Modelling of synchrotron SAXS patterns of silicalite-1 zeolite during crystallization†

Alexander Aerts,a Lana R. A. Follens,a Ellen Biermans,b Sara Bals,b Gustaaf Van Tendeloo,b Benoit Loppinet,c Christine E. A. Kirschhocka and Johan A. Martens*a

Received 24th August 2010, Accepted 14th December 2010
DOI: 10.1039/c0cp01592j

Synchrotron small angle X-ray scattering (SAXS) was used to characterize silicalite-1 zeolite crystallization from TEO/TPAOH/water clear sol. SAXS patterns were recorded over a broad range of length scales, enabling the simultaneous monitoring of nanoparticles and crystals occurring at various stages of the synthesis. A simple two-population model accurately described the patterns. Nanoparticles were modeled by polydisperse core–shell spheres and crystals by monodisperse oblate ellipsoids. These models were consistent with TEM images. The SAXS results, in conjunction with in situ light scattering, showed that nucleation of crystals occurred in a short period of time. Crystals were uniform in size and shape and became increasingly anisotropic during growth. In the presence of nanoparticles, crystal growth was fast. During crystal growth, the number of nanoparticles decreased gradually but their size was constant. These observations suggested that the nanoparticles were growth units in an aggregative crystal growth mechanism. Crystals grown in the presence of nanoparticles developed a faceted habit and intergrowths. In the final stages of growth, nanoparticles were depleted. Concurrently, the crystal growth rate decreased significantly.

1. Introduction

Small-angle X-ray scattering (SAXS) is a powerful method to monitor zeolite formation.1–7 The technique has been applied frequently to the synthesis of silicalite-1 zeolite (MFI topology) from a clear sol. This synthesis is one of the most important model systems to study the mechanism of zeolite crystallization. A clear sol is obtained by hydrolyzing tetraethylorthosilicate (TEOS) in aqueous tetrapropylammonium hydroxide (TPAOH) at room temperature. The as-prepared sol contains silica precursor nanoparticles measuring less than ~10 nm. Upon hydrothermal treatment or after prolonged aging at room temperature, silicalite-1 crystals nucleate and start growing to reach a final size of the order of 100 nm.

SAXS was used to determine nanoparticles size, shape and internal structure and to characterize their colloidal interactions in the clear sol.2,3,8–12 SAXS in parallel with small-angle neutron scattering (SANS) revealed that nanoparticles in as-prepared sols possess a silica-rich core/TPA-rich shell structure.9 Monodisperse oblate ellipsoids8 and polydisperse spheres9 have been proposed for the nanoparticle shape. The core–shell structure is maintained during induction and initial stage of crystal growth.2 During the induction stage, nanoparticles increase in size and decrease in number density.2,9

A distinction is made between concentrated clear sols, i.e. those with a molar water : TEOS ratio of ~10–15 and dilute ones, water : TEOS > 238.3 SAXS patterns of concentrated sols show a prominent correlation peak, indicating the presence of repulsive inter-nanoparticle interactions. In dilute systems, these interactions do not influence the scattering pattern. This facilitates modelling of SAXS patterns to determine the properties of the nanoparticles. Dilution leads to an increase of the nanoparticle size and condensation of the silicate framework.12

Crystal nucleation and early growth in dilute systems, aged at room temperature for several months, were investigated with SAXS in combination with cryogenic transmission electron microscopy (cryo-TEM).9 It was found that crystal growth is initiated by aggregation of a fraction of nanoparticles in the clear sol. Evidence for nanoparticle aggregation during

† Electronic supplementary information (ESI) available: Comparison of nanoparticle models for SAXS simulation. See DOI: 10.1039/c0cp01592j
the initial stages of the crystallization was also found in concentrated sols at room temperature\textsuperscript{13} and after hydrothermal treatment.\textsuperscript{14}

In dilute sols, only two particle populations are typically observed with SAXS during crystallization, viz. nanoparticles and crystals (or aggregates of nanoparticles that may evolve into crystals).\textsuperscript{15} In concentrated sols, on the other hand, an additional population of smaller interacting nanoparticles ($<3$ nm), termed primary units, is present,\textsuperscript{1} although not all authors adopt this three-population interpretation.\textsuperscript{16,17} The crystallization at hydrothermal conditions in concentrated sols has been monitored in great detail using synchrotron SAXS over an extended range of length scales by de Moor et al.\textsuperscript{1} However, quantitative analysis by modelling of the full SAXS patterns was not performed, probably due to complexities (three particle populations, combined with interparticle interactions) arising from the concentrated nature of these sols.

