.

TABLE I
Microwave synthesis of aluminosilicate zeolites

Zeolite	Reference
Analcime	23, 25
Faujasite (cubic, zeolites X & Y)	17, 18, 19, 21, 23
Faujasite (hexagonal)	19
Hydroxycancrinite	25
Hydroxysodalite	17, 23, 24, 25
Phillipsite	25
Zeolite A	16, 17, 22, 23, 24
Zeolite F (Linde)	25
Zeolite P	25
Zeolite Beta	19
ZSM-5	16, 18, 19, 27, 28, 31
TS-1	19

4. MICROWAVE SYNTHESIS OF ZEOLITIC ALUMINOPHOSPHATES

Microporous aluminophosphate polymorphs $AlPO_4$-n have neutral frameworks, no associated cations and no significant catalytic activity[2]. However, the substitution of heteroelements into these structures introduces possibilities for many types of catalysis. For example, silica and/or metal substitution (affording the SAPO-n, MeAPSO-n and MeAPO-n families) produces a net negative framework charge (for Me^{n+} where $n < 3$) and therefore potential acid sites, whilst the presence of framework transition metal atoms may give redox activity. In addition, there are also possibilities for using $AlPO_4$-n materials as supports for catalytically active extra-framework species.

4.1. Synthesis of AlPO₄-5 and Derivatives

The first aluminophosphate material to be synthesised by microwave heating was the cobalt substituted derivative CoAPO-5, made using a triethylamine template in a fluoride-containing system[32]. The authors were particularly interested in obtaining large single crystals and succeeded in preparing well-formed hexagonal rods up to about 75 μm in length and having an aspect ratio of around 3 : 1. Interestingly, the crystals are dichroic in polarised light, a observation believed to reflect the distorted tetrahedral geometry of the Co^{2+} ions in the lattice. The authors comment on the rapidity of the synthesis (*ca* 20 min at 170–200 °C) but do not provide any direct comparison with oven heating.

An early study of Mg-AlPO₄-5 synthesis established the short reaction time required (20 min at 174 °C, microwave; 24 h at 200 °C, conventional oven)[33]. Large AlPO₄-5 crystals (up to 130×40 μm) were prepared in a similar manner to the CoAPO-5 by the same research group[34] and it was found that crystals 40×15 μm in size could be grown in 60 s at 180 °C. A large series of parameters (composition, temperature, heating time) was investigated in order to determine their effect upon the synthesis. An interesting point concerned the use of a 2-stage synthesis in which the (opaque) mother liquor from a 60-second synthesis was decanted and heated again at 180 °C for 60 s. Although the particle size distribution in the first stage product was fairly broad and included amorphous material, the product from the second step, although slightly smaller, had a very narrow size distribution and was free from unreacted material or other impurities.

Although it should be noted that the original authors of the studies on CoAPO-5 (ref.[32]) and AlPO₄-5 (ref.[34]) optimised their syntheses for microwave heating, the same reaction compositions have subsequently been used in a comparative study of the synthesis of AlPO₄-5 and CoAPO-5 by thermal and microwave methods in the temperature range 160–180 °C (ref.[35]). The thermal preparation of CoAPO-5 required *ca* 3 h at 180 °C for completion and produced blue hexagonal rods of up to 200 μm in length. At 175 °C (fibre optic probe), the microwave synthesis was complete in 10 min although the crystals were smaller (60 μm). The syntheses of AlPO₄-5 tended to be slower than those of

the cobalt analogue. The conventionally heated preparation yielded crystals up to 200 µm in size in reactions which took about 12 h to reach completion at 180 °C. At a similar temperature, microwave heating required about 30 min to complete the reaction (largest crystals 70 µm). However, for both $AlPO_4$-5 and its cobalt analogue, crystals around 50 µm in size were found amongst the amorphous material at the earliest times observable in the microwave experiments (3 min). From these observations and those of the Berlin group[34], it is clear that crystal growth rates (0.5 dl/dt) in the range 10–20 µm min^{-1} are possible in these systems. It was also apparent that the $AlPO_4$-5 product was considerably more stable than the cobalt material under the reaction conditions. Extension of the synthesis times had little effect upon the $AlPO_4$-5 crystals whereas the cobalt analogue decomposed quite rapidly to a pink residue. The 2-stage synthesis (re-heating of a decanted mother liquor) was also investigated for thermal and microwave syntheses of both $AlPO_4$-5 and CoAPO-5. Only in the case originally reported[34] (microwave/$AlPO_4$-5) was a product of narrow particle size distribution (24 × 7 µm) obtained. Finally (as a qualitative generalisation based on optical microscopy), the overall quality of the crystals produced by the microwave syntheses was better than that of the thermal samples.

