Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Synthesis of isoreticular CAU-1 compounds: Effects of linker and heating methods on the kinetics of the synthesis

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Comparison of the EDXRD and the ADXD measurement

The EDXRD patterns of CAU-1-NH_2 were recorded using a nitrogen-cooled germanium solid-state detector positioned at approximately 1.90° 2theta. The detector contains 2048 channels, which recording the data in an energy range of 6-57 keV. The beam is collimated to a dimension of 20µm x 20µm by wolfram-collimators. The d-spacing is given by the equation:

$$E = 6.199/(d \sin\Theta)$$

The energy calibration of the detector was performed using a glass containing a series of heavy elements with well separated fluorescence lines. The angle of the detector in the conventional and MW set-up, were calibrated using the set of Bragg peaks measured from a pre-made sample of CAU-1-NH_2. A comparison of an EDXRD with an ADXD measurement is given in Figure S1.

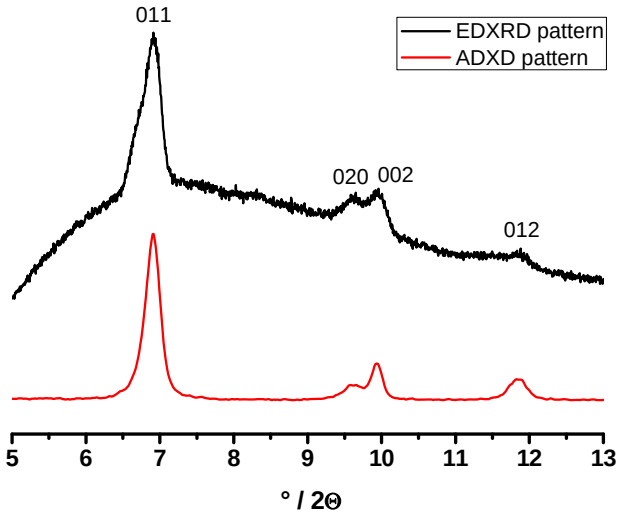

Figure S1: Comparison of ADXD data recorded from a dry sample of CAU-1-NH_2 synthesised at 140 °C using MW-assisted heating (bottom) and the corresponding EDXRD measurement during in-situ crystallisation study (top).

Preferred orientation

To exclude the presence of preferred orientation the 011, 020, 002 and 012 Bragg reflections of the EDXRD measurements were used to calculate the extent of crystallization (α) (conventional synthesis of CAU-1-NH_2 at 145 °C). The corresponding curves α(t) are shown in Figure 2. Since superimposable curves are obtained the presence of preferred orientation can be excluded.

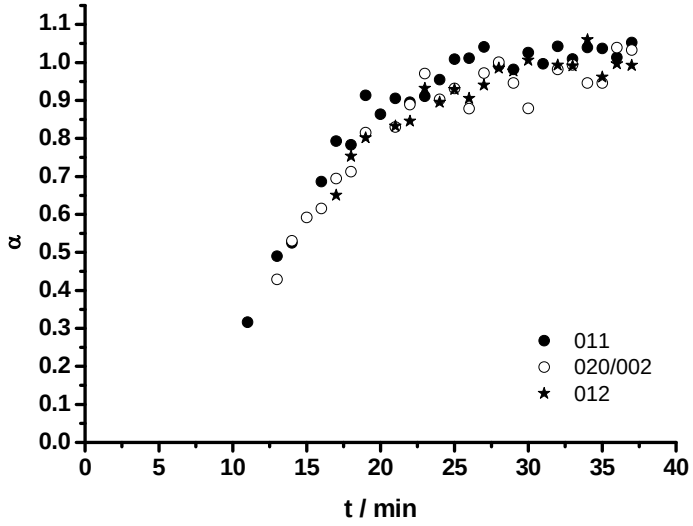

Figure S2. Plots of extent of crystallization (α) vs. reaction time (t) obtained by integration of the 011, 020, 002 and 012 Bragg peaks during the conventional synthesis of CAU-1-NH_2 at 145 °C. The areas of the 020 and 002 Bragg peaks were treated as a single peak due to a nearly complete overlap.