Previous quantitative SAXS studies primarily focused at characterization of as-prepared sols, containing nanoparticles only, and of sols during the early stages of crystal growth. As opposed to early crystals, which are aggregate-like, final crystals have a well-developed faceted habit. Based on this observation, it was suggested that crystals finally undergo Ostwald ripening and grow by addition of small silicate oligomers rather than nanoparticles. The evolution of nanoparticles in parallel with high yields of growing crystals in later stages of the crystallization has received much less attention, in part because the length scale accessible by laboratory SAXS instruments (typically less than $\sim 100$ nm) is not sufficient to resolve large crystals, especially in dilute sols, where crystals are known to grow to sizes well above 100 nm.\textsuperscript{18} For such sizes, the wide $q$-range provided by synchrotron SAXS instruments is required.

In the present work, silicalite-1 crystallization from dilute clear sol was studied by synchrotron SAXS and TEM. Full pattern modeling yielded quantitative structural information on the evolution of nanoparticles and crystals during the later stages of crystal growth. To complement the SAXS study, nucleation and initial crystal growth were monitored by \textit{in situ} dynamic and static light scattering (DLS and SLS).

2. Experimental

Sample synthesis: TEOS was hydrolyzed in 40 wt\% aqueous TPAOH at room temperature resulting in a clear solution with a molar TEOS : TPAOH : H$_2$O ratio of 25 : 9 : 152; 15 min after hydrolysis, water was added to a ratio of 25 : 9 : 1500. Clear sols were heated at 95 °C for times between 0 and 26 h before quenching to room temperature, yielding samples at various stages of the crystallization.

SAXS patterns were recorded at the ID02 beamline of the European Synchrotron radiation facility (ESRF). Samples heated for 0, 8, 10, 12, 14, 16, 20 and 26 h were measured in a quartz flow-through capillary (diameter 1.6 mm) at a sample-to-detector distance of 0.86 m and a wavelength of $\lambda = 9.18 \times 10^{-11}$ m. Samples heated for 8, 12, 16, 20 and 26 h were also measured at a distance of 7.01 m with $\lambda = 9.95 \times 10^{-11}$ m. Two-dimensional SAXS patterns were recorded with a Frelon Kodak CCD camera. Standard data treatment involved various detector corrections for flat field response, spatial distortion, and dark current of the CCD, and normalization by the incident flux, exposure time and the angular acceptance of the detector pixel elements. The 2D patterns were corrected based on sample transmission and the thickness of the capillary. The obtained intensities are absolute in units of cm$^{-1}$. Water was measured as a background, and subtracted from the sample patterns. The measured scattering of water in the region $1 < q < 4$ was $1.7 \times 10^{-2}$ cm$^{-1}$, in good agreement with the value reported by Orthaber \textit{et al.} (1.63 $\times 10^{-2}$ cm$^{-1}$).\textsuperscript{19} SAXS modelling was performed using the NIST SANS package for the Igor Pro software from Wavemetrics.\textsuperscript{20}

\textit{In situ} DLS was performed on a custom made setup at the FORTH institute in Heraklion, Greece. The setup consists of a temperature controlled copper sample holder with an opening through which a continuous wave, frequency doubled Nd-Yag laser having a wavelength of 532 nm passes the sample. The scattered intensity at 90° (corresponding to a wave vector magnitude $q = 0.022$ nm$^{-1}$) was collected and autocorrelated. Measurements between 2 and 10 h were carried out \textit{in situ} at 95 °C. The experimental autocorrelation functions were analyzed by inverse Laplace transformation using the CONTIN algorithm.

TEM images were obtained using a Philips CM20 microscope, after spreading liquid samples diluted with ethanol on a holey carbon copper grid.

