Abstract: Aluminium dihydroxyterephthalate \([\text{Al}_8(\text{OH})_4(\text{OCH}_3)_8\text{H}_2\text{O}]\) is a metal–organic framework (MOF) that was synthesized under solvothermal conditions and characterized by X-ray powder diffraction, IR spectroscopy, sorption measurements, as well as thermogravimetric and elemental analysis. CAU-1-(OH)_2 is isoreticular to CAU-1 and its pores are lined with OH groups. It is stable under ambient conditions and in water, and it exhibits permanent porosity and two types of cavities with effective diameters of approximately 1 and 0.45 nm. The crystallization of CAU-1-(OH)_2 was studied by in situ energy-dispersive X-ray diffraction (EDXRD) experiments in the 120–145°C temperature range. Two heating methods—conventional and microwave—were investigated. The latter leads to shorter induction periods as well as shorter reaction times. Whereas CAU-1-(OH)_2 is formed at all investigated temperatures using conventional heating, it is only observed below 130°C using microwave heating. The calculation of the activation energy of the crystallization of CAU-1-(OH)_2 exhibits similar values for microwave and conventional synthesis.

Keywords: aluminum terephthalate • CAU-1 • metal–organic frameworks • microwave chemistry • X-ray diffraction

Introduction

Metal–organic frameworks (MOFs) belong to the family of crystalline porous materials and are promising multifunctional compounds. They are investigated for their potential applications in the fields of gas and liquid separation, catalysis, drug delivery, as well as electrode materials in batteries. The success of hybrid frameworks is based on the diversity of metal oxide clusters that can be connected by a large variety of organic linkers. It is possible to tune the pore size as well as the chemical properties of such MOFs. Although many MOFs are easily hydrolyzed, Al-containing compounds are the focus of intensive research since they exhibit good thermal and chemical stabilities. Very promising Al-containing candidates for introducing functional groups are the well-known compounds Al-MIL-53 and CAU-1. For example, Himsl et al. synthesized a hydroxyl-functionalized Al-MIL-53 that shows a significant increase in hydrogen adsorption after Li doping.

The synthesis of isoreticular frameworks by using functionalized or larger organic linker molecules as starting materials poses challenges, since the different organic linker molecules can drastically influence the reaction conditions due to their different basicity and solubility. A tedious trial-and-error approach is often required to get the pure product. High-throughput (HT) methods are a valuable tool for the systematic and efficient investigation of compositional and process parameters in solvothermal reactions. Recently, we successfully employed this method to synthesize isoreticular structures of Fe-MIL-53, Fe-MIL-88, Fe-MIL-101, as well as Cr-MIL-101 by using aminoterephthalic acid and 2,6-naphthalenedicarboxylic acid, respectively.

In the course of these studies, the influence of the solvent, the reaction temperature, and time were investigated. Jhung et al. have recently explored the effect of the type of heating on the formation of Cr-MIL-101, that is, conventional versus microwave heating. At the same temperature, microwave heating leads to smaller crystals, a narrower particle-size distribution, and faster reaction times compared to the synthesis using conventional solvothermal techniques. Only few
other studies on the use of microwave heating for the synthesis of MOFs have been reported.\[25,26\]

Although HT methods allow for the systematic investigation of synthesis fields, no information on the reaction mechanism, the induction time, the reaction rate, or the formation of intermediate phases are obtained. Time-resolved energy-dispersive X-ray diffraction (in situ EDXRD) using white-beam X-rays from a synchrotron source is a powerful method to study crystallization processes since they can penetrate the reaction vessels. Studies on inorganic materials that range from transition-metal oxides to zeolites have been described in the literature.\[27–31\] Up to now, only three EDXRD MOF crystallization studies—that is, the formation of HKUST-1, Fe-MIL-53, and MOF-14—have been reported.\[32,33\] In addition, light scattering was used to examine the formation of MOF-5.\[34\]

Herein, we present the results of the in situ investigation and the detailed characterization of the highly porous compound CAU-1-(OH)\(_2\) that contains 2,5-dihydroxyterephthalate ions ([Al\(_8\)(OH)\(_4\)\((\text{OCH}_3)\)_8(BDC(OH)\(_2\))\(_6\)]\(\times\)H\(_2\)O). In addition, the in situ crystallization of CAU-1-(OH)\(_2\) by means of EDXRD techniques using microwave and conventional heating is described.