In a synthesis system based on tetraethylammonium hydroxide rather than triethylamine, crystals of $AlPO_4$-5 down to about 50 nm in size were synthesised at 50–60 °C in around 10–25 min by microwave heating[36]. Also, whilst large $AlPO_4$-5 crystals have found applications in spectroscopy, non-linear optics and one-dimensional membranes[34b], a different approach has been investigated for the preparation of aligned aluminophosphate crystals[37]: a membrane of vertically aligned $AlPO_4$-5 crystals was prepared on floating anodised alumina using microwave heating.

Molecular sieves of the $AlPO_4$-5 type containing ions of various metals isomorphously substituted into the framework have been synthesised by microwave and conventional methods[38a] (MeAPO-5, Me = Mn, Co, Ni, Mg, Zn, Zr and Si). Acidity and catalytic properties were studied but the microwave products were not described separately. A related study in which M = Co, Si has also recently been reported[38b].

4.2. Other Aluminophosphate Molecular Sieves

A comparison has been made between VPI-5 syntheses at reflux temperature and under autoclave conditions using both conventional and microwave heating in both cases[39]. Differences in reaction rate and product phase distribution were observed but beyond the expected effect of temperature in the oven-heated reactions (ca 99 and 132 °C), further comparisons are difficult because the temperatures in the microwave experiments were not measured.

A similar uncertainty over reaction temperature applies in an investigation of the synthesis of $AlPO_4$-11, the large-pore gallophosphate cloverite and a dense $GaPO_4$ phase[40]. Synthesis times were reduced by more than an order of magnitude compared with comparative runs carried out using conventional heating. However, impurity

phases were observed in many cases and the temperatures in the microwave experiments were estimated from the vapour pressures. The temperature of the body of the reaction mixture could thus have been considerably different from that assumed.

A study of the microwave crystallisation of Ti-cloverite[41] mentions comparative thermal preparations but does not provide details. However, it was found that the microwave samples were of higher crystallinity than those synthesised in a furnace. Using an empirical 120–170 °C temperature programme in a laboratory microwave oven, crystals up to 60 μm in size were obtained.

The metalloaluminophosphates MeAPO-44, MeAPSO-44 (*i.e.* containing Me, Al, P, and Si) and MeAPO-5 were prepared with Me = Co, Mn by microwave synthesis[42] and (for Me = Co only) by conventional heating[42b]. Although detailed comparisons were made of acidity, stability and other properties, the microwave-prepared samples were not discussed separately. However, synthesis times were greatly reduced (4–24 h, thermal; 20–30 min, microwave) and it was noted that the crystals obtained by microwave synthesis were characterised by more uniform and more perfect habits.

Table II summarises published work on the microwave synthesis of zeolitic alumino- and gallophosphates.

5. SYNTHESIS OF OTHER CRYSTALLINE MOLECULAR SIEVES

Several microporous manganese oxides with layer and tunnel structures have been prepared by a variety of techniques including microwave heating[43]. Synthetic todorokite (OMS-1) is an octahedral molecular sieve with one-dimensional 6.9 Å channels. A total microwave synthesis (reagent mixing, precipitation, hydrothermal treatment all in the

