

Influence of aging and dilution on the crystallization of silicate-1

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Influence of Aging and Dilution on the Crystallization of Silicalite-1

PETER-PAUL E. A. DE MOOR, THEO P. M. BEELEN AND RUTGER A. VAN SANTEN

Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: ppaul@sg3.chem.tue.nl

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Abstract

The correlation between the formation of colloidal aggregates and the crystallization of silicalite-1 from a clear solution has been investigated with *in situ* combined small-angle X-ray scattering and wide-angle X-ray scattering, and *in situ* ultra-small-angle X-ray scattering using synchrotron radiation. Increasing the aging time at room temperature of the synthesis mixture prior to heating to the reaction temperature reduced the induction period and increased the crystal growth rate without affecting the formation of colloidal aggregates. Dilution of the synthesis mixtures did not influence the nucleation and crystal growth rate, and did not affect the formation of colloidal aggregates.

1. Introduction

Although a considerable amount of information is available describing numerous synthesis routes of zeolites (Barrer, 1982; Jacobs & Martens, 1987), mechanisms directing to a given crystalline structure are still poorly understood. In particular, events in the early stages of the synthesis are of critical importance in determining the course of the crystallization (Twomey, Mackay, Kuipers & Thompson, 1994). Even relatively slow processes taking place at room temperature prior to heating to the appropriate crystallization temperature are known to have a major influence on the induction period and crystallization rate, and even on the zeolite formed (Katovic, Subotic, Smith, Depotovic & Curic, 1989).

A question of considerable debate is the nature of the gel phase and its role in the nucleation and growth mechanisms. If there is a liquid-phase ion-transplantation mechanism (Gabelica, Nagy, Debras & Derouane, 1984), nucleation and crystal growth occur only in the liquid phase. The gel phase acts as a source of nutrients for the crystallization process (Iton, Trouw, Brun & Epperson, 1992). On the other hand, in the solid hydrogel reconstruction mechanism (Chang & Bell, 1991; Serrano, Uguina, Overjero, van Grieken & Camacho, 1996), nucleation and crystal growth occur in the heterogeneous gel or at the gel surface by a recon-

struction or aging mechanism and can be classified as a solid–solid transformation.

To study (trans)formation processes in synthesis gels on a colloidal scale, spectroscopic methods like nuclear magnetic resonance and infrared spectroscopy are not informative. Also, colloidal aggregates and gels are extremely vulnerable, so only *in situ* techniques can provide reliable information. In a previous paper (Dokter, van Garderen, Beelen, van Santen & Bras, 1995), we reported on the crystallization of silicalite-1 from a clear solution, and described a provisional mechanism in which the (trans)formations on a colloidal scale were correlated with the onset of crystallization. This mechanism includes two aggregation and two densification steps at a colloidal scale. In a later study (de Moor, Beelen & van Santen, 1996), a more complete set of data and a wider Q range probed with small-angle X-ray scattering persuaded us to another interpretation of the scattering patterns, involving only one aggregation step. So, although the synthesis mixture keeps its initial low viscosity and no percolating gel phase is formed at any stage during the reaction, amorphous colloidal aggregates with a size of up to 9 nm are formed in the clear solution prior to the onset of crystallization. Here, we report on ultra-small-angle X-ray scattering (USAXS) data that confirm this new interpretation.

To find a correlation between the effects on the processes on a colloidal scale and the crystallization behaviour, we studied the influence of aging at room temperature prior to heating to reaction temperature and the influence of dilution in the synthesis of silicalite-1 from a clear solution using *in situ* combined small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS).

2. Experimental

2.1. Silicalite-1 synthesis

The recipe used is based on a patent of Exxon Chemical (Exxon Chemical, 1993). The procedure described and the composition [0.434 Na₂O/1.22 (TPA)₂O/10 SiO₂/116 H₂O] is the same as used by Dokter, van

Garderen, Beelen, van Santen & Bras (1995) and we refer to this system as the 'standard system'.

1.40 g NaOH (Merck, p.a.) was dissolved in 100 g tetrapropylammonium hydroxide solution (Merck, 20 wt% solution in H₂O) with gentle mixing at room temperature, followed by spoonwise addition of 27.0 g silicic acid powder (Baker, 10.2 wt% H₂O). Thereafter, the homogeneous dispersion was boiled under stirring for approximately 10 min to obtain a clear solution. The solution was cooled down to room temperature in a water bath, corrected for loss of water during boiling and filtered through a paper filter (Schleicher & Schüll, Schwarzband). *In situ* SAXS/WAXS experiments were performed on samples with aging times of 0.25, 72, 312 and 624 h between filtration and heating to reaction temperature. The samples with SiO₂/H₂O ratios of 10/292, 10/646 and 10/999 (two-, four- and sixfold dilutions, respectively) were prepared by addition of the appropriate amount of distilled water to a reaction mixture having the standard composition after the filtration. The reactions were performed in a specially designed rotating (2 cycles min⁻¹) cell (de Moor, Beeten, Diat & van Santen, 1997) at 398 K.

