



	Experiment title: In-situ time-resolved SAXS/WAXS studies of the formation of ZIF-8 nanocrystals	Experiment number: SC-2803
Beamline: ID 02	Date of experiment: from: 23/10/2009 to: 26/10/2009	Date of report: 23/08/2011
Shifts: 9 [#]	Local contact(s): Dr. Jeremie Gummel, Dr. Theyencheri Narayanan	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Dr. Michael Wiebcke, *Janosch Cravillon, and *Christian A. Schröder, Leibniz University Hanover, Institute of Inorganic Chemistry, Germany *Roman Nayuk, and Professor Dr. Klaus Huber, University of Paderborn, Department of Chemistry, Germany [#] 6 shifts out of the total of 9 shifts were used for the in-situ SAXS/WAXS studies reported here (as applied for in the proposal), 3 additional shifts were granted to Prof. K. Huber for in-situ SAXS studies on the formation of amorphous CaCO ₃ nanoparticles reported separately.		

Report:

The work resulted in the following publication:

“Fast Nucleation and Growth of ZIF-8 Nanocrystals Monitored by Time-Resolved In Situ Small-Angle and Wide-Angle X-Ray Scattering” by J. Cravillon, C. A. Schröder, R. Nayuk, J. Gummel, K. Huber, M. Wiebcke, *Angew. Chem. Int. Ed.* **2011**, 50, 8067-8071.

Since the format of a communication in *Angewandte Chemie* does not consider an Abstract, a Report is presented instead.

ZIF-8 (Zeolitic Imidazolate Framework-8) is a prototypical crystalline microporous coordination polymer (or metal-organic framework, MOF). This novel class of materials is currently widely investigated for potential applications in separation, catalysis, etc. At present, design of MOF synthesis is significantly hampered by the poor understanding of the mechanisms of crystallization. The series of in-situ SAXS/WAXS studies performed at ID02 on the formation of ZIF-8 nanocrystals, in continuation of our time-resolved in-situ static light scattering investigations,¹ enabled for the first time direct insight into MOF nucleation from supersaturated homogenous solutions.

To define the starting point of the fast crystallization reaction as precisely as possible the time-resolved scattering measurements were combined with a stopped-flow device for rapid turbulent mixing of methanolic Zn(NO₃)₂·6H₂O and 2-methylimidazole (Hmim) solutions (total molar ratio Zn : Hmim : MeOH = 1 : 4 : 1000). Good results could be obtained when the solutions were injected with a rate of 2 mL/s into the quartz glass capillary (1.5 mm diameter) that served as the scattering cell. The distance between the SAXS detector and the

scattering cell (1.08 m) was chosen as close as possible to enable monitoring the earliest (smallest) particles. Within an experiment, SAXS and WAXS measurements were repeated every 1 s for periods that lasted up to 800 s.

Figs. 1a and 1c show experimental SAXS and WAXS patterns, respectively. Two features can be identified in the SAXS patterns. The feature of a residual intensity at momentum transfer $q > \sim 0.9 \text{ nm}^{-1}$ is observed already in the first measurement at 1 s and originates from very small particles (denoted clusters hereafter), i.e. the clusters form spontaneously upon combining the component solutions. The feature at $q < \sim 0.9 \text{ nm}^{-1}$ is first observed after 15 s and originates from the formation of particles. While the intensity corresponding to the particles increases with time, a simultaneous decrease of the intensity corresponding to the clusters is observed, indicating that the formation of particles is correlated with a depletion of clusters (Fig. 1b). All Bragg reflections that appear in the WAXS patterns belong to the cubic body-centered lattice of ZIF-8, revealing that pure-phase ZIF-8 nanocrystals are generated. Fig. 1d shows a plot of the extent of crystallization versus time produced by normalization of the integrated intensity of the 211 reflection in the WAXS patterns at various times to the intensity at 800 s. The fast crystallization process slows down at ~ 300 s and is followed by a much slower process (most likely Ostwald ripening) which may even exceed our last measurement at 800 s, where the maximum in intensity (and the end of the reaction) has not yet been reached.

