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Modifying zeolite particle morphology and size using water/oil/surfactant mixtures as confined domains for zeolite growth†

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Here we report the synthesis of silicalite-1 particles using microemulsions wherein the particle size and morphology can be varied.

Precise control over particle size and morphology is emerging as a critical issue in the design of nanostructured materials. The explosive growth of nanoparticle synthesis is a good example of this.[1–4] While numerous advances have been made in nanoparticle synthesis these have been generally restricted to materials possessing relatively simple structures (fcc, bcc, hcp) with small unit cells. By contrast there is much less work demonstrating such morphological control over more complex materials such as zeolites. Recent work by Lai and coworkers has shown that one possible approach to this end is to use different structure directing agents to influence crystal growth.[5] Another approach is to use microemulsions as confined spaces or "nanoreactors" for material growth, as has been shown extensively to be successful for the synthesis of structurally simple nanoparticles.[6] In this vein Dutta and colleagues have studied the nucleation of the zincophosphate analogue of FAU in microemulsions, though controlling morphology was not the goal of their studies.[7,8] Yates and colleagues have recently employed microemulsions for the synthesis of $ALPO_4$-5 fibrils.[9,10] Manna *et al.* reported work on MFI syntheses in AOT emulsions in the presence of fluoride.[11] However, no work to date on microporous silicates has shown that different morphologies and particle sizes can be obtained based on emulsion composition. This is what we report here, namely that we can make particles of silicalite-1 with different morphologies (spheres and plates) based on the emulsion composition, and that also we can change the size of the spherical particles based on the emulsion composition. In all cases the particles are different from what one obtains from the corresponding synthesis *without* the microemulsion. Also given the low synthesis temperatures (below 373 K) we have determined the phase behavior of our mixtures at the actual synthesis conditions. Our work demonstrates that different emulsion microstructures can be used to change the morphology and size of the silicalite-1 particles, suggesting this to be a versatile and useful approach for fabricating complex crystalline solids that possess unique morphological properties.

The water/oil/surfactant system chosen was heptane/water/IGEPAL CO-520 and CO–720/butanol. IGEPAL are commercially available polyoxyethylene(x)nonylphenyl ethers with mean ethoxylation degrees of 5 (CO-520) and 12 (CO-720). Phase diagrams for the heptane/water/IGEPAL/butanol systems were determined over the temperature range of 298–368 K; by visual inspection. The phase diagram where the water was replaced by an equivalent amount of silicalite-1 synthesis mixture (by weight) was also determined (ESI†). The silicalite-1 mixture has a molar composition of 1 TEOS : 0.36 TPAOH : 20 H_20. The IGEPAL : butanol weight ratio was fixed at 1 : 1 or 2 : 1. Synthesis mixtures were prepared as follows: fixed amounts of heptane, surfactant, and butanol were mixed together at room temperature. The corresponding amounts of TPAOH, deionized water, and TEOS were then added sequentially. The mixtures were vigorously shaken for five minutes, at which point they were placed in an oven at the desired temperature and allow to react under quiescent conditions for a given period of time. Samples were collected by filtration, washed with copious quantities of ethanol, acetone, and water and then air-dried. All samples reported are silicalite-1 by powder X-ray diffraction (ESI†).

Fig. 1 shows Field Emission SEM images of samples made in two-phase microemulsions at 368 K. The two-phase mixture has a composition (by weight) of heptane : CO-520 + butanol : silicalite-1 mixture of 0.577 : 0.337 : 0.086 with a surfactant : butanol weight ratio of 1 : 1 at 368 K for 120 hours. As can be seen the particles are large platelets. This is contrast to a synthesis without the emulsion, (*i.e.* 1 TEOS : 0.36 TPAOH : 20 H_2O at 368 K) which leads to spherical/ellipsoidal particles between 100–300 nm in diameter.[12,13] High magnification FE-SEM images of this sample (Fig. 1, bottom) show the individual plates are formed by smaller zeolite particles (< 500 nm). We hypothesize these materials form at the oil/water interface, which essentially acts as a site for the particles to aggregate and coalesce. The instability of zeolite particles in this mixture as compared to clear solution syntheses of similar composition is likely a result of some of the TPAOH partitioning into the oil rich phase, though we have no direct evidence for this. Current work is focusing on growing plates where the zeolite crystal domains are much larger, ideally making plates that are single crystals. As such, current work is studying syntheses where nucleation is suppressed as compared to growth.