TABLE II
Microwave synthesis of zeolitic alumino- and gallophosphates

Material	Reference
AlPO$_4$-5	34, 35, 36, 37, 53
CoAPO-5	32, 35, 38, 42a
MgAPO-5	33, 38
MnAPO-5	38, 42b
MeAPO-5 (Me = Ni, Zn, Zr, Si)	38
AlPO$_4$-11	40
MeAPO-44 & MeAPSO-44 (Me = Co, Mn)	42
VPI-5	39
Cloverite	40
Ti-Cloverite	41

microwave field) has been employed to give a pure phase material with increased catalytic activity[43b]. Considerable reduction of synthesis time (at least threefold) was achieved and differences from conventionally synthesised samples were also seen in FTIR, SEM, surface area and extent of crystallinity. No clear reasons for the differences were apparent but the effect upon the catalytic properties was startling. In the conversion of ethylbenzene to styrene, the microwave sample (BET surface area 48 m^2 g^{-1}) was six times as active as the conventionally synthesised material (27 m^2 g^{-1}) but the selectivity to styrene (as opposed to CO_2) fell from 95% (conventional) to 3% for the microwaved material. In the microwave synthesis of cryptomelane, the product was formed at an unusually low temperature (320 °C – rather than 370 °C, conventional heating). Similarly, bixbyite, which usually forms at temperatures above 600 °C in conventional preparations, was obtained at 470 °C (ref.[43c]).

6. MICROWAVE SYNTHESIS OF MESOPOROUS MATERIALS

Although the mesoporous aluminosilicates of the M41S family (pore size *ca* 20–100 Å) lack the strong acidity characteristic of crystalline zeolites, they can act as hosts for both structural heteroatoms and anchored functional groups. These materials therefore have considerable potential as selective catalysts for the transformation of larger molecules[3,4]. Using aged precursor gels (mixed silica source), Si,Al-MCM-41 of good thermal stability has been synthesised at 150 °C (optimum) within about one hour[44]. The beneficial effect of the microwave heating was attributed to the acceleration of the condensation reactions of the silicate network. A paper describing several different routes to Si- and Si,Al-MCM-41 mentions the synthesis of these materials in a 650 W microwave oven in 1–30 min (ref.[45a]) whilst the mechanism of MCM-41 formation under microwave heating has been studied using photoluminescence spectroscopy[45b].

7. MICROWAVE TECHNIQUES IN THE MODIFICATION OF ZEOLITE CATALYSTS

Zeolitic catalysts are commonly modified by ion exchange or impregnation[4] and it is possible that any necessary heat input could be supplied by microwave heating, as has been achieved for other types of catalyst[46].

Rapid microwave-assisted replacement of Na^+ by Co^{2+} in faujasite and sodalite has been reported[23]. A series of La,H-ZSM-5 samples with different degrees of La^{3+} exchange has been prepared by microwave methods and their acidity characterised and correlated with catalytic cracking activity[47a]. Palladium clusters have been encaged in zeolite Y following microwave-mediated ion exchange between $[Pd(NH_3)_4](NO_3)_2 \cdot H_2O$ and Na-Y. Following XRD and XPS characterisation, the products were found to be effective catalysts for the complete oxidation of CO at room temperature[47b].

Cu/ZSM-5 catalysts are active in NO_x reduction and CO activation and several papers describe their preparation by microwave methods. $CuCl_2$ has been dispersed in Na-

ZSM-5 by microwave heating of the mixed solids[48]. Up to a critical weight ratio, no peak at the melting point of $CuCl_2$ was seen in DTA curves and XRD patterns exhibit only the peaks assigned to the zeolite. Infrared studies indicated that more CO was absorbed on the product than was the case with Cu-ZSM-5 prepared by ion exchange from $CuCl_2$ solution. Copper chloride was also dispersed by microwave treatment into the channels of Na-Y and similar phenomena were observed using salts of lithium, gold, nickel and ruthenium. Further results on the derived intrazeolite Au(I) carbonyl and nitrosyl complexes have also been given[49].

