In situ observation of the growth of silicalite nuclei by small-angle X-ray and neutron scattering

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Small-angle X-ray and neutron scattering provide evidence for the formation and growth of crystal nuclei from a clear homogeneous solution in the synthesis of silicalite using tetrapropylammonium (TPA) ions as the structure directing agent.

It has been the goal of our work for some time to identify the first steps in the template-induced structuring process in zeolite synthesis using scattering methods.[1,2] Our approach has been to find gel systems and, most recently, clear sol systems from which the scattering is so simple that a quantitative interpretation of the scattering can be given in terms of either of the classical mechanisms[3] of liquid-phase ion transport or solid hydrogel transformation. We report on the tetrapropylammonium (TPA) ion templated synthesis of silicalite from a totally clear non-gelling solution. *In situ* small-angle X-ray scattering from this system has been studied as a function of time after heating to 100 °C. At this temperature, heating for 36 h produces crystalline silicalite as the only product. This has been confirmed by high-angle diffraction. Small-angle X-ray scattering (SAXS) on the solution before crystallisation allows the time evolution of the scattering species to be followed. Small-angle neutron scattering (SANS) as a function of D_2O–H_2O contrast[4] is then used to show that the scattering species are indeed templated.

The synthesis mixture was a 'water white' solution with a silicon : TPA ratio of 8.3 : 1. It was prepared by stirring a TPABr (Aldrich) solution into a sodium silicate solution (E-Brand, PQ Corporation) to give a clear homogeneous solution with the following molar composition 1.0 SiO_2 : 0.297 Na_2O : 0.12 TPABr : 120.0 H_2O.

For the SAXS experiments, aliquots of a freshly mixed solution were sealed in a 1.0 mm capillary and placed in the precisely controllable high-temperature stage on our small-angle camera which was set at 100.0 ± 0.2 °C.

We have been able to perform *in situ* measurements of the scattering function as the reaction proceeds. Since good scattering functions were able to be recorded for exposure times of 30 min, the early and later stage time developments of the scattering function could be studied with reasonable precision. Guinier plots were constructed by plotting the log of the intensity, I, *vs.* the square of the momentum transfer, Q ($=4\pi\sin\theta/\lambda$, where θ is the half scattering angle), for each run from which the radius of gyration, R_g, and scattering intensities $I(0)$, were determined from the slope and intercept of the curve, respectively.

To demonstrate inclusion of the template in the scattering particles and at the same time introduce the most rigorous control experiment (whereby only the degree of deuteriation of the template is changed in the mixture) we use isotopic substitution and small-angle neutron scattering. The intensity $I(Q)$ of the small-angle scattering from a solid particle depends on the difference in scattering length density ($\rho_m - \rho_s$) between the solid, ρ_m, and solvent, ρ_s, phases, as given by

$$I(Q) = k\,(\rho_m - \rho_s)^2 S(Q) \qquad (1)$$

By independently labelling the templated solid and solvent isotopically with hydrogen or deuterium, the scattering intensity as a function of solvent scattering length density can be measured. When the scattering length density of the fluid and solid components are matched ($\rho_m = \rho_s$), the scattering intensity will be nulled [$I(0) = 0$]. Hence the scattering length density of the particles can be determined. The scattering length densities for crystalline silicalite containing [$^1H_{28}$]TPA, [$^2H_{28}$]TPA and dense amorphous silica are given in ref. 1. In this study, which is very similar to previous experiments,[1,2] the scattering length density of the solvent was varied by changing the D_2O : H_2O ratio in the solution. Also, by using both hydrogenated ([$^1H_{28}$]TPA) and deuteriated ([$^2H_{28}$]TPA) template, the scattering length density of the 'particles' was varied. The solutions were heated for 5 h at 100 °C before being measured. This particular heating time was chosen so that the scattering from the samples was strong enough to enable reliable data to be gathered with sampling times between 4 and 5 h, yet still provide evidence for the incorporation of the template in the scattering species at the earliest possible stage of growth as observed by SAXS. A contrast variation series of SANS measurements for each template was made. The SANS patterns were measured on the small-angle diffractometer SAD at IPNS, Argonne National Laboratory.

