Remarkable synergy between microwave heating and the addition of seed crystals in zeolite synthesis—a suggestion verified

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A recent suggestion that there can be a nucleation-related bottleneck in microwave zeolite synthesis has been verified: ZSM-5 has been synthesised very rapidly in seeded systems with and without an organic template.

Microwave dielectric heating is becoming an increasingly important accessory in chemical synthesis.[1–3] Remarkable reductions in synthesis time (by up to a factor of 10^3)[4] are observed and selectivity to particular product isomers has been achieved in naphthalene sulfonation.[5] Following an early study,[6] the microwave-mediated synthesis of micro- and mesoporous materials has been the subject of a number of recent reports, with zeolites,[7,8] $AlPO_4$-type materials[9,10] and MCM-41[11] being successfully prepared. In the microwave synthesis of zeolite Y, crystallisation of undesired phases is suppressed[7] and phase selectivity can be maintained at an unusually high synthesis temperature (150 °C).[12]

The crystallisation of zeotype materials is frequently constrained by limitations at the nucleation stage so that it is common practice to age reaction mixtures or add nucleants to them.[13] There are two potential effects of these procedures on the synthesis reaction: (*a*) reduction of the induction period preceding the detection of crystalline product and (*b*) promotion of a dominant crystalline phase (usually that of the seeding material). Thus, overall synthesis time can be shortened and product purity improved. Different aspects of these two effects have been demonstrated in recent studies on the synthesis of zeolite A with conventional[14] and microwave[8] heating. In one report,[8] microwave heating of zeolite A reaction mixtures which had been aged for various periods led to reaction times as short as 1 min and it was suggested that the rearrangement of the synthesis mixture to yield nuclei was the bottleneck in a microwave synthesis. We demonstrate below using a different zeolite system as a model that this is indeed the case and furthermore that the effects achievable by microwave heating and seeding techniques are strongly synergistic.

The synthesis of zeolite ZSM-5 has been studied using two optimised reaction systems.‡ In the first case, Na, TPA-ZSM-5 was synthesised using the composition:[12] $5.0\ Na_2O : 0.2\ Al_2O_3 : 60\ SiO_2 : 4.0\ TPABr : 900\ H_2O$ where the silica source was a silica sol, the alumina source was sodium aluminate and TPA is the templating cation tetrapropylammonium. The second system used similar reagents but contained no organic template:[15] $10.0\ Na_2O : 1.0\ Al_2O_3 : 60\ SiO_2 : 3000\ H_2O$.

In each case, reactions were carried out in the presence and absence of seed material and using both microwave and traditional heating methods. The seed employed (5% by mass of total silica) was a fully characterised TPA-silicalite (Al-free ZSM-5) sol[16,17] consisting of near-monodisperse nanometre-sized crystalline zeolite particles in water. Reaction temperature was 175 °C throughout and times were recorded from the start of the heating period.

The results are illustrated in Fig. 1. In the unseeded TPA-templated thermal preparation [curve (*e*)], crystalline MFI product was detected (XRD) after 2 h and the synthesis was complete at 5.5 h. Carrying out the reaction at the same indicated temperature using microwave heating reduced the synthesis time to 3 h following the appearance of crystallinity at t = 1 h [curve (*d*)]. The crystallisation of the oven-heated mixture was considerably accelerated by the presence of the nanosized seed material with 15% crystallinity apparent after only 1 h and completion in 2 h [curve (*c*)]. However, the combined effect of nanocrystal seeding and microwave heating produced the remarkable result seen in curve (*a*) where crystallisation was almost complete by the time that the reaction mixture had reached working temperature (3 min).

With no organic template and in the absence of seed crystals, no crystalline product was found after 3 h of microwave heating, whilst only a trace of product was detectable by X-ray diffraction after 7 h of oven heating. The inclusion of colloidal seed material brought reaction rates within the time frame of Fig. 1, although the thermal reaction was the slowest recorded overall [curve (*f*)]. However, the corresponding microwave-mediated synthesis [curve (*b*)] was only a little slower than its templated counterpart [curve (*a*)].

These results may be rationalised by consideration of three factors contributing to the overall reaction time, namely (1) thermal lag, (2) the induction period and (3) crystal growth. The first of these probably accounts for about 0.5 h in the experiments with the oven-heated autoclaves (as determined by separate tests). This is essentially eliminated in the microwave experiments, where the rise to operating temperature of the reactor contents is extremely rapid ($\leqslant$3 min). It is clear from Fig. 1 that, although the induction period is reduced by the presence of the nanocrystal seed, a notable synergism occurs when microwave heating is additionally employed. Possible reasons for this are discussed in more detail below. The third factor allows for a reaction time adjustment which depends on the pattern of nucleation and crystal growth. The unseeded TPABr-containing compositions produce products of broader particle size range (up to *ca.* 5 μm thermal, 12 μm microwave) than the seeded preparations ($\leqslant$1 μm), necessitating a longer period of crystal growth for the largest crystals to reach their final size. There are also differences in linear growth rate (templated synthesis > inorganic and microwave > thermal). A more detailed study of crystal growth rates[18] will be reported elsewhere.