In a related study[50], catalysts for the syngas to methanol reaction were prepared from H-ZSM-5 by (*1*) solution ion exchange with Cu(II) acetate, (*2*) thermal (≥400 °C) solid state exchange with $CuCl_2$ and (*3*) microwave solid state ion exchange with $CuCl_2$. Unusually, methods (*1*) and (*3*) were found to give products containing mainly Cu^+ whereas method (*2*) afforded largely Cu^{2+}. However, no firm conclusion can be drawn as the temperature of the microwave reaction was not recorded. Some ambiguity also exists in a further similar study[51]. Microwave products at the directly-measured temperature of 145–158 °C had BET surface areas (around 900 $m^2 g^{-1}$) that were comparable with those of catalysts prepared thermally at 850 °C. However, it is stated elsewhere in the report that the microwave samples were further heat-treated to 550 °C in air to convert $Cu(NO_3)_2$ to CuO and it is unclear to which evaluated samples this applies. Further recent work on microwave-assisted dispersion of inorganic materials into zeolites includes the systems MgO/KL (ref.[52a]), $ZnCl_2$/Na-Y (ref.[52b]) and [MoO_3, $CuCl_2$, $NiX_2\cdot6 H_2O$ (X = Cl, NO_3)]/Na-ZSM-5, Na-Y, MCM-41 (ref.[52c]). Finally, in a development which may have future implications for zeolite photocatalysis, the rapid syntheses achievable by microwave methods have been exploited in the encapsulation of unstable dye molecules during the crystallisation of $AlPO_4$-5 (ref.[53]).

8. MICROWAVE ACTIVATION OF CATALYTIC REACTIONS

Reports have appeared in which catalytic reactions have been carried out under conditions of microwave irradiation[46]. Although few of these have involved zeolite catalysts, this is a growing field for research and a brief summary of relevant topics is given below. The cautionary comments on specific microwave effects made in section 2.3 should be noted again here, especially in the light of recent further investigations[6a,7].

Porous catalysts have been employed in a number of solid-in-liquid reactions in which microwave heating has been used. Unfortunately, there is often no "control" data and comparison with conventional heating is therefore difficult. However, a comparison has been made in the case of hexane oxidation by hydrogen peroxide in the presence of TS-1 at 100 °C (ref.[54]). Rates and conversions were found to be higher when microwave heating was used although peroxide usage efficiency was lower. Direct microwave activation of the hydrogen peroxide was considered improbable and the action of "hot spots" was thought to be the most likely cause of the observed effects. It

is interesting to note that the isomer ratio of hexan-2-ol to hexan-3-ol was found to be lower for microwave than conventional heating indicating a larger contribution of a free radical mechanism in the microwave case.

Many reactions have been carried out in which the reagents are impregnated on to a solid (often a clay) catalyst and in this supported state are heated by microwave radiation[6k]. Examples of such "dry media" reactions include (*a*) dibenzylamine alkylation using Na-Y zeolite[55], (*b*) Michael additions of ethyl acetate to imidazole catalysed by alkali-exchanged montmorillonites[56], (*c*) oxidation of secondary and benzylic alcohols to the corresponding carbonyl compounds by *t*-butyl hydroperoxide in the presence of 3A molecular sieve[57], (*d*) the Knoevenagel condensation of carbonyl compounds with malononitrile on silica gel[58], (*e*) benzylation of sodium phenylsulfinate on sodalite and zeolite 13X (ref.[59]) and (*f*) a group of organic rearrangements, dehydrogenations and dehydrations carried out on Na-Y and Cu(II)-Y (ref.[60]). Again, meaningful comparisons with thermal reactions are rare. However, in case (*a*), higher yields at similar (nominal) temperatures and reaction times were obtained with microwave heating than with conventional heating. Once again the selective heating of polar active sites or the presence of other "hot spots" in the solid was suggested as a reasonable explanation of the results obtained. In (*f*), higher selectivity in the isomerisation of citronellal to cyclic alcohols was obtained with microwave heating (3 min, temperature unknown) than with conventional heating (30 h, 180 °C). In the dehydrogenation of tetralin on a Na-Y/CuO mixture, reaction was observed only in the case of microwave heating.

A particularly interesting situation arises with a fluid passing over a supported catalyst. In theory, differential heating through microwave dielectric loss could act on the fluid phase, on the solid support or on the supported catalyst itself. An example of this situation arises with the catalytic oxidation of ethylene over a platinum/alumina catalyst. This reaction has been studied using both microwave and conventional heating[61]. In this case, conversion rates for microwave and classical heating were equivalent where the microwave temperature was some 6–8 °C lower than the conventional. This difference was believed to be real but could also be explained by uncertainties in the measurement of the temperature of the solid. An example has recently been reported of an esterification reaction in a continuous flow reactor in which selective heating of the catalyst particles created hot spots, resulting in an increased reaction rate[7e]. The temperature of the active site was calculated to be 9–18 K above the bulk temperature. The nearest parallel involving zeolites appears to lie in cases where zeolites have been used to aid microwave pyrolysis. In the cracking of neopentane, an increased proportion of methane was found when microwave rather than conventional heating was employed[62], although once again there is uncertainty over temperature measurement. A nickel zeolite designated M-SR115-Ni (M = Al, Si) was reported to crack benzene to acetylene with around 90% selectivity under microwave irradiation, although no activity was

found with conventional heating[63]. A patent exists on the decarbonisation of cracking catalysts using microwaves[64].