3. Results

3.1 Small angle X-ray scattering

SAXS patterns at different heating times are shown in Fig. 1. The unheated sol only contained nanoparticles, revealed by an intensity decay above $q = 0.2$ nm$^{-1}$. After 8 h, the increase of scattering intensity at lower $q$ indicated that larger, secondary particles had formed. Simultaneously, Bragg reflections, characteristic for the MFI structure, emerged

![Fig. 1](https://example.com/f1.png)
around \( q = 6 \text{ nm}^{-1} \), proving that the secondary particles were MFI-type zeolite crystals (the enlarged Bragg region is provided as ESI†). Oscillations below \( q = 0.1 \text{ nm}^{-1} \) were attributed to form factor scattering of these crystals. The presence of oscillations indicated that the crystal size and shape were rather uniform.

The evolution of the patterns above \( q = 0.2 \text{ nm}^{-1} \) suggested that nanoparticles coexisted with crystals until 16 h of hydrothermal treatment. The simultaneous presence of nanoparticles and crystals was confirmed by TEM (see next section). Thereafter, nanoparticles were depleted. In the low-\( q \) region, the intensity increased strongly until 20 h, indicating crystal growth. After 20 h, the crystal growth rate decreased significantly.

The scattering of crystals exhibited a power law decay up to \( q \approx 0.6 \text{ nm}^{-1} \). This power law arises from Porod scattering of the crystal–solvent interface. The theoretical exponent for a perfectly smooth interface is \(-4\).\(^{21}\) The fitted exponent was equal to \( x = -3.8 \), corresponding to a surface fractal dimension \( D_s = 6 + x = 2.2\).\(^{21}\) This value indicates that the crystal surface is nearly smooth down to length scales of a few nanometres.

3.2 TEM

Fig. 2 shows TEM images of the sols heated 8 h and 16 h, spread on a TEM sample grid. The image of the 8 h sol showed silicalite-1 crystals embedded in a grainy matrix (Fig. 2a). A magnification of this image revealed that the grainy matrix consisted of agglomerated nanoparticles (Fig. 2b). This agglomeration probably occurred during the TEM sample preparation, because SANS revealed no significant interparticle interaction. On the basis of the TEM images, the nanoparticles were size-polydisperse with an average diameter of 6.0 ± 1.9 nm (ESI†). The crystals are easily identified by dark uniform contrast, appearing as disks with an average diameter of about 200 nm and a height of \( \sim 70 \) nm. In this morphology, the circular projection corresponds to the (010) crystallographic face of the MFI structure,\(^{22}\) which was confirmed by electron diffraction (Fig. 2c).

In the sol heated 16 h, the shape of the crystals stayed and have an average diameter of about 460 nm and a height of \( \sim 170 \) nm. The presence of agglomerated nanoparticles was much less pronounced or even absent near the crystals (Fig. 2d). The overall crystal morphology was invariable during heating. In the sol heated 16 h additional 90° intergrowths were observed (dark contrast areas on crystals, Fig. 2d), a characteristic morphological feature of silicalite-1.

3.3 Simulation of SAXS patterns

The qualitative analysis of SANS data and the TEM results allowed formulating a model for quantitative interpretation of the SANS patterns. The total intensity at different heating times \( t \) is \( I_{\text{total}}(q,t) \), where the scattering vector \( q = 4\pi \sin(\theta)/\lambda \), with \( \theta \) being the scattering angle. We assume that the total intensity is the sum of contributions by nanoparticles \( I_{np}(q,t) \), one of crystals \( I_{cr}(q,t) \) and a \( q \)-independent background \( B(t) \):

\[
I_{\text{total}}(q,t) = I_{np}(q,t) + I_{cr}(q,t) + B(t) \quad (1)
\]

In this model, it is assumed that nanoparticles and crystals do not interact, which implies that their relative positions in the sol are uncorrelated. Each intensity term is approximated by a scattering equation of the type:

\[
I(q,t) = N(t)V(t)\Delta \rho^2(t)P(q,t)S(q,t) \quad (2)
\]

where \( N \) is the number density, \( V \) is the particle volume, \( \Delta \rho \) is the contrast, and \( P \) and \( S \) are the form and structure factors, respectively. In the case of a polydisperse assembly, proper averaging of \( N \), \( V \) and \( P \) was performed.