**Results and Discussion**

**High-throughput syntheses of CAU-1-(OH)\(_2\):** For the discovery of CAU-1-(OH)\(_2\), high-throughput methods were applied. Solvothermal reactions of AlCl\(_3\)6H\(_2\)O and 2,5-dihydroxyterephthalic acid in methanol were performed by varying chemical (molar ratio of Al\(^{3+}\)/linker = 3:1 in methanol and a reaction temperature of 125 °C). The synthesis optimization of CAU-1-(OH)\(_2\) was carried out in a 24-reactor multivessel with a total volume of 2 mL. The synthesis of CAU-1-(OH)\(_2\) is very pH-sensitive, and a base, preferentially NaOH, as an additive is needed. The synthesis of CAU-1-(OH)\(_2\) was also carried out under higher concentration of reactants. As expected, the powder patterns of CAU-1-(OH)\(_2\) and CAU-1 are very similar (Figure S5) and thus only small changes in the lattice parameters are observed (CAU-1-(OH)\(_2\): \(a=b=18.320(5), c=17.711(6) \text{ Å}; V=5945(1) \text{ Å}^3\) (Table S2); CAU-1: \(a=b=18.3517(1), c=17.7720(1) \text{ Å}; V=5985.33(8) \text{ Å}^3\)). The title compound is isoreticular to CAU-1, and its structure consists of eight distorted AlO\(_x\) polyhedra that form the octameric brick [Al\(_8\)(OH)\(_4\)(OCH\(_3\))\(_8\)]\(^{2+}\). Within this brick the AlO\(_4\) polyhedra are connected through hydroxide groups (corner-sharing) and methoxide groups (edge-sharing). Each octameric brick is bridged by twelve linker molecules, that is, dihydroxyterephthalate ions, to twelve other eight-ring units and thus a three-dimensional network is formed. A detailed description is given in the literature.\[35\]

**Thermal investigation of CAU-1-(OH)\(_2\):** The thermal behavior of CAU-1-(OH)\(_2\) was studied by thermogravimetric (TG) and temperature-dependent X-ray powder diffraction (TDXRD) measurements. The TG curve (Figure S6 in the Supporting Information) of CAU-1-(OH)\(_2\) shows a two-step weight loss. The first step (50–130 °C) corresponds to the release of approximately 18 water molecules per formula unit (obsd 29.0%, calcd 27.5%). At higher temperatures (above 300 °C), the decomposition of the frameworks takes place and AlO\(_3\) is formed. Based on the formation of AlO\(_3\), the observed and calculated total weight loss compare well. (obsd 82.0%, calcd 83.1%). These results are in a good agreement with the temperature-dependent XRPD measurements (Figure S7). Between 70 and 120 °C, a strong change of reflection intensities is observed that corresponds to the desorption of enclosed water molecules. Above 300 °C only an X-ray amorphous product is obtained.

**Sorption studies on CAU-1-(OH)\(_2\):** Based on the TG data, an activation procedure at 130 °C and 10\(^{-3}\) mbar for 3 h was used. The N\(_2\) sorption isotherm of CAU-1-(OH)\(_2\) exhibits a type-I behavior (Figure 1) according to the IUPAC classification.\[36\] The apparent specific Brunauer–Emmett–Teller (BET) surface area calculated from the N\(_2\) sorption isotherm is approximately 1350 m\(^2\)/g. The micropore volume is 0.50 cm\(^3\)/g. These values are in good agreement with the data obtained for CAU-1 (1370 m\(^2\)/g, 0.52 cm\(^3\)/g).\[17\] The result of the H\(_2\)O sorption experiment is also shown in Figure 1. The total amount of adsorbed water vapor is approximately 520 cm\(^3\)/g at p/p\(_0\)=0.9, which is corresponds to 27 wt% of adsorbed water molecules. In contrast to the N\(_2\) sorption isotherm, the water-vapor sorption isotherm shows two adsorption steps, which may be due to the tetragonal and octahedral cages. The desorption shows a slight hysteresis due to the strong intermolecular interaction of the sorbate. CAU-1-(OH)\(_2\) exhibits a great stability against water. After the H\(_2\)O sorption experiment, the re-
corded powder pattern of CAU-1-(OH)$_2$ showed no loss of crystallinity. The methane excess uptake of CAU-1-(OH)$_2$ was measured at 25°C up to 50 bar (Figure 2). Under these conditions, maximum uptake was not fully reached. The excess methane uptake in CAU-1-(OH)$_2$ at 50 bar corresponds to 8.0 wt%. For comparison, MIL-101 has an uptake of 9.7 wt% at 35 bar. The CO$_2$ sorption isotherms of CAU-1-(OH)$_2$ are also presented in Figure 2. Two high-pressure measurements were performed at 20 and 30°C up to 20 bar; the third measurement was carried out at 298 K and up to 1 bar. Under these conditions, maximum uptake was not fully accomplished. However, the isotherm at 20°C is nearly linear up to 20 bar and shows an uptake of 30.5 wt% CO$_2$. This value is comparable to those of well-known MOFs like MIL-53(Al) (30.5 wt% at 30 bar and 31°C) and Cu-BTC (32.0 wt% at 35 bar and 25°C) and well above those obtained typically with zeolites (e.g., Zeolite 5A: 22.3 wt% at 14 bar and 25°C). The highest values of CO$_2$ uptake found for MOFs are around 68.6 wt% (at 50 bar and 25°C). Looking at the pressure range up to 1 bar, CAU-1-(OH)$_2$ adsorbs at 298 K about 13.1 wt% CO$_2$, which is relatively high compared to the adsorbed amount of CH$_4$ (0.9 wt%, Figure 2, inset). This different sorption behavior can be explained by the stronger host–guest interactions of the adsorbent with CO$_2$.