Two clear ruby mica sheets were used as windows, the spacing provided by a polytetrafluoroethylene ring (thickness 0.5 mm).

2.2. Data collection and analysis

The time-resolved combined SAXS and WAXS measurements were performed at station 8.2 (Bras *et al.*, 1993) of the Synchrotron Radiation Source (Daresbury Laboratory, Warrington, England). The length of the vacuum chamber between the sample and the SAXS detector was 3.5 m. Both the SAXS and WAXS spectra were recorded with position-sensitive detectors. The wavelength of the X-rays was 1.54 Å and $\Delta\lambda/\lambda < 4 \times 10^{-3}$.

Before the experiment, a 2 min scan of the scattering of the reaction mixture was recorded at room temperature. After heating of the cell to 398 K within another 2 min, data collection was started (start of reaction time). The intensity of the scattered X-rays was sufficient to collect a small-angle and wide-angle X-ray scattering pattern with an acceptable signal-to-noise ratio every 2 min.

Both SAXS and WAXS patterns were corrected for the intensity of the X-ray source and detector sensitivity prior to background subtraction. The scattering signal of water between two mica windows at 398 K was used as background. The WAXS pattern was used to determine the start of the crystallization and to check for crystalline phases other than silicalite-1. Since the resolution of the WAXS detector is too low to determine the width of the peaks with sufficient accuracy, the height of the highest peak in the pattern of silicalite-1 (501 reflection at $2\theta = 23.2^\circ$) was taken as a measure for the crystallinity of the sample in this study. The SAXS and WAXS

detectors were calibrated with the scattering pattern of a specimen of wet rat-tail collagen and sample of zeolite NaA, respectively.

USAXS data were collected with a Bonse-Hart camera on the small-angle scattering station of BL4/ID2 at the European Synchrotron Radiation Facility (ESRF) in Grenoble (Bösecke, Diat & Rasmussen, 1995). Details of the set-up are given by Diat *et al.* (1995). For background correction, we used the scattering pattern of water at 398 K.

3. Results

3.1. SAXS/WAXS and USAXS on the 'standard system'

The SAXS patterns recorded after several reaction times during the synthesis of silicalite-1 from a reaction mixture having the standard concentration given in the experimental section are shown in Fig. 1(a). For a fresh sample and short reaction times (<15 min), the scattering intensity is almost constant over the whole Q region measured. After reaction times longer than 20 min, an increased intensity at $-1.15 < \log Q < -0.8$ is observed, which is most probably due to the presence of a population of scattering particles with a size of up to

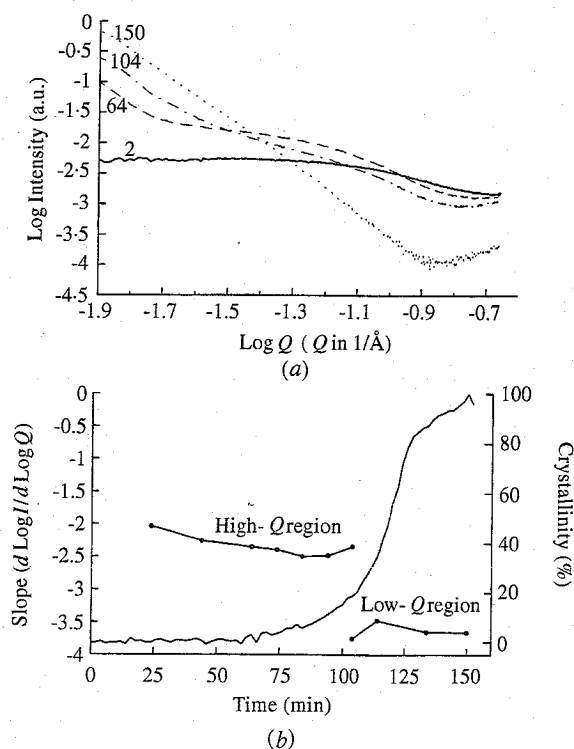


Fig. 1. (a) Overview of the SAXS patterns recorded during the synthesis of silicalite-1 from a clear solution (standard composition), aged at room temperature for only 15 min prior to heating to reaction temperature. The labels at the curves correspond to the reaction time in minutes. (b) The slope in two regions of the $\log I$ versus $\log Q$ plot of the SAXS pattern and the crystallinity. The maximum height of the 501 reflection has been arbitrarily set to correspond with 100% crystallinity.