9. CONCLUSIONS

9.1. Rate Effects

Some concluding assessment is necessary on the topic of microwave effects in microporous materials synthesis. If we accept the views (section 2.3) that (i) specific activation at a controlled temperature in homogeneous media is unlikely[6a] and (ii) a combination of rapid heating and up to 30 °C of superheating can provide reductions in reaction time of 10–50-fold based on purely conventional arguments[5c], then we may question whether any further explanations of experimental observations are necessary. It is also clear from the work described in earlier sections that there is considerable ambiguity in some published work because of uncertainties in reaction temperature (estimated, or not measured at all) and in the possible presence of temperature gradients (*e.g.* bulk *vs* surface). In several instances, earlier claims of specific effects in organic synthesis have, on further investigation, proved to be unjustified[6a,7]. In cases where there have been no kinetic measurements, the actual reaction times quoted may also be misleading. However, a major additional factor to be considered is that zeolite-type synthesis reactions are virtually never homogeneous. In addition to the true solution phase, macroscopic gel, colloidal material and/or crystals will be present[65]. Therefore the dielectric – the reaction mixture – is a heterogeneous medium.

A discussion of the mode of action of microwave heating in zeolite and zeotype synthesis has been given by several authors[17,28,34a,39,43b]. Jansen *et al.*[17] attribute the rapid crystallisation observed in the microwave experiment to the fast dissolution of the gel. This in turn was ascribed to the rotational dynamics of the water molecules under the influence of the microwave field. This is said to destroy far more hydrogen bridges of water molecules than conventional heating[66] resulting in so-called active water molecules[67] which have a higher potential to dissolve the gel because their lone pairs and OH groups are available to attack the gel bondings.

These ideas have been taken up by Girnus *et al.*[34a] who in addition suggest an influence of the microwave field on the condensation rate of Al–O–P bondings and simultaneous separation of water to give a special gel structure (a self-assembled organic–inorganic molecular microarray). Carmona *et al.*[39] go even further, suggesting a microwave activation to change the coordination of aluminium in the gel from octahedral to tetrahedral to yield the specific Al(O)/Al(T) ratio in the gel precursor necessary to direct the crystallisation of VPI-5. The mechanism for this is that the coupling of the microwaves with the hydration shell water is more effective than that to the free water, thus weakening the cation–water bonding besides yielding a higher heating efficiency.

It is difficult to assess the significance of the arguments given above. At present, there seems to be little supporting evidence to substantiate an intrinsically higher nucleophilicity for water under microwave conditions. The microwave photon is not sufficiently energetic to break even hydrogen bonds and the frequently propounded idea that microwaves rotate dipolar groups is misleading[7c]. Given the uncertainties in some of the experimental data and the caveats expressed earlier (section 2.3), it is perhaps better to look initially for simpler and more conventional explanations.

Other authors have attempted to clarify the reasons for the reduced timescale in zeolite synthesis under microwave conditions by analysing the separate contributions of various factors to the overall reaction time[28], namely (i) thermal lag, (ii) the induction period before crystalline product is detected and (iii) crystal growth. Thermal lag is always present in conventional syntheses although its extent will depend on equipment design. The effect will be greatest for large metal autoclaves heated externally and can be difficult to estimate if there is no internal measurement of temperature. Such heating-up time is essentially eliminated in microwave experiments, where the rise to operating temperature of the reactor contents is extremely rapid (usually ≤ 3 min).