Based on the TEM images of Fig. 2, the crystal population was described using the form factor \( P_{cr}(q) \) for monodisperse oblate ellipsoids of rotation, having a short polar (rotation) axis \( a \) and a long equatorial axis \( b \). Inter-crystal structure

![Fig. 2](image-url)
factor contributions were assumed negligible, i.e. \( S_{\text{c}}(q) = 1 \). At early heating times, this assumption is justified because the crystal concentration is low. For the large crystals present at later times, structure factor contributions, if present at all, can be expected to be unimportant in the measured \( q \) range.\(^{21}\)

For the nanoparticles, different models have been proposed in the literature. We tested several models and found the best agreement for size-polydisperse spherical cores composed of SiO\(_2\), surrounded by a TPAOH shell of constant thickness (see ESI†). The incorporation of a shell presented a significant improvement of the fits in the high \( q \) region, which is dominated by scattering at the nanoparticle–solvent interface. The core–shell structure is in accordance with observations by Fedeyko et al.\(^{8}\) The polydispersity of the silica cores was assumed to follow a narrow Schultz distribution, in agreement with TEM and previous reports.\(^{9}\) Schultz-type distributions are predicted by thermodynamic equilibrium theories for surfactant micelles.\(^{23}\) The origin of nanoparticle formation described as micelle self-assembly\(^{8}\) suggests that the Schultz distribution is indeed a physically relevant choice.

Monodisperse nanoparticles with a specific shape, such as oblate ellipsoids proposed by Fedeyko et al.,\(^{8}\) did not describe the data accurately. This was clear especially in the high \( q \) region where sharp oscillations expected for monodisperse ellipsoidal core–shell nanoparticles were not observed, despite the high resolution and low noise level of the synchrotron data (ESI†).

The scattering pattern of the unheated sol (0 h) showed a broad intensity maximum (Fig. 1), indicating a slight contribution of a structure factor \( S_{\text{np}}(q) \) caused by nanoparticle interactions. For the 0 h sample, this structure factor was accounted for with the Hayter–Penfold mean spherical approximation for repulsive electrostatic interactions. When nanoparticles and crystals are simultaneously present (sols heated 8 h or longer), accurate modelling of the structure factor contribution was not possible. In these systems, \( S_{\text{np}}(q) \) is assumed to be equal to 1. This approximation did not introduce large errors, because the structure factor contribution was already relatively small for the unheated sol and is not expected to increase in the course of crystallization when nanoparticles are depleted.

The contrast \( \Delta \rho \) in eqn (2) is equal to the difference of scattering length density (SLD) between nanoparticles or crystals, and solvent. In the present SAXS experiment, the scattering length density (SLD) between nanoparticles or crystals are depleted.

Table 1: Mass density \( \rho \) and scattering length density (SLD) used for the various components in the SAXS simulation

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical composition</th>
<th>( \rho / \text{g cm}^{-3} )</th>
<th>SLD ((\times 10^{-5} \text{ nm}^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>( \text{H}_2\text{O} )</td>
<td>1</td>
<td>9.4</td>
</tr>
<tr>
<td>Nanoparticle shell</td>
<td>TPAOH</td>
<td>0.87</td>
<td>8.2</td>
</tr>
<tr>
<td>Nanoparticle core</td>
<td>SiO(_2)</td>
<td>1.8</td>
<td>15.3</td>
</tr>
<tr>
<td>Crystal</td>
<td>TPA-MFI</td>
<td>2.05</td>
<td>17.7</td>
</tr>
</tbody>
</table>

\( q = 5 \text{ nm}^{-1} \) (Fig. 3a and S1 of the ESI†). The small intensity decay above \( q = 5 \text{ nm}^{-1} \) is probably caused by scattering of oligomeric silicate species. In the present work, this decay was taken as a part of the background. From 8 h onwards, crystals were observed (Fig. 3b–d). The oscillations of crystal scattering were described in detail by a uniform oblate ellipsoid shape, validating the model assumptions.

The excellent agreement of the two-population model with all experimental patterns proved that particles with sizes between nanoparticles and crystals were not present in significant amounts. For the crystallization mechanism this implies that no nucleation of new crystals occurred in the period 8–26 h.

