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refinement gave almost identical parameters and R values. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository numbers CSD-401026 (room-temperature form) and CSD-401027 (low-temperature form).

- [8] C. J. J. van Loon, J. D. Ijdo, *Acta Crystallogr. Sect. B* **1975**, *31*, 770–773.
 [9] P. W. Selwood, *Magnetochemistry*, Interscience, New York, **1956**.
 [10] H. Lucken, personal Communication; H. Lucken, L. Maque, *Z. Anorg. Allg. Chem.* **1982**, *490*, 64–76.
 [11] P. Güthlich, *Angew. Chem.* **1994**, *106*, 2109–2141; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024–2054.
 [12] W. Klemm, L. Grimm, *Z. Anorg. Allg. Chem.* **1942**, *249*, 198–208, 209–218.
 [13] J. Lewis, D. J. Machin, I. E. Newnham, R. S. Nyholm, *J. Chem. Soc.* **1962**, 2036–2041.

Homogeneous versus Heterogeneous Zeolite Nucleation

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A question of considerable debate in zeolite synthesis is the nature of the precursor gel from which the zeolite is formed and whether nucleation occurs within the gel or from the mother liquid of the synthesis mixture.^[1, 2] For the synthesis of ZSM-5 and silicalite considerable evidence supports the hypothesis that crystallization occurs by transformation of the precursor gel.^[3–4] On the other hand, it has also been demonstrated that the zeolite can be formed directly from the liquid phase without the intermediacy of a gel phase.^[5] Here we report on a silicalite synthesis in which the silicalite crystallites do not nucleate in a separate gel phase, but directly from the liquid phase. Even in this experimental system, in which no gel phase was expected, precursor aggregates were observed with simultaneous, real-time small- and wide-angle X-ray scattering (SAXS-WAXS). These aggregates reorganize in analogy to the heterogeneous reaction mixture before nucleation and subsequent crystallization.^[2, 6]

Time-resolved small- and wide-angle X-ray scattering can be applied to study aggregation, gelation, and crystallization processes under in situ conditions. We recently reported a SAXS-WAXS study of the gel morphology changes that occur during silicalite formation in a synthesis mixture with a separate gel phase. We found significant gel transformations before nucleation of silicalite crystallites. The gel morphology could be analyzed in terms of primary particles with a radius of 14 nm and an initial surface fractal dimension of 2.7, indicating a rough surface, which reorganized into smoother particles during reaction.^[2, 6] We concluded that nucleation proceeds within the gel.

The simultaneous small- and wide-angle X-ray scattering experiments were performed using beamline 8.2 at the Synchrotron Radiation Source (Daresbury Laboratories, United Kingdom). Details concerning camera geometry and data collection were presented elsewhere.^[7] The spatial resolution of the

SAXS quadrant detector is 400 μm , and it can handle up to 300 000 counts per second.^[8] The WAXS detector is a curved knife-edge INEL detector with a spatial resolution of 50 μm and can handle up to 100 000 counts per second.^[9] The scattering ranges covered are $0.01 < Q < 0.175 \text{ \AA}^{-1}$ and $0.8 < Q < 3.4 \text{ \AA}^{-1}$ for the SAXS and WAXS detectors, respectively. The SAXS data were corrected for background scattering and solvent using a procedure introduced by Vonk.^[10] Fractal dimensions were determined from the parts of the scattering curves where behavior followed the power law, and particle and aggregate sizes were determined from the point of deviation from this behavior. In the determination of the slope of the scattering curve, two possible sources of error may be distinguished. The first is the natural noise present in the data, which is small, however, compared to the error introduced during background subtraction ($D_f \pm 0.05$). The crystallinity of the final product was determined with in-house XRD, which was calibrated with a fully crystalline sample of silicalite. The relation between a scattering spectrum and the species responsible for the scattering is shown in Figures 1a and 1b. For mass fractal aggregates