SAXS data evaluation based on the Guinier approximation and the Porod invariant that is independent from any assumption of particle shape² has been performed after subtraction of the scattering contribution of the clusters for the period from 22 to 60 s. The radius of gyration (R_g), weight-averaged molar mass (M_p) and number density (N/V) of the particles obtained accordingly increase with time (Figs. 2a and 2b). This can only be interpreted with a particle growth accompanied by a continuous nucleation of new particles. In order to demonstrate that nucleation and/or growth of the particles occur at the expense of clusters, the mass concentration of clusters as a function of time has been estimated by taking the scattering intensity at a fixed q value (Fig. 2b). The intensity starts to decrease with the first observation of particles in the SAXS pattern at 15 s. At about 60 s, the clusters are nearly consumed while the particle number density appears to approach a constant value, indicating

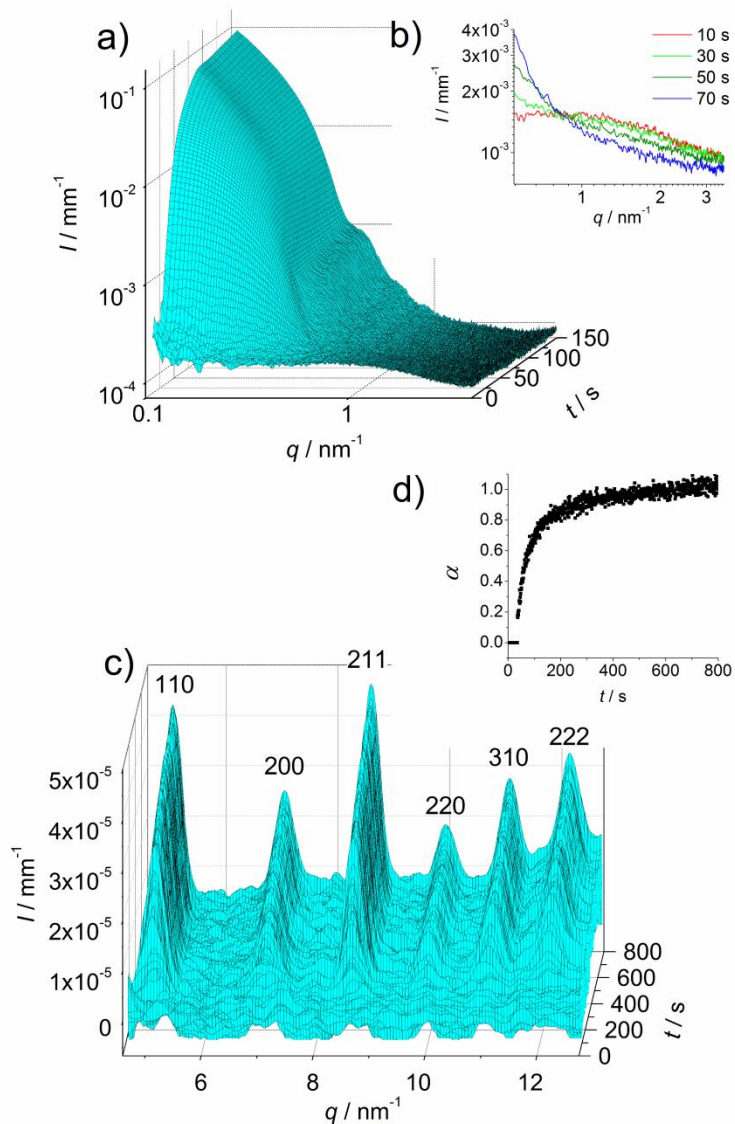


Fig. 1. (a) SAXS patterns for the first 150 s. (b) High- q region of selected SAXS patterns originating from the clusters. (c) WAXS patterns between 1 and 800 s with the indices of the Bragg reflections indicated. (d) Extent of crystallization (α) versus time (t).

that the nucleation process ceases by this time. At the same time the extent of crystallization is $\alpha \approx 0.5$ (Fig. 1d). The fact that the gradual disappearance of clusters is parallel with the approach of a constant number of particles suggests that the clusters are involved in the particle nucleation process.

The SAXS patterns before the appearance of particles could be fitted with a model of monodisperse homogeneous spheres, yielding for the clusters a radius of 1.1 nm. This value should be taken as an average size estimate, as the clusters may be polydisperse. After the appearance of particles, that is, after 22 s, the SAXS patterns could be fitted with a bimodal model of polydisperse spheres (modeling the particles) and monodisperse spheres or an additive Lorentzian function for random fluctuations (modeling the clusters), resulting in values for the radius and polydispersity of the particles that support the above model-independent data evaluation. The first point in time at which the ZIF-8 structure is established in the particles cannot be determined from the WAXS data because a few unit cells are needed for the generation of Bragg reflections and the sensitivity of WAXS is lower than that of SAXS. Thus, we cannot say whether the first particles are already crystalline or amorphous and then reorganize into the ZIF-8 structure. Extrapolation of the experimental extent of crystallization versus time data (Fig. 1d) to $\alpha = 0$ yields a time of ~ 22 s which may be taken as the time where the periodic ZIF-8 structure emerges.