### 3.4 Evolution of nanoparticles and crystals in the crystal growth stage

Nanoparticles in the 0 h sol had an average core diameter of \( \phi_{\text{np,core}} = 3.1 \pm 0.8 \text{ nm} \), where the error equals the standard deviation \( \sigma \) of the Schultz distribution. The shell thickness was 0.3 nm. Consequently, the average diameter of core and shell combined was 3.7 nm. This value was in good agreement with the hydrodynamic diameter determined with DLS (4.2 nm). The nanoparticle surface charge density, derived from the structure factor contribution, was \(-3.7 \mu \text{C cm}^{-2}\), which is a physically meaningful value for silica surfaces.\(^{26}\)

The most significant increase of the nanoparticle core size occurred during the first hours of heating (Fig. 4a), in accordance with previous reports.\(^{2,8}\) Between 8 and 16 h, i.e. during crystal growth, the nanoparticle core diameter was 5.4 nm on average. Core diameter, shell thickness and polydispersity reached a maximal value after 12–14 h. Until 14 h, the nanoparticle core volume fraction \( \phi_{\text{np,core}} \) was \( \text{ca.} \ 8 \times 10^{-3} \) (Fig. 4b). It is noteworthy that after 16 h the core volume fraction strongly decreased to \( 3 \times 10^{-3} \) while the core diameter remained around 5.0 nm. This evolution indicated consumption of entire nanoparticles in the crystal growth process rather than shrinkage or dissolution.

Sols heated 20 and 26 h contained a small amount (\( \phi_{\text{np,core}} = 5 \times 10^{-4} \)) of residual nanoparticles with a core diameter smaller than 1.5 nm. This reduced size suggested that these residual particles may consist of large silicate oligomers. However, estimates of nanoparticle size after 20 h are considered less accurate, because the scattering intensity in the relevant \( q \) range \((1–6 \text{ nm}^{-1})\) was only marginally larger than the background due to the small nanoparticle size and low volume fraction (Fig. 3).

The evolution of the oblate ellipsoidal diameters and volume fraction of crystals is shown in Fig. 5. The first crystals (after 8 h of heating) had a minor (polar) diameter \( d_{\text{cr,rad}} \) of
98 nm and a major (equatorial) diameter $d_{cr,b}$ of 188 nm (Fig. 5a). These dimensions and shape are in excellent agreement with the TEM observations (Fig. 2). The crystal volume fraction $f_{cr}$ in this early stage of crystallization was very low (Fig. 5b) as to be anticipated due to the large crystal size and the diluted conditions.

The ellipsoid diameters $d_{cr,a}$ and $d_{cr,b}$ both increased with heating time (Fig. 5a), but the growth rate along the long axis $b$ was larger (Fig. 5a). Consequently, the ellipsoid aspect ratio ($d_{cr,b}/d_{cr,a}$) increased monotonously with heating time (Fig. 5a). The linear crystal growth rate in both directions decreased after 20 h.

Until 20 h the crystal volume fraction increased at an almost constant rate of $2.6 \times 10^{-4}$ h$^{-1}$ (Fig. 5). From 20 h onwards, the rate decreased strongly to $0.5 \times 10^{-4}$ h$^{-1}$. This change of volumetric crystal growth rate coincided with decrease of the linear growth rate of the ellipsoidal axes, the aspect ratio, and was concurrent with the depletion of $\sim 5$ nm nanoparticles.

The number densities of nanoparticles $N_{np}$ and crystals $N_{cr}$ were calculated using the relation $N = \phi V$ (Fig. 6). For the nanoparticles, the core volume fraction $\phi_{np,core}$ and average core volume $V_{np,core}$ were used. The number density of nanoparticles $N_{np}$ was of the order of $10^{17}$ mL$^{-1}$ and that of the
crystals $N_{cr}$ is $10^{11}$ mL$^{-1}$ (Fig. 6). The number density of nanoparticles showed a pronounced decrease during the first hours of heating. This initial decrease was in agreement with previous observations. During the further course of the crystallization, the number of nanoparticles decreased at a slower, almost constant rate. Linear extrapolation of the data between 8 and 16 h suggested that the number of nanoparticles reached zero after 20 h. After 20–26 h the nanoparticle number density again increased. These data are not included in Fig. 6 because the size determination of these residual nanoparticles was probably inaccurate as discussed above.

The number density of the crystals was almost constant from 8 h onwards (Fig. 6). Again, this pointed out that nucleation was restricted to heating times before 8 h.