Fig. 1. a) Schematic representation of an aggregate with mass fractal and surface fractal properties; b) the corresponding plot of $\log I$ versus $\log Q$ of the small-angle scattering spectrum. $S(Q)$ = structure factor, $P(Q)$ = form factor, I = scattered intensity, Q = scattering vector, D_f = mass fractal dimension, D_s = surface fractal dimension, r_g = radius of gyration of the aggregate, r_0 = radius of gyration of primary particles.

the scattered intensity will be dominated by the structure factor, providing information about the correlation between the various primary building units present in the aggregates^[11] [Eq. (a)]. Here $Q = 2\pi/\lambda \sin(2\theta)$, λ = wavelength, 2θ = scattering angle, $P(Q)$ = form factor, $S(Q)$ = structure factor, and D_f = mass fractal dimension.

$$I(Q) \sim P(Q)S(Q) \sim S(Q) \sim Q^{-D_f} \quad (a)$$

On the scale of the primary building units the form factor of the primary building units becomes dominant in the scattering pattern, thus providing information about the surface structure of these units^[12] [Eq. (b)], where D_s , the surface fractal

$$I(Q) \sim P(Q) \sim Q^{-(6-D_s)} \quad (b)$$

dimension, ranges between 2 and 3. The surface fractal dimension equals 2 for a nonfractal, completely smooth surface, thus resulting in the well-known Porod relation^[13] [Eq. (c)].

$$I(Q) \sim Q^{-4} \quad (c)$$

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If D_s increases, the roughness of the surface increases. When $D_s \rightarrow 3$ and $D_f \rightarrow 3$, then a homogeneous distribution of mass and voids (possibly filled) throughout the sample is obtained.^[14] Experimentally the parameter D_f (fractal dimension) can be determined from a plot of $\log I(Q)$ versus $\log Q$. The slope of the scattering curve α is equivalent to $-D_f$ for mass fractal scattering and equivalent to $-(6 - D_s)$ for surface fractal scattering.

The reaction mixture studied here was prepared from silicic acid powder (Baker 10.2 wt% water), NaOH pellets (Merck, >99 wt%) and tetrapropylammonium hydroxide (TPA) (Fluka 20 wt%) in the following molar ratios: $\text{SiO}_2/\text{TPA} = 4.1$, $\text{SiO}_2/\text{NaOH} = 11.5$, $\text{H}_2\text{O}/\text{SiO}_2 = 11$.^[15] NaOH was added to the TPAOH solution with gentle stirring. The silicic acid was added to the solution and stirred until a homogeneous dispersion was obtained. This solution was heated for approximately 10 min to obtain a clear synthesis mixture. Water was added to correct for the loss due to evaporation. This synthesis mixture usually remains clear during reaction until crystallization, detectable with standard X-ray diffraction, occurs.^[15] The reaction temperature was $120^\circ\text{C} \pm 5^\circ\text{C}$.

Our results indicate that in the homogeneous system cluster aggregation occurs before crystallization, in analogy to the heterogeneous system.^[12, 6] SAXS curves and corresponding schematic aggregate structures are shown in Figures 2 and 3, respectively. As Figures 2a and 3b show, the morphology ($D_f = 2.2$), observed after a reaction time of 5 min is typical for aggregates condensed according to reaction-limited cluster-cluster aggregation.^[16] The low rate of reaction is due to the effect of the structure-directing TPA ions.^[17]

The aggregates formed under these conditions have a diameter d of approximately 6.4 nm ($d = 2 \cdot r_g$; r_g = radius of gyration). These aggregates are composed of primary particles with a radius smaller than 1.6 nm, the upper limit of the Q -values of the available SAXS range. These primary particles may be hydrated tetrapropylammonium-silicate clusters. Burkett and Davis have provided evidence for the existence of preorganized organic-inorganic composite structures in the synthesis of ZSM-5.^[18] Short-range intermolecular interactions exist between the protons of TPA and silicon atoms of the zeolite precursor phase before development of the long-range order characteristic of the ZSM-5 structure.^[18] Other authors observed specific silicate anions in various aqueous silica solutions

Fig. 2. Plot of $\log I$ versus $\log Q$ of the small-angle X-ray scattering spectra of the clear silicalite synthesis mixture after reaction times of a) 5 min, b) 35 min, c) 75 min, and d) 105 min.