In situ EDXRD investigations: Time-resolved EDXRD measurements of the crystallization of CAU-1-(OH)$_2$ were performed on beamline F3 at HASYLAB (DESY, Hamburg, Germany). The starting reagents were dissolved at the desired reaction temperature, and crystallization of CAU-1-(OH)$_2$ was investigated starting from clear solutions. After the reaction, dispersions with particles between 250 and 1200 nm in diameter, depending on the reaction temperature, and a zeta potential of around 28 mV were obtained. The spectra were recorded at an energy range from 6 to 57 keV. A typical diffraction pattern is shown in Figure S8 in the Supporting information. The four peaks that are observed correspond to the 011, 020, 002, and 121 reflections. The kinetic analyses were done by integrating the 011 reflection, which has the highest intensity. As an example, the results of the crystallization process at 125°C using conventional heating are shown in Figure 3. The 011 reflection is observed at 27 keV for the conventional setup that corresponds to an interplanar spacing of 12.77 Å. After an induction time of around 50 min, all four product peaks appeared simultaneously (Figure S9) and grew to the maximum intensity within 100 min. The induction time (t$_0$) represents the time until a detectable size of product particles was formed. During this time nucleation took place. The reaction time corresponds to the period from the first appearance of a reflection to its maximum intensity. The induction time as well as the crystal growth depend strongly on the reaction temperature. To acquire information about the kinetic parameters of the crystallization of CAU-1-(OH)$_2$, the crystallization reactions were carried out at seven different
temperatures in the range 120–145°C by using conventional and microwave heating. The conventional heating was performed using a setup developed by Bensch et al.\[43\] For the microwave heating, a new setup was implemented. This was realized by a slight modification of the commercially available Biotage Initiator microwave oven, which was placed in the beam path at beamline F3, HASYLAB (Figure S10). This reactor allows an accurate monitoring of the reaction temperature, stirring rate, and pressure (for details, see the Experimental Section). The comparison of induction and reaction times using conventional and microwave (MW) heating in the crystal growth of CAU-1-(OH)\(_2\) between 120–145°C is shown in Figure 4. For both heating methods, shorter induction and reaction times with increasing temperature are observed. At the same temperature, the microwave crystallization of CAU-1-(OH)\(_2\) is considerably faster; shorter induction as well as reaction times are found. Above 130°C, conventional heating led to the desired product but no product formation was observed in the microwave reactor. Such a decrease in reaction time using microwave heating instead of conventional heating is generally observed in the literature for organic reactions\[44\] as well as for MOF synthesis of MIL-53\[45\] or MIL-101.\[24\] These studies were performed by quenching the reaction after well-defined reaction times, which can lead to misleading results. According to the literature, the increase in synthesis rates using MW heating are caused by the creation of so-called hot spots, the increase in the heating rate of the reaction mixture or superheating of the reaction mixture.\[46,47\] In ex situ experiments on the crystal growth of the microporous materials silicate-1, VSB-5, and HKUST-1, Jhung et al. also observed accelerated syntheses by microwave irradiation.\[48,49\] They suggest a higher population of nuclei for microwave syntheses than for conventional syntheses at the same temperature, which leads to a decrease in crystal sizes. These results are in a good agreement with the measured hydrodynamic diameters of CAU-1-(OH)\(_2\) synthesized by conventional and MW heating (Figure S12). For the kinetic evaluation of the data, the extent of reaction \(\alpha\) and the induction times were determined. The extent of the reaction \(\alpha(t)\) is given as the ratio of the intensity at time \(t\) to the intensity at time \(t_\infty\) [Eq. (1)]:\[50\]