Determination of t_0

The parameter t_0, which is the time until the first crystallites are observed in the EDXRD spectra, is one of the key parameter for the kinetic modelling using the Avrami-Eroféev expression. Therefore, the determination of t_0 was done very carefully for each measurement. As an example the determination of t_0 is shown for the microwave-assisted synthesis of CAU-1-NH_2 at 125 °C. The data were accumulated in 1 min intervals. Between a reaction time of 12 min and 14 min the first product peaks appears in the EDXRD spectra (Figure S3, top) at ~23 keV. Due to the low intensity of the Bragg peaks at the beginning of the reaction, the exact time of t_0 was often difficult to determine. Hence, in addition contour plots of the EDXRD spectra were calculated to verify the estimated t_0 values (Figure S3, bottom). In good agreement a time of 13 min was determined for t_0 for the MW-assisted synthesis of CAU-1-NH_2 at 125 °C using both methods.

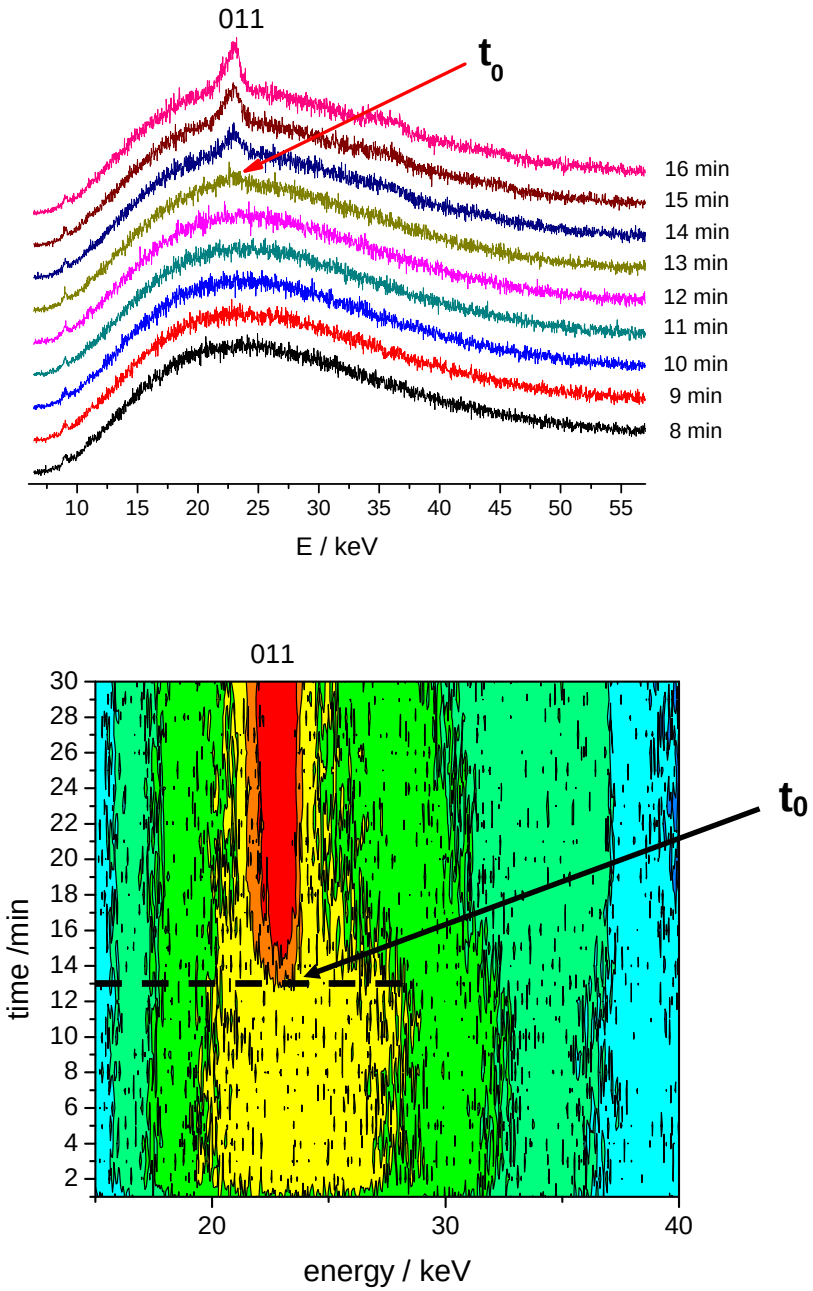

Figure S3. Plots of the EDXRD spectra (top) and the contour plot (bottom) of the MW-assisted synthesis of CAU-1-NH_2 to determine t_0. For both methods the 011 Bragg Peak occurs at a reaction time of 13 min at ~23 keV.

Dynamic light scattering

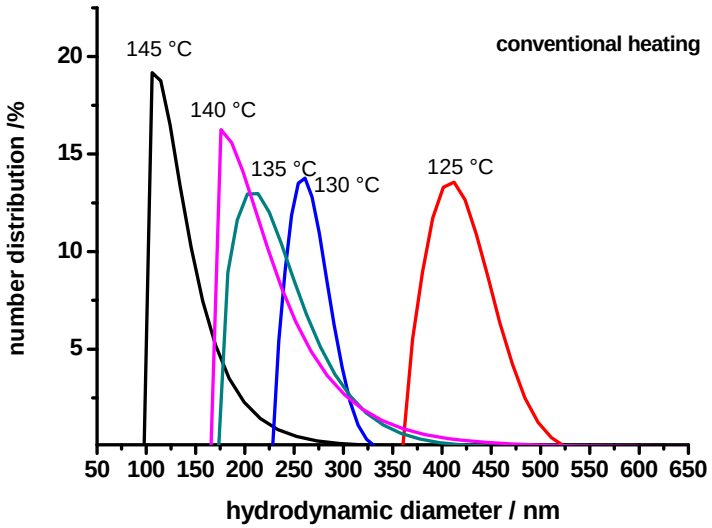

Figure S2: Differential number distribution curves of the hydrodynamic diameters of CAU-1 particles synthesized by conventional electrical heating as determined by dynamic light scattering measurements.

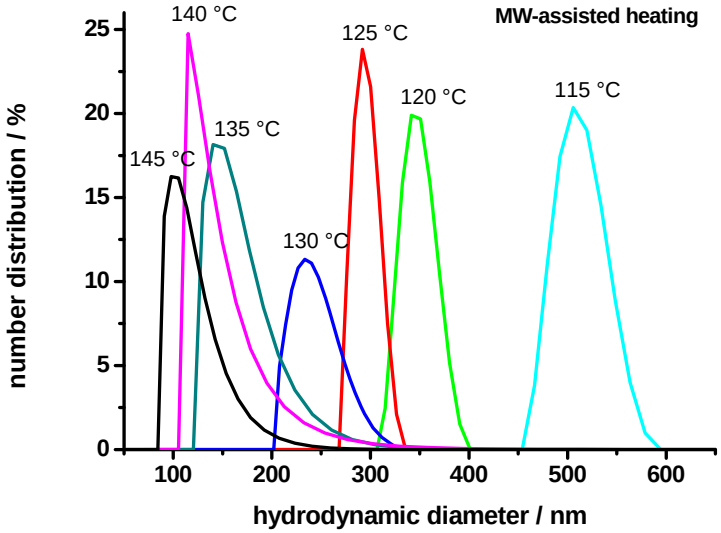

Figure S3: Differential number distribution curves of the hydrodynamic diameters of CAU-1 particles synthesized by MW-assisted heating as determined by dynamic light scattering measurements.