Fig. 3. Mechanism of microstructural random packing, subsequent ordering, and crystallization. a) Silicate/TPA clusters in solution; b) primary fractal aggregates formed from the silicate/TPA clusters (6.4 nm, Fig. 1a); c) densification of these primary fractal aggregates (Fig. 1b); d) combination of the densified aggregates into a secondary fractal structure and crystallization (Fig. 1c); and e) densification of the secondary aggregates and crystal growth.

which may be building blocks for zeolites or precursors of zeolites.^[19, 20]

The observed silica/TPA clusters start to densify (Figs. 2b and 3c) with time into denser mass fractal aggregates and subsequently into surface fractal aggregates (Fig. 4). After a reaction

Fig. 4. Plot of crystallinity C (from WAXS) and microstructure (from SAXS) as a function of time t . The scattering slopes α obtained with SAXS are divided in the scattering slope at high Q (small radius) ($\circ$) and the scattering slope at small Q (large radius) ($\bullet$) to clearly demonstrate the consistency between the microstructure and crystallization ($\square$).

time of 35 min at 120°C the plot of $\log I(Q)$ versus $\log Q$ shows a Porod slope ($\alpha = -4$), indicative of a homogeneous dense silica/TPA structure with a smooth surface ($D_s = 2$). The size of this structure increases only very slightly (to 7.2 nm) with time. The fact that it does not decrease upon densification indicates that additional primary particles (TPA surrounded with silicate anions) are transported from solution or other silica aggregates to the densifying cluster. The size of these densified silica/TPA

particles is approximately equal to 20 silicalite unit cells. After this densification, the 7.2-nm particles aggregate again into a new, secondary fractal aggregate (Figs. 2c and 3d). The occurrence of crystalline structures is observed simultaneously with WAXS.

Figure 4 shows the time progression of the scattering slope α at large values of Q (small particles) and at small values of Q (large particles or clusters), and the degree of crystallinity as determined with WAXS. The WAXS curves are shown in Figure 5. From these plots we may conclude that crystallization

Fig. 5. WAXS spectra of clear silicalite synthesis mixtures demonstrate crystallization between 50 and 125 min of reaction. I = intensity, Q = scattering vector, t = time.

starts as soon as the dense silica/TPA particles 7.2 nm in diameter have been formed and aggregation into the larger secondary aggregate starts. Growth of zeolite particles occurs by transformation of the 7.2-nm silica/TPA particles that form the new secondary fractal structure (Fig. 2c). Crystallization occurs again via a surface fractal aggregate (Fig. 4) to a completely smooth (energetically more favorable) structure (Figs. 2d and 3e). They grow rapidly to a size larger than the upper size limit (low Q -limit) of the available SAXS range ($d > 52$ nm).

Crystal growth occurs by combination of the densified primary aggregates into kinetically determined secondary aggregates, indicative for growth by combination of already growing nuclei, which subsequently densify into energetically more favorable, dense, smooth particles. These results are in agreement with the results obtained by Twomey et al. who deduced from size distributions of crystals obtained from light-scattering experiments that nucleation is a continuous process and that growth occurs by agglomeration of nuclei.^[21]

One interesting feature of the results presented here is that also in the homogeneous system a precursor aggregate is formed before crystallization, which is indicative of a gel transformation or gel reorganization mechanism of zeolite crystallization even in a clear silicalite solution. This is in contrast to the direct homogeneous crystallization.

For silicalite synthesized from a gelatinous reaction mixture^[2] it was concluded that crystallization proceeded also according to a gel transformation mechanism. No mass fractality was observed during these experiments. The different silica source (Aerosil 380) leads to very compact amorphous surface fractal precursor particles with a initial particle size of 14 nm. Crystallization, however, starts only after the surface fractal amorphous particles have been transformed into smooth par-

ticles with $D_s = 2$. An analogous feature was observed in this study. The mass fractal aggregate had to transform into smooth, homogeneous, dense structures before crystallization starts. From this we may conclude that homogeneous and heterogeneous crystallization both require an intermediate gel phase before nucleation and crystallization can occur.