Leaving aside all consideration of crystal growth at this stage, the induction period is itself made up of two components: (i) digestion and equilibration of the reactants and (ii) the crystal nucleation period. From the experimental evidence[17,24,28], it seems very likely that the reagent digestion steps are much faster in microwave than in thermal heating. Studies on the microwave crystallisation of zeolite A (ref.[24]) and ZSM-5 (ref.[28]) have shown that there is a nucleation-related bottleneck in such syntheses. Allowing for an accelerated equilibration stage, there is always a relatively long period in an "unseeded" synthesis before crystals appear. This time can be reduced by appropriate ageing of the reaction mixture, adding a portion of an aged mixture or including seed crystals. These procedures provide crystal nuclei, proto-nuclei or crystal surfaces which remove the need for the reaction mixture to self-nucleate. However, an additional effect can be seen from Fig. 3 (ref.[28]). If curves *4*, *2* and *3*, *1* are compared, it can be seen that although the induction period is considerably reduced when nanometre-sized seed crystals are added to a conventionally heated synthesis mixture, the induction period is essentially *eliminated* when microwave heating is employed.

The third factor to be considered is the effect upon synthesis time of different patterns of crystal nucleation and growth. Quite different results may be observed when reaction conditions (other than composition and temperature) are varied[68]. The growth time for a final crystal size of ≤ 1 μm (Fig. 3, curves *1* and *2*) will clearly be less than for a product where the largest crystals are an order of magnitude larger (curves *3* and *4*). There may also be an additional effect due to differences in crystal linear growth rate under the reaction conditions.

In summary, the reduction in overall reaction rate between comparable thermal and microwave zeolite syntheses can be attributed to differences in the thermal lag of the

system, the observed induction period and the pattern of crystal nucleation and growth. Several of these differences have entirely straightforward causes but the following observations in the microwave-mediated reactions cannot immediately be explained: (i) the apparent rapidity of the reactant equilibration steps and (ii) the virtually instantaneous activation of the nanocrystal seed. The most probable causes lie in differential microwave heating effects due to the heterogeneity of the dielectric (*i.e.* the reaction mixture) which at all times contains colloidal or particulate material. Local superheating could result from a number of energy-loss mechanisms[5a]: (i) dipolar polarisation losses varying with local composition, (ii) interfacial (Maxwell–Wagner) polarisation losses and (iii) conduction losses associated with clusters or arrays of ions. If such mechanisms for localised heating contribute to an acceleration of gel digestion and equilibration steps, an even more significant effect may be occurring at crystal surfaces. Microwave energisation of the hydroxylated surface or of associated water molecules in the boundary layer may be linked to specific energy dissipation through modes (ii) and (iii) above. This could account for the rapid activation of seed crystals under microwave conditions seen in curve *1* of Fig. 3.

In a study of the synthesis of the octahedral molecular sieve OMS-1, there are some interesting observations which counter the perception that microwave heating invariably increases overall reaction rate[43b]. Reduction of permanganate was complete when conventional heating was used but did not proceed to completion under microwave conditions, even after heating ten times longer than in the thermal preparation at the same temperature. It was also found that the large differences in crystallisation rate between microwave and conventional heating reported for other microporous materials were not so pronounced with the manganese oxide materials under study. This was attributed to the fact that these materials are themselves very good absorbers of microwave energy, so that less microwave power was required to maintain temperature and the water itself was receiving a relatively small fraction of the total power input.

9.2. Selectivity

In section 2.4., it was suggested that there are at least two mechanisms by which selectivity in zeolite synthesis might reasonably be brought about through the agency of microwave heating. Following the demonstration of the effect of high heating rates in naphthalene sulfonation by Stuerga *et al.*[9], it might be expected that zeolite synthesis, where products are usually under kinetic control, would furnish additional examples. It has been found that, in the microwave synthesis of zeolite Y, crystallisation of undesired phases is suppressed[18] and phase selectivity can be maintained at an unusually high synthesis temperature[19] (150 °C). This selectivity is attributable, at least in part, to the effect observed by Stuerga and colleagues since the rival rates of nucleation and growth of competing phases Y and P under different conditions of mixing and heating have been known for many years[69]. In this case, microwave heating allows the phase

purity of the zeolite Y product to be maintained even under conditions (150 °C) where zeolite P would normally dominate in a thermal synthesis. Figure 4 shows the XRD patterns for (unseeded) zeolite Y synthesis at 150 °C (refs[19,21]). Under microwave heating (Fig. 4a), pure zeolite Y is formed in 20 min and is stable under the reaction conditions for a total of 120 min. With the same reaction mixture and conventional heating (Fig. 4b), only 10% conversion to zeolite Y is observed in the first 45 min, the rest of the material being amorphous. After 90 min, amorphous material, zeolite Y and zeolite P coexist, showing that the crystallisation of Na-Y does not reach completion before the P-type impurity nucleates. After 180 min of conventional heating, Na-Y has completely disappeared leaving a tetragonal P-type zeolite with an XRD pattern resembling that of gobbinsite.