The distribution of Bragg crystalline domains inside crystals could be determined by comparison of the intensity of Bragg peaks with the volume fraction of ellipsoidal crystals. A linear scaling was observed (Fig. 7). Therefore, the crystalline domains were uniformly distributed, as opposed to a fractal arrangement. This observation, however, does not exclude the presence of fractal aggregates before 8 h. In the frame of crystal growth mechanisms involving addition of nanoparticles or crystal–crystal aggregation, a fractal distribution of crystalline domains should be expected in the case of diffusion limited aggregation.

### 3.5 Crystal nucleation

The evolution of crystal size during the nucleation stage (0–8 h) was monitored by in situ DLS and SLS (Fig. 8a). The use of in situ DLS and SLS, as pioneered by Schoeman, is restricted to nucleation and early growth because too large crystals cause multiple scattering and the sols have to be diluted prior to measurement.

The first particles resolved next to the nanoparticle population were observed between 3–4 h and had a hydrodynamic diameter of 20–30 nm. We further use the term “crystals” for these early particles, bearing in mind that initially they might not be fully crystalline. These crystals grew linearly with time and after 8 h, their hydrodynamic diameter was 134 nm. This hydrodynamic diameter was in agreement with the equivalent spherical diameter of 126 nm, calculated from the SAXS data and corrected for reduced diffusion of oblate ellipsoids compared to spheres.

The fraction of SLS intensity scattered by crystals increased according to a power law (Fig. 8b). The relative crystal number $N_{cr}$ during the first 8 h of heating was calculated from the hydrodynamic diameter and the SLS intensity according to the equation $N_{cr} \approx I_{SLS}(q)^{-1}d_h^{-6}$. Here, $P(q)$ is the crystal form factor at the $q$-value of the light scattering experiment, approximated by Guinier’s law. Fig. 9 shows the evolution of the crystal number, scaled to the value determined with SAXS after 8 h. The light scattering data revealed that the crystal number remains constant from 4–5 h onwards. Thus, nucleation of new crystals was confined to the short period between 3–5 h. Between 3–4 h, the number of crystals appeared to decrease, suggesting crystal–crystal aggregation could have occurred. However, the small crystal size combined

![Fig. 6](https://example.com/fig6.png)

Fig. 6 (circles) Nanoparticle number density after different heating times at 95 °C; (diamonds) crystal number density.

![Fig. 7](https://example.com/fig7.png)

Fig. 7 Intensity of Bragg reflections versus oblate ellipsoidal crystal volume fraction determined from the SAXS.

![Fig. 8](https://example.com/fig8.png)

Fig. 8 (a) DLS hydrodynamic crystal diameter and (b) SLS intensity scattered by crystals measured in situ during crystallization at 95 °C. The SLS data are plotted on a log–log plot to reveal the power law behaviour.

![Fig. 9](https://example.com/fig9.png)

Fig. 9 Crystal number density during the first 8 h of the crystallization derived from in situ DLS and SLS, scaled to the 8 h value derived from SAXS.
with the very low volume fraction may affect the reliability of
the extracted number densities.

4. Discussion

The core–shell structure of the nanoparticles is confirmed by
the SAXS analyses. The nanoparticle cores are best described
as polydisperse and spherical, although a non-spherical
particle shape cannot be fully excluded. Monodisperse, non-
spherical particles are not supported by the data. The shell
thickness increases during crystal growth, in agreement with
the blurring of the core/shell interface attributed to successive
incorporation of increasing amounts of a structure directing
agent (TPA) into the core.29 The resulting changes of the
nanoparticle core density may be the cause for observation of
the maximum in the volume fraction at 12 h (Fig. 4b). The core–shell structure and the particle size are maintained during
the period of fast crystal growth (until 20 h).

The nucleation of crystals is restricted to a surprisingly short
timespan, occurring predominantly between 3–5 h. Cryo-TEM
observations showed that the nucleation is probably due to
ggregation of nanoparticles.9 The first crystals observed with
DLS in the present work are composed of ~ 50 nanoparticles,
and the number of nanoparticles taking part in nucleus
formation is 1 in 105 at most.