Fig. 3. summarizes the species detected by SAXS/WAXS during the fast nucleation and early growth of ZIF-8 nanocrystals. Clusters with a diameter of ~ 2 nm form in solution from the Zn^{2+} and Hmim precursors and transform into ZIF-8 particles. The nucleation of particles continues while the existing particles grow by attachment of monomers until the clusters are consumed. The prenucleation clusters and nanoparticles/nanocrystals hint at a complex crystallization process that may not follow classical nucleation theory and exhibits similarities with chemical systems, such as zeolites where prenucleation clusters of a similar size have been previously also observed during crystallization from clear solutions.

[1] J. Cravillon, R. Nayuk, S. Springer, A. Feldhoff, K. Huber, M. Wiebcke, *Chem. Mater.* **2011**, 23, 2130-2141.

[2] J. Liu, S. Pancera, V. Boyko, A. Shukla, T. Narayanan, K. Huber, *Langmuir* **2010**, 26, 17405.

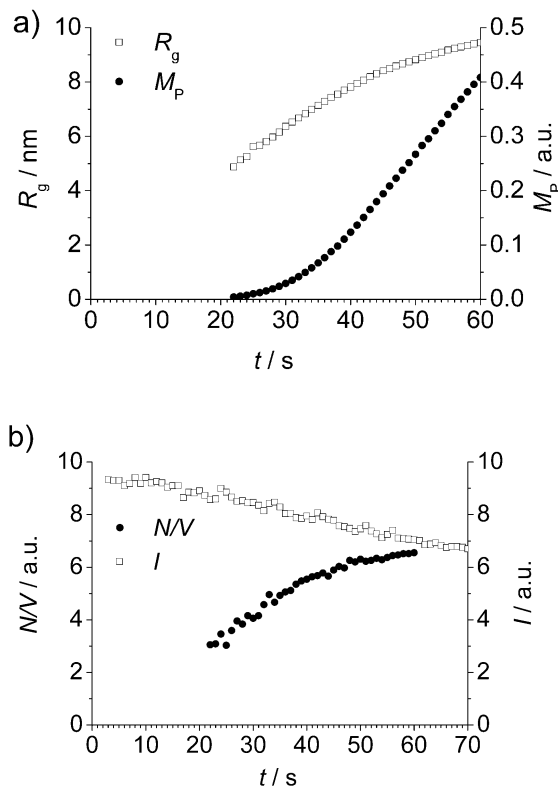


Fig. 2. (a) Radius of gyration (R_g) and weight-averaged molar mass (M_p) of the particles versus time (t). (b) Number density (N/V) of the particles and intensity at $q = 1.502 \text{ nm}^{-1}$ taken as an estimate of the mass concentration of the

already crystalline or amorphous and then reorganize into the ZIF-8 structure. Extrapolation of the experimental extent of crystallization versus time data (Fig. 1d) to $\alpha = 0$ yields a time of ~ 22 s which may be taken as the time where the periodic ZIF-8 structure emerges.

Fig. 3. summarizes the species detected by SAXS/WAXS during the fast nucleation and early growth of ZIF-8 nanocrystals. Clusters with a diameter of ~ 2 nm form in solution from the Zn^{2+} and Hmim precursors and transform into ZIF-8 particles. The nucleation of particles continues while the existing particles grow by attachment of monomers until the clusters are consumed. The prenucleation clusters and nanoparticles/nanocrystals hint at a complex crystallization process that may not follow classical nucleation theory and exhibits similarities with chemical systems, such as zeolites where prenucleation clusters of a similar size have been previously also observed during crystallization from clear solutions.

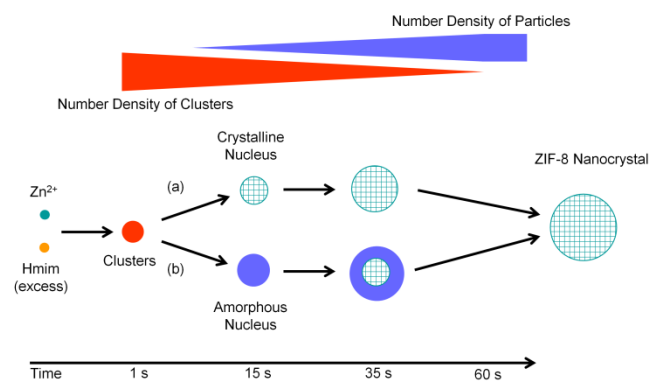


Fig. 3. Species occurring during nucleation and growth of ZIF-8 nanocrystals. Two possible alternative particle nucleation pathways (a) and (b) are considered.