9 nm. The slope of a linear fit in the center of this region is approximately -2.1 . These particles are believed to be aggregates of silica particles that are amorphous, since no indication of any bands is present in the WAXS pattern. At reaction times longer than 40 min the intensity in the low- Q region starts to increase and after about 64 min a small linear region in the $\log I$ versus $\log Q$ plot appears. At the same time, the scattered intensity at $2\theta = 23.2^\circ$ in the WAXS pattern starts to increase, pointing to the formation of silicalite-1 crystals (see Fig. 1*b*). At longer reaction times, the increased intensity at small angles in the SAXS patterns forms a linear region with a slope of approximately -3.6 , which agrees with scattering at a crystal with surface-fractal properties (surface-fractal dimension 2.4) (Bale & Schmidt, 1984; Schmidt, 1989). Recent *in situ* USAXS experiments (de Moor, Beelen, Diat & van Santen, 1997) on a system with the same composition provided data over a much larger Q range with significant overlap with the SAXS experiments. Fig. 2 shows that the measured USAXS and SAXS patterns agree in the overlap region. These data confirm that the increased intensity in the low- Q region of the SAXS pattern is indeed part of a larger region with a slope of about -3.6 .

At reaction times longer than 64 min, two effects can be observed. Both the scattered in the low- Q region and the 501 reflection (Fig. 1*b*) increase, corresponding to an increase in the amount of crystalline product. At high- Q values, the scattered intensity from the colloidal aggregates lowers, indicating a decrease in their concentration. The slope of the $\log I$ versus $\log Q$ curve in the appropriate region shows a decrease from -2.0 to -2.5 when the reaction time increases from 20 to 90 min (see curve denoted 'high- Q region' in Fig. 1*b*). This could be in accord with a densification of aggregates by a reconstruction or aging process, but the range of the linear fit is too small for us to draw any definite conclusions in terms of mass-fractal dimensions of these aggregates (Teixeira, 1986). However, in contrast with the results of Dokter, van Garderen, Beelen, van Santen

& Bras (1995) on a system with the same composition, but aged for 7 d at room temperature prior to the SAXS/WAXS experiment, the densification of these aggregates into smooth particles (characterized by a slope of -4 in the $\log I$ versus $\log Q$ plot) is not found.

At reaction times longer than 120 min, no scattering intensity from the colloidal aggregates could be observed, corresponding to complete consumption in the crystallization process. Now, the scattering pattern shows a smooth bend at $\log Q \simeq -1.3$. For $\log Q$ values smaller than -1.3 , a slope of approximately -3.6 (surface-fractal dimension -2.4) is found, while for larger ($\log Q$ values a slope of -4 is found. This suggests that the growing crystals show surface-fractal properties on a length scale larger than 12 nm, while they are smooth on smaller length scales.

3.2. Effect of aging time at room temperature

The WAXS patterns showed that silicalite-1 was formed in all syntheses and that it was the only detectable crystalline material present. The intensity of the 501 reflection of silicalite-1 in the WAXS pattern for samples with different aging times prior to heating to reaction temperature is shown in Fig. 3. In all syntheses, a sigmoidal crystallization is found. At increasing aging time at room temperature, both the maximum intensity of the 501 band and the induction period decrease. The SAXS patterns for the different syntheses all showed strong similarity with those shown in Fig. 1*a*). Since the same aggregate size and slope in the $\log I$ versus $\log Q$ plot were found on the same time scale, no influence of the aging on the scattering of the aggregates was observed. Even for aging longer than 7 d, no indication has been found of the densification of the aggregates to smooth particles, characterized by a slope of -4 in the scattering curve, as described by Dokter, van Garderen, Beelen, van Santen & Bras (1995). The only influence of the aging was found on the time scale at which the

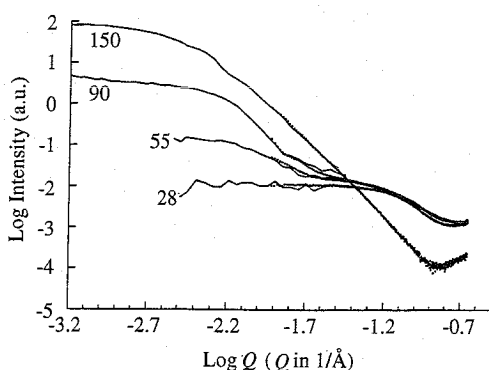


Fig. 2. USAXS data (full lines) combined with the SAXS data (dotted lines) for a standard synthesis mixture without aging at room temperature prior to heating to reaction temperature. The labels on the curves correspond to the reaction time in min.