In the gel phase nucleation and crystallization occur more slowly than in the homogeneous phase, because the gel formed must first dissolve before a new phase is formed, from which crystallization can occur. This dissolution step is not required in the homogeneous phase, in which the mass transport and subsequent formation of the primary and secondary clusters seem to be the rate-determining steps. Instant crystallization may be achieved when the precursors are prepared in such a way that the desired gel phase for nucleation is obtained directly.

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- [1] M. E. Davis, R. F. Lobo, *Chem. Mater.* **1992**, 4, 756.
- [2] Z. Gabelica, J. B. Nagy, G. Debras, E. G. Derouane, *Proc. Int. Zeolite Conf. 6th 1983*, **1984**, 914.
- [3] W. H. Dokter, T. P. M. Beelen, H. F. van Garderen, C. P. J. Rummens, R. A. van Santen, J. D. F. Ramsay, *Coll. Surf. A* **1994**, 85, 89.
- [4] W. Xu, J. Li, W. Li, H. Zhang, B. Liang, *Zeolites* **1989**, 9, 468.
- [5] L. E. Iton, F. Trouw, T. O. Brun, J. E. Eperson, J. W. White, S. J. Henderson, *Langmuir* **1992**, 8, 1045.
- [6] W. H. Dokter, T. P. M. Beelen, H. F. van Garderen, R. A. van Santen, W. Bras, G. E. Derbyshire, G. R. Mant, *J. Appl. Crystallogr.* **1994**, 27, 901.
- [7] W. Bras, G. E. Derbyshire, A. J. Ryan, G. R. Mant, A. Felton, R. A. Lewis, C. J. Hall, G. N. Greaves, *Nucl. Instrum. Methods Phys. Res. Sect. A* **1993**, 326, 587.
- [8] R. A. Lewis, N. S. Fore, W. Helsby, C. Hall, A. Jones, B. Parker, I. Sumner, J. S. Worgan, C. Budtz-Jorgensen, *Rev. Sci. Instrum.* **1992**, 63 (1), 642.
- [9] M. Evain, P. Deniard, A. Jouanneaux, R. Brec, *J. Appl. Crystallogr.* **1993**, 26, 563.
- [10] C. G. Vonk, *J. Appl. Crystallogr.* **1973**, 6, 81.
- [11] J. E. Martin, A. J. Hurd, *J. Appl. Crystallogr.* **1987**, 20, 61.
- [12] H. D. Bale, P. W. Schmidt, *Phys. Rev. Lett.* **1983**, 53, 596.
- [13] G. Porod, *Kolloid Z.* **1951**, 124, 83.
- [14] D. W. Schaeffer, A. J. Hurd, *Aerosol Sci. Technol.* **1990**, 12, 876.
- [15] J. Verduyn (PCT), **1992**, EP-A02386.
- [16] R. Jullien, M. Kolb, *J. Phys. A* **1984**, 17, L639.
- [17] E. M. Flanigan in *Introduction to zeolite science and practice* (Eds.: H. Van Bekkum, E. M. Flanigan, J. C. Jansen), Elsevier, Amsterdam, **1991**, p. 13.
- [18] S. L. Burkett, M. E. Davis, *J. Phys. Chem.* **1994**, in press.
- [19] P. W. J. G. Wijnen, T. P. M. Beelen, J. W. de Haan, L. J. M. van de Ven, R. A. van Santen, *Colloids Surf.* **1990**, 45, 255.
- [20] D. Hoebbel, A. Vargha, B. Fahlke, G. Engelhardt, *Z. Anorg. Allg. Chem.* **1985**, 521, 61.
- [21] T. A. M. Twomey, M. Mackay, H. P. C. E. Kuipers, R. W. Thompson, *Zeolites* **1994**, 14, 162.