The second potential mechanism for selectivity does not yet appear to have been observed in the synthesis of microporous materials themselves, unless a negative example is considered. The differential heating effects possible in a non-homogeneous medium could conceivably encourage the formation of one phase rather than another. In a case discussed earlier (section 3.3.5), zeolite formation was suppressed because of the immobilisation of key reagents through differential heating[27]. Positive examples of the effect exist in the microwave activation of catalytic reactions (section 8) and it is possible that the cryptomelane/bixbyite system[43c] may prove to be the first demonstration in zeolite-type synthesis.

10. OUTLOOK

There is no doubt that the technique of microwave dielectric heating is becoming of increasing importance in chemical synthesis and that it is of great utility in the field of zeolite synthesis and modification. The most apparent advantages are those of the rapid
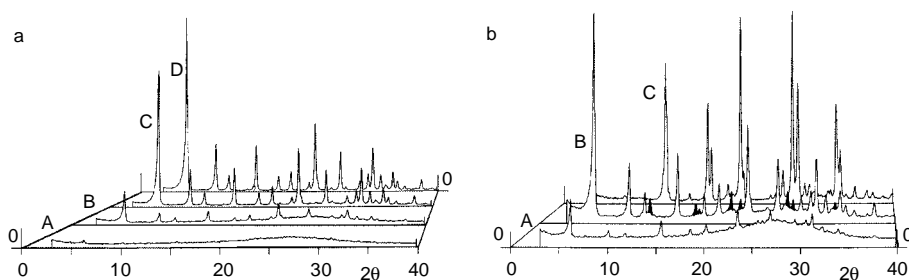

FIG. 4

XRD patterns of the products synthesised at 150 °C from the (unseeded) reaction composition 6.2 Na_2O–1.0 Al_2O_3–10 SiO_2–240 H_2O: a microwave heating (A 5 min, B 10 min, C 15 min, D 20 min) to give pure Na-Y; b conventional heating (A 45 min, B 90 min, C 180 min) to give (finally) zeolite P

heating rate to the working temperature and the significant shortening of reaction time which is found in virtually every case. Conventional thermal methods are not displaced by microwave techniques and may in some instances be preferable. However, microwave synthesis does offer a high probability of rapid (and in some cases selective) reaction to give a pure product of good crystal quality.

If we wish to obtain further advantages from microwave-mediated synthesis, the key parameter is "microwave selectivity". For some useful difference from conventional heating, a system needs some component to be selectively sensitive to microwave energy input or at least to heating rate. Key factors are the relative values of reaction activation parameters, polarity and dielectric properties of reaction components, the nature of interfaces (particularly solid surfaces) and the presence of ions or conducting particles.

Finally it should be noted that there is much work to be done in assessing the dielectric properties of potential reaction components and products in microwave synthesis. However, it should be remembered that the earliest work on zeolites in a microwave heating environment was exactly along these lines[12–14] (section 3). Dielectric measurements on zeolites themselves continue[70] and have been used to follow the progress of zeolite crystallisation[71]. A study on the microwave heating of a series of zeolites concluded that strong absorption of microwave energy is associated with the presence of cations in large cavities[72]. Highly dispersed and reduced cobalt metal atom clusters have been produced in zeolites X and Y by subjecting them to plasmas generated via a microwave discharge[73] whilst a similar method has been used to produce zeolite-supported, gold-based metallic catalysts[74]. In a separate development, rapid syntheses of sodalite and zeolites A, X and Y have been achieved using induction heating[75]: in this case, an alternating magnetic field is used to generate heat within the sample via mobile ions which provide an induced current.

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