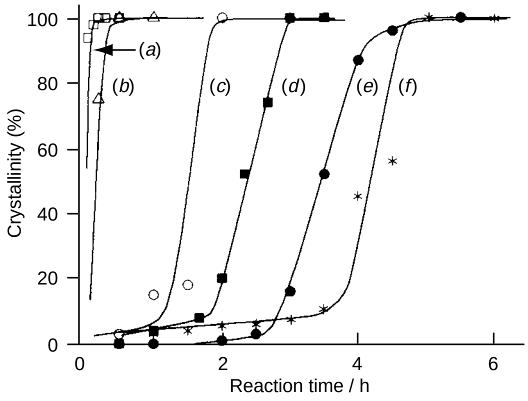

Fig. 1 Growth curves for ZSM-5: (*a*) seeded, TPA, microwave; (*b*) seeded, inorganic, microwave; (*c*) seeded, TPA, thermal; (*d*) unseeded, TPA, microwave; (*e*) unseeded, TPA, thermal; (*f*) seeded, inorganic, thermal

The results above confirm the suggested[8] nucleation-related bottleneck. However, it is useful to make a distinction between the equilibration of the reaction mixture (as evidenced by, for example, changes in pH and silicate anion distribution) and the generation of nuclei, since it can be shown that these are separate, although interlinked, processes.[19] In both the zeolite A and the ZSM-5 cases (but perhaps not universally), the microwave heating rate far outstrips the crystal nucleation rate so that no zeolite product is formed at short heating times in the absence of added seed crystals or sources of nuclei. However, in the earlier work,[8] it was also proposed that the almost instantaneous heat-up allowed the reaction to take place in a synthesis mixture that had hardly changed during the heating process. The very rapid onset of crystal growth which occurs under microwave heating conditions in the presence of added nanocrystalline seed [*e.g.* curve (*a*) *vs.* curve (*d*)] confirms that it is the time to form nuclei rather than the preceding equilibration of the reaction mixture which is the slowest step. However, such rapid and complete crystallisation could not occur unless any slow reagent digestion steps were complete. Hence, the reaction mixture has to be regarded as essentially fully equilibrated rather than hardly changed.

Finally, we consider the differences apparent from Fig. 1 between comparable microwave and thermal reactions. Since both thermal and microwave syntheses are carried out under conditions of controlled and measured temperature, a significant overall temperature difference due to microwave superheating[3] is unlikely. A more probable cause lies 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:[3] (*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. Thus, one component of the enhanced rates observed in the microwave syntheses may derive from an acceleration of reagent digestion and aluminosilicate equilibration processes to produce a medium which is more homogeneous on a molecular scale. However, perhaps an even more significant effect may be occurring at crystal surfaces where 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 curves (*a*) and (*b*) of Fig. 1.

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Notes and References

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‡ *Experimental details* for the zeolite syntheses: TPA-templated composition: sodium aluminate (0.49 g, BDH, 21.3 mass% Na, 20.8 mass% Al) dissolved in a solution of sodium hydroxide (1.80 g, Prolabo AR) in water (35 g) was added with stirring to a solution of tetrapropylammonium bromide (5.03 g, ABM Chemicals) in 42.5 g of Ludox AS 40 silica sol (40 mass% SiO_2, Dupont). To one half of this mixture was added water (7.5 g) and, to the other, an aqueous colloidal sol of TPA-silicalite (7.5 g, 5.8 mass% solids, mean particle size *ca.* 70 nm). Reaction mixture aliquots were heated in PTFE-lined autoclaves at 175 °C either in a conventional oven or in a CEM MDS-2100 microwave reactor (2.45 GHz).

Inorganic composition: aluminium nitrate nonahydrate (12.75 g, Merck AR) dissolved in water (100 g) was added to a vigorously stirred solution of sodium hydroxide (17.65 g, Prolabo AR) in water (150 g). The resulting clear solution was added to a mixture of Syton X 30 silica sol (203.8 g, 30 mass% SiO_2, Monsanto) and water (456 g). Further water or silicalite sol was added as above to give a seed concentration of 5% by mass (based on total silica) and the comparative syntheses carried out as before.

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