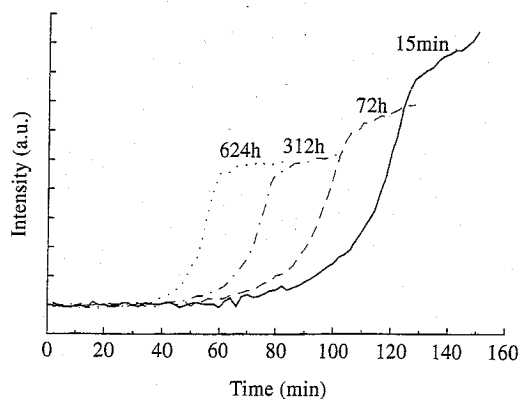


Fig. 3. The crystallinity as a function of time (standard composition) for different aging times at room temperature prior to heating to the reaction temperature.

features described in previous section related to the onset of crystallization took place.

3.3. Variation of $\text{SiO}_2/\text{H}_2\text{O}$

As expected, the intensity of the Bragg reflections in the crystallizing diluted systems is lower than in the standard system, corresponding to the silica concentration in the system. Therefore, in Fig. 4 the height of the 501 reflection is normalized for the silica concentration in the sample, showing that the crystallization behaviour is independent of the silica concentration for $\text{SiO}_2/\text{H}_2\text{O}$ ratios between 10/116 and 10/999.

Generally, the SAXS patterns for the diluted systems showed the same features as described for the 'standard system', as shown in Fig. 1. However, there were two differences concerning the formation of the amorphous colloidal aggregates, which become clear when one compares the lines for the different $\text{SiO}_2/\text{H}_2\text{O}$ ratios denoted 'high- Q region' in Fig. 5. First, the aggregates are formed in an earlier stage in the diluted synthesis mixtures compared to the standard one. Second, the slope in the appropriate region of the $\log I$ versus $\log Q$ plot decreases to the lower values upon an increase of the dilution. The size of the aggregates is found to be constant up to 9 nm for all syntheses.

4. Discussion

The SAXS and USAXS patterns show the same features for all synthesis. For fresh synthesis mixtures, the scattered intensity is almost constant over the whole Q range measured. Therefore, it is believed that the silicic acid powder is dissolved completely during the 10 min boiling of the synthesis mixture, and that only silica monomers, oligomers or polymers with a size smaller than 2.5 nm are present in the solution (primary parti-

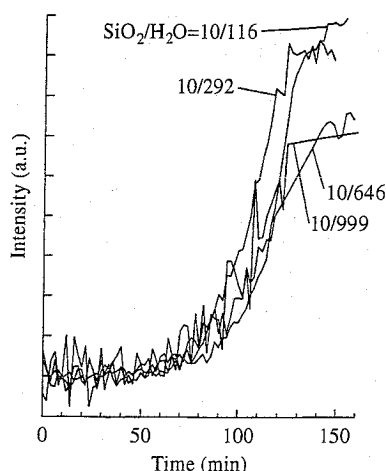


Fig. 4. Crystallinity for synthesis of silicalite-1 at various $\text{SiO}_2/\text{H}_2\text{O}$ ratios as a function of time. The intensity of the 501 reflection has been normalized for the silica concentration in the synthesis mixture.

cles). After heating to 398 K, colloidal aggregates with sizes up to 9 nm are formed within several tens of minutes. These are believed to be amorphous, since no indication of any band is found in the WAXS pattern at this stage. At the onset of crystallization as determined by the intensity of the 501 reflection, the intensity in the low- Q region of the SAXS spectrum increases, pointing to the formation of relatively large crystals (< 50 nm). This interpretation is confirmed by the USAXS patterns. At this stage, three types of siliceous component are present in the synthesis mixture: primary particles (smaller than 2.5 nm), amorphous colloidal aggregates (up to 9 nm) and crystals (larger than 50 nm). Cundy, Henty & Plaisted (1995) quantitatively determined each type of siliceous component with *ex situ* chemical methods. Our *in situ* combined SAXS/WAXS results agree with their results. At long reaction times, the scattering from the aggregates completely disappears and crystallization continues. This suggests a solution-mediated growth mechanism, in which the primary particles are smaller than 2.5 nm. This is in accord with the mechanism proposed by Burkett & Davis (1994, 1995). In this mechanism, the structure-directing role of organic templates is explained in terms of interactions between the organic molecules, water and the silicate species. The water, organized in a hydrophobic hydration sphere around the organic molecules, is replaced by silicate species (Flanigen *et al.*, 1978). Thus, the geometry of the organic species is translated into the inorganic component through multipositional molecular-level interactions. These organic-inorganic composite species then combine to form materials containing longer-range order.