For our SAXS experiments the scattering function was first measured over 30 min periods for 6 h to achieve short time intervals of observation. In a second experiment (to get better statistics after longer heating times) the data were taken in 2 h intervals up to a total time of 32 h. A water sample (1.0 mm capillary) was used in the analysis for background correction. Flux and transmission measurements were taken before and after the runs to provide absolute intensities. The parameters from a Guinier analysis for each run are summarised in Table 1.

Table 1 *In situ* SAXS study of the crystallisation of silicalite at 100 °C

t/h	R_g/Å	$I(0)$
0	—	—
0.5	22	5
1	34	22
1.5	44	54
2	47	72
2.5	53	75
3	57	89
4	62	129
6	69	166
8	75	197
10	75	198
12	79	209
14	81	216
16	82	215
18	81	203
20	85	195
22	85	184
26	85	167
32	84	112

The results for the two experiments showed excellent agreement, and therefore have been combined.

The SAXS pattern for the unheated silicalite solution showed little scattering above the water background. After heating for 30 min the radius of gyration (fitted over nearly the whole of the scattering function) was of the order of 22 Å (see Fig. 1). With continued heating the radius grew and the intensity of scattering increased to a maximum at 14 h (Table 1). From this point in time, there was a continual decrease in the scattering intensity and no change in the radius of gyration.

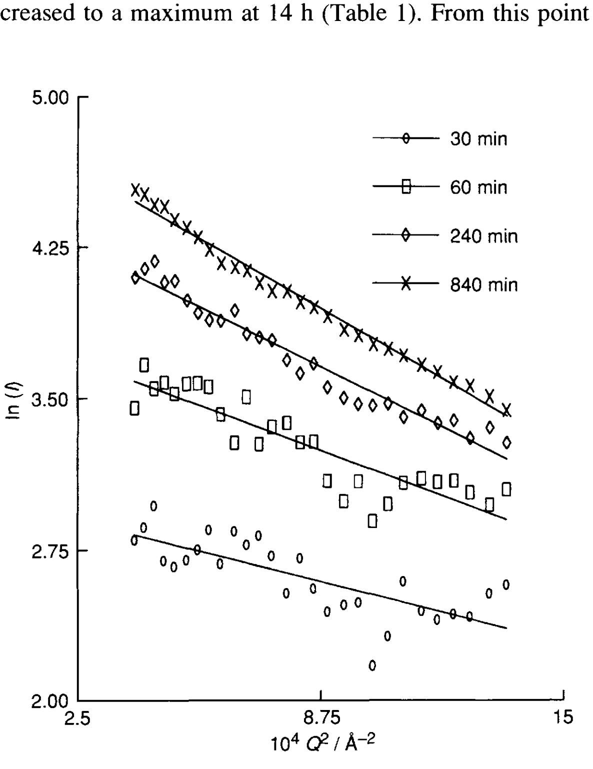

Fig. 1 Guinier plots illustrating an increase in the radius of gyration with heating time

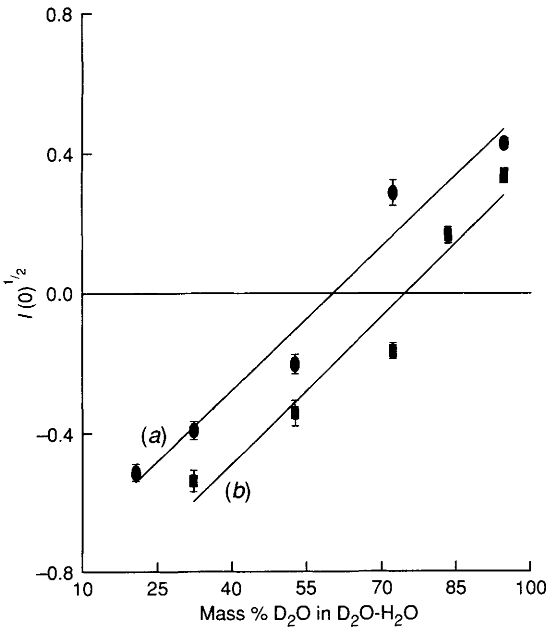

Fig. 2 Contrast variation plots of the SANS intensities for silicalite solutions heated for 5 h at 100 °C with (*a*) [$^1H_{28}$]TPA template and (*b*) [$^2H_{28}$]TPA template