We can also grow spherical particles of silicalite-1 at a synthesis temperature of 353 K; these are shown in Fig. 2. We also observe that the particle size depends on the emulsion composition for a given zeolite synthesis stoichiometry. For the heptane : CO-520 + butanol : silicalite-1 mixture system the particle size changes from approximately 1.5 μm (0.185 : 0.649 : 0.166) to a mixture of small (1.5 μm) and larger (4 μm) particles (0.167 : 0.460 : 0.373) to only

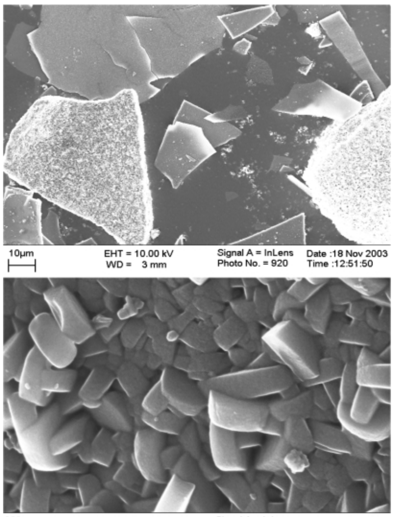

Fig. 1 Low (top) and high (bottom) magnification FE-SEMs of as-synthesized silicalite-1 samples made in two-phase water/oil/surfactant mixtures. Scale bars are 10 μm (top) and 200 nm (bottom).

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† Electronic supplementary information (ESI) available: XRD patterns of samples in Fig. 1 and 2, phase diagram of synthesis mixture at 353 K, FE-SEM images of fused spheres. See http://www.rsc.org/suppdata/cc/b3/b315646j/

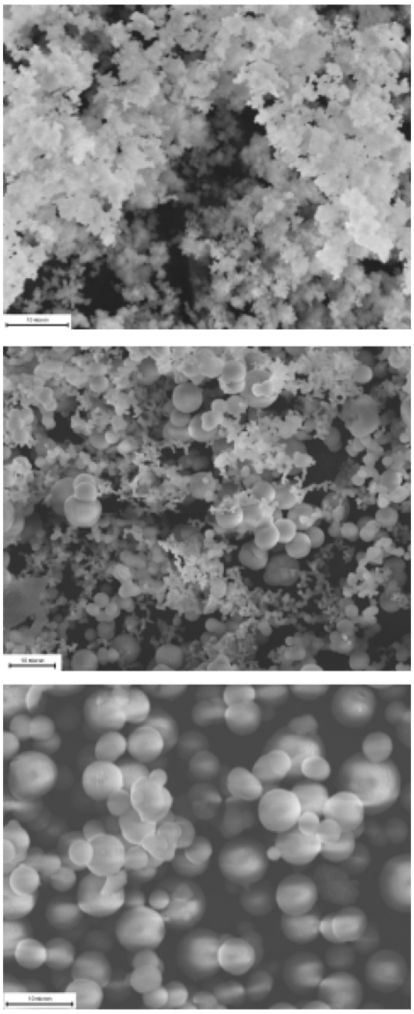

Fig. 2 SEM images of silicalite-1 spheres synthesized at 353 K, compositions given in text. Scale bar is 10 μm for all images.

larger particles (0.162 : 0.405 : 0.433) (Points A, B, C on the phase diagram in the ESI). DLS measurements verify the particle size distributions and are consistent with the SEM results. After calcination, these samples possess micropore volumes (0.11 cm^3 g^{-1}) in line with the expected value for silicalite-1. It can be clearly seen from the SEM images that a systematic increase in the particle size is observed as the surfactant content is decreased yet in all cases a spherical morphology is obtained. Moreover by XRD all materials are silicalite-1 yet the crystallinity is observed to improve as the "aqueous" fraction increases and the surfactant fraction decreases. We also notice some particles which appear fused (ESI). This would be consistent with either coalescence of individual particles due water droplet exchange, or the result of a highly interconnected water network as the water content increases. Two of the mixtures (B and C) are near the one phase/two boundary; B is on the one phase side and C is on the two phase side. However, platelets are not made in any of these cases. Mixtures B and C are near the phase boundary, however the mixture used to make platelets is well inside the two-phase region. We show these samples to illustrate this as a possible route to tuning the size of the particles while retaining morphological control and to illustrate the complexities of this "pseudo tertiary" system. Although it seems reasonable to hypothesize that increasing the water content of the emulsions (*e.g.* large water droplets) is the reason for an increase in particle size, we have no corroborating evidence for this. We are currently attempting to develop a more fundamental description of what controls the formation of plates *versus* spheres.

All samples above are in contrast to the particle sizes obtained from clear solution syntheses of silicalite-1 made using the same reaction mixture *without the oil and surfactant* (*i.e.* 1 TEOS : 0.36 TPAOH : 20 H_2O) at temperatures between 353–368 K, which are ellipsoidal particles between 100–300 nm in size.[12,13] As the synthesis temperature decreases the particle size generally does as well.[12] The SEM images are strong evidence that the synthesis of zeolite silicalite-1 in the presence of the microemulsion leads to different particle morphologies and sizes than that obtained from a normal clear solution synthesis.

In summary here we demonstrate the ability to synthesize samples of silicalite-1 wherein the particle morphology is dramatically different from what is obtained from the corresponding clear solutions. We also have the ability to tune particle size while simultaneously controlling morphology. We are currently developing a fundamental explanation to rationalize and understand our results using small-angle scattering and electron microscopy. We are also exploring means to improve the quality of the platelets (*i.e.* growing "single-crystal" plates with controlled crystal growth). Demonstrating the latter point would have profound implications for the zeolite science community and the application of zeolites in emerging technologies such as microdevices, sensors, and seeds for thin film formation.

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