In this study, no influence of the aging upon the formation of aggregates has been observed. However, upon increasing aging at room temperature, the nucleation period decreases and the crystallization rate increases. In another study (de Moor, Beelen & van Santen, 1997), we found silicalite-1 crystallizes from solutions with

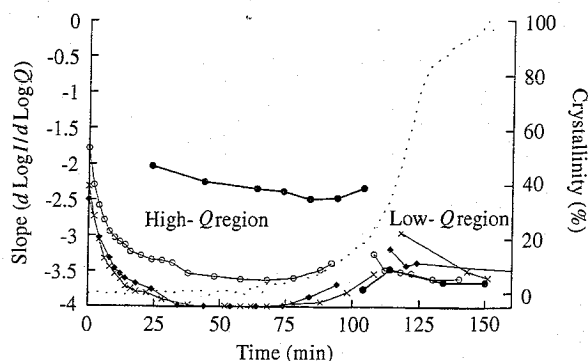


Fig. 5. The slope in two regions of the $\log I$ versus $\log Q$ plot of the SAXS pattern for systems with different $\text{SiO}_2/\text{H}_2\text{O}$ ratios: \bullet 10/116; \circ 10/292; \blacklozenge 10/646; \times 10/999. Only the crystallization curve of the 'standard system' with $\text{SiO}_2/\text{H}_2\text{O} = 10/116$ is shown.

SiO_2/OH^- smaller than 2.65, while no amorphous colloidal aggregates could be detected with SAXS. These results suggest that neither nucleation, nor the growth rate of silicalite-1 depend on the formation of colloidal aggregates or gels, and that they act as a source of nutrients and do not play an active role in the nucleation and growth process. For systems with varying $\text{SiO}_2/\text{H}_2\text{O}$ ratios, the induction period and crystallinity growth rate are found to be constant. This means that the diffusion of nutrients to the crystal surface is not rate-determining in the growth process, and agrees with a surface-reaction-controlled crystallization mechanism as suggested by Schoeman, Sterte & Otterstedt (1994). In such a case, the crystal surface will be covered with a layer of amorphous or semicrystalline material that is still subject to reorganization processes. This may be the explanation for why no smooth crystals (characterized by a slope of -4 in the $\log I$ versus $\log Q$ plot) are found.

In this study, for all syntheses the SiO_2/OH^- ratio was 3.02 and the formation of aggregates was observed. Here, we found a decrease in the slope of the $\log I$ versus $\log Q$ plot for the scattering from the aggregates with a decrease in $\text{SiO}_2/\text{H}_2\text{O}$ at constant SiO_2/OH^- . For $\text{SiO}_2/\text{H}_2\text{O} = 10/116$, a slope of -2.5 is found, corresponding to a mass-fractal dimension of 2.5, while for $\text{SiO}_2/\text{H}_2\text{O} = 10/292$ a slope of approximately -3.6 is observed, pointing to the formation of aggregates with surface-fractal properties. For more dilute systems ($\text{SiO}_2/\text{H}_2\text{O} = 10/646$ and $10/999$), the formation of smooth particles with a Euclidean surface dimension of 2 (slope -4) is found. However, since the range of the linear region is small, it is not possible to draw any definite conclusions in terms of mass-fractal dimensions, but these results suggest that the $\text{OH}^-/\text{H}_2\text{O}$ ratio influences the structure of the colloidal aggregates.

5. Conclusions

We showed that *in situ* investigation of synthesis mixtures with X-ray scattering techniques can provide valuable information on the correlation between (trans)formations on a colloidal scale and the nucleation and growth of zeolite crystals.

Room-temperature aging of the synthesis mixtures prior to the heating to reaction temperature reduced the induction period and increased the crystal growth without having an effect on the formation of amorphous colloidal aggregates.

Dilution of the reaction mixtures prior to heating to the reaction temperature was found not to affect the nucleation and crystal growth rate, but affected the formation of colloidal aggregates. The change in slope in the scattering curves is probably related to a change of the structure of the aggregates formed due to a variation of the $\text{OH}^-/\text{H}_2\text{O}$ ratio in the reaction mixture.

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