Our small-angle neutron scattering study using hydrogen and deuterium contrast variation provides the means of detecting whether template has been incorporated into the scattering species, *e.g.* the R_g = 81 Å particles. Contrast variation plots for [$^1H_{28}$]TPA and [$^2H_{28}$]TPA are shown in Fig. 2. It is obvious from the two plots that the scattering from the silicalite solution is sensitive to the isotopic labelling of the TPA template. For [$^1H_{28}$]TPA and [$^2H_{28}$]TPA template the contrast null point occurs at 60 and 75 mass% D_2O–H_2O, respectively. These results compare very well with the predicted and experimental values for scattering length density equivalents of mass% D_2O–H_2O for zeolite materials given in ref. 1. This proves that the R_g = 81 Å 'particles' have a density which is nearly that of a fully densified silicalite particle containing the tetrapropylammonium template and in turn suggests that we are observing the nucleation process.

Further proof of the silicalite structure of these 'particles' is obtained using IR spectroscopy. The IR spectrum of a freeze-dried sample from a solution heated for 11 h at 100 °C (the solution remained clear and contained no sediment) shows a band at 560 cm^{-1} which is characteristic of the silicalite framework.[5] The X-ray diffraction pattern obtained from this sample is apparently amorphous indicating that the silicalite structures present are of the order of only a few unit cells. Consequently, as found elsewhere,[5] there is no high-angle diffraction pattern. In addition, SEM analysis reveals particles 500 nm in diameter in a solution that has been heated for 18 h.

These results are consistent with two possible models. The first interpretation is that particles of nucleated silicalite grow to a size of R_g = 81 ± 5 Å and that above this size they rapidly aggregate into larger secondary particles. The radii of these particles must be >250 Å as they are not detected by our SAXS camera whose minimum Q is about 0.01 $Å^{-1}$. The second interpretation would be that the 81 Å particles are not the nuclei from which macroscopic crystals grow, but instead, they redissolve [hence the decrease in $I(0)$] and act as a source of material for growth of other nuclei in the solution that are not distinguishable by SAXS.

Using small-angle X-ray and neutron scattering we have been able to directly monitor the transformations occurring during the induction period for the template induced growth of particles whose size is about 200 Å and whose composition is close to that of silicalite. These may be the nuclei for macroscopic silicalite crystals. Also we have found a way of measuring phenomena related to the early stages of growth of silicalite from a clear homogeneous preparation heated at 100 °C with no apparent gel phase. At present, we are investigating the temperature dependence of this early growth phase and its subsequent development to determine thermodynamic and kinetic parameters. This work and ageing phenomena without heating will be reported soon.

References

1 L. E. Iton, F. Trouw, T. O. Brun, J. E. Epperson, J. W. White and S. J. Henderson, *Langmuir*, 1992, **8**, 1045.
2 J. Dougherty, L. E. Iton and J. W. White, *Zeolites*, 1995, **15**, 640.
3 Z. Gabelica, J. B. Nagy, G. Debras and E. G. Derouane, in *Proceedings of the Sixth International Zeolite Conference*, ed. D. Olson and A. Bisio, Butterworths, Guildford, 1984.
4 G. E. Bacon, *Neutron Diffraction*, Oxford University Press, Melbourne, 1975, 3rd edn.
5 P. A. Jacobs, E. G. Derouane and J. Weitkamp, *J. Chem. Soc., Chem. Commun.*, 1981, 591.

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