An increase of the aspect ratio during crystal growth
was observed (Fig. 5a). Extrapolating this trend to earlier
crystallization times suggests that the nucleus shape on average is
less anisotropic. Therefore, anisotropy of the crystals grown in
dilute clear sol seems to develop predominantly during crystal
growth, rather than originating from a strongly anisotropic
nucleus.

In the presence of 5–6 nm nanoparticles, i.e. until 20 h, the
volumetric crystal growth rate is 5 times higher than in their
absence at later stages. This suggests an active role for the
nanoparticles during the crystal growth, also at crystal yields
larger than 5%. The nanoparticle size does not decrease
significantly during crystal growth, but their number decreases
at an almost constant rate. This supports crystal growth by
direct addition of nanoparticles to the crystal surface. Solution
mediated growth involving gradual dissolution of nanoparticles
to supply silicate oligomers for growth is less plausible in view
of the present data, although additional techniques such as
cryo-TEM are necessary to provide direct evidence.

The above considerations suggest that growth by addition
of nanoparticles is the dominant mechanism until 20 h,
supplying the major part of the crystal mass. Interestingly,
typical crystal features such as facets and intergrowths develop
during fast growth through nanoparticle addition. This might suggest that the attaching nanoparticles already are of
anisotropic nature themselves.

The crystals have a uniform non-fractal distribution of
crystalline domains, supporting the proposal that the aggregation
of nanoparticles is surface reaction limited.30

After depletion of 5–6 nm nanoparticles, crystals still grow,
although at a much-reduced rate. Growth by oligomers is
probably dominant in this stage. Oligomers in sols with
compositions comparable to the presently investigated system
are mostly the monomer and dimer.12 Most probably silicate monomer and dimer contribute to
crystal growth already during the period of fast growth.
Growth by oligomer addition, together with smoothing out
of the irregularities by Ostwald ripening, readily explains the
smooth surface of the crystals already at early stages.

5. Conclusions

Synchrotron SAXS was used to characterize the evolution of
nanoparticles and crystals during crystallization of silicalite-1
zeolite. Crystals in dilute clear sol nucleated from nanoparticles
in a short period of time. After nucleation, crystals showed a
period of fast growth depleting the population of 5–6 nm
nanoparticles, and accounting for the majority of crystal mass.
These events were followed by a period of slow growth in the
absence of nanoparticles. Nanoparticles maintained a silica-rich
core/TPA-rich shell structure throughout the crystallization.
The results suggested the occurrence of two competing crystal
growth mechanisms. During fast crystal growth, nanoparticle
aggregation to the crystal surface is the dominant mechanism.
Crystals at this stage already developed silicalite-1 type
morphology, showed intergrowths and became anisotropic.
Crystal growth by silicate oligomers becomes important when
the nanoparticles are depleted. This process was characterized
by a reduced growth rate. The present study demonstrates that
synchrotron SAXS applied to the relatively simple dilute clear
sol system provides a quantitative characterization of the
entire crystallization process. Therefore, the results are
encouraging to conduct an in situ synchrotron SAXS study of
this system in the future.

Acknowledgements

We acknowledge the European Synchrotron Radiation
Facility for provision of synchrotron radiation facilities and
we would like to thank Anuj Shukla and Emanuela di Cola for
assistance in using beamline ID02. We acknowledge Basavaraj
Madivala, currently at the University of Delaware, Chemical
Engineering, for assistance during the synchrotron X-ray
measurements. A.A. and S.B. are grateful to the Flemish
FWO for a post-doctoral scholarship. L.R.A.F., C.E.A.K.,
J.A.M. and S.B. acknowledge financial support by ESA and
the Belgian ProdeX office. The work was supported by the
Belgian government through the IAP-PAI network and by the
Flemish government through long term structural funding to
J.A.M. (Methusalem). S.B. and G.V.T. acknowledge financial
support from the European Union under the Framework 6
program under a contract for an Integrated Infrastructure
Initiative (Reference 026019 ESTEEM).

Notes and references

1 P. de Moor, T. Beelen, B. Komanschek, L. Beck, P. Wagner,
12762.
3 C. Cheng and D. Shantz, Curr. Opin. Colloid Interface Sci., 2005,
10, 188.
2008, 130, 17284.

This journal is © the Owner Societies 2011
27 B. Schoeman, Zeolites, 1997, 18, 97.