\[
\alpha(t) = \frac{I(t)}{I(t_\infty)}
\]

The crystallization kinetics can be calculated using the Avrami–Erofeev expression, which relates \(\alpha(t)\) to the reduced time \(t_{\text{red}} = (t-t_0)/a\) as [Eq. (2)]:

\[
\ln[-\ln(1-\alpha)] = m \ln(k) + m \ln(t_{\text{red}})
\]

Plotting \(\ln[-\ln(1-\alpha)]\) versus \(\ln(t_{\text{red}})\) (Sharp–Hancock plot) leads to a straight line if the reaction follows the same mechanism during the complete reaction time.\[50\] The reaction exponent \(m\) can be derived from the slope of the curve, whereas the intercept yields the rate constant \(k\). The plots of extent of crystallization and the corresponding Sharp–Hancock plots are listed in the Supporting Information (Figure S13). The kinetic parameters extracted from the Sharp–Hancock plots are shown in Table 1. The parameter \(t_0\) denotes the starting time for the crystal growth of CAU-1-(OH)\(_2\). The Avrami exponent \(m\) contains information about the mechanism of the process studied and the growth geometry. Due to the low intensity of the Bragg peaks at the beginning of the reaction, we estimate the error of \(t_0\) according to the reaction rate in the range between \(\pm 5\) min for reactions at 115°C using conventional heating and \(\pm 1\) min using MW heating at 130°C. The error in the determination of the end of reaction was calculated at the scattering of the data at \(\alpha = 1\). Here we found an average error of 5%. Errors involved in fitting the peaks were found to be comparatively small. Altogether, including the error resulting for the determination of the Avrami exponent \(m\) by linear regression, a maximum error of \(\pm 0.2\) for \(m\) and a maximum error of \(\pm 3 \times 10^{-4} \text{s}^{-1}\) for the rate constant was found for all reactions. It should be noted that the reaction mechanism models are empirical. Using the Avrami equation is the most commonly employed approach for kinetic studies of solvothermal reactions and has been applied widely to many reaction systems, that is, crystallization of zeolites, thioan-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\multicolumn{2}{|c|}{\textbf{Reaction temperatures (°C)}} & \textbf{\(t_\infty\) [min]} & \textbf{\(k \left[ \text{s}^{-1} \right]\)} & \textbf{\(m\)} \\
\hline
120 & MW & 50 & 74 & 9.12 \times 10^{-4} & 2.50 \times 10^{-4} & 0.74 & 1.06 \\
125 & MW & 27 & 59 & 1.53 \times 10^{-3} & 6.46 \times 10^{-4} & 0.66 & 1.10 \\
130 & MW & 19 & 35 & 2.56 \times 10^{-3} & 7.40 \times 10^{-4} & 0.74 & 1.06 \\
135 & MW & 15 & - & 2.11 \times 10^{-3} & - & 1.06 \\
140 & MW & 15 & - & 2.08 \times 10^{-3} & - & 1.06 \\
145 & MW & 11 & - & 3.18 \times 10^{-3} & - & 1.07 \\
\hline
\end{tabular}
\caption{Rate constants \((k)\) and reaction exponents \((m)\) of microwave (MW) and conventional (con) synthesis obtained by evaluation of Sharp–Hancock plots.}
\end{table}
timonates, or metal–organic frameworks.\textsuperscript{[27,28,32]} Nevertheless, this method allows one to extract the rate constants and enables the comparison of reactions, for example, at different temperatures. The observed values of Avrami exponents are in the range of 1.0–1.1 and 0.6–0.8 for reactions that use conventional and MW heating, respectively. This indicates a rather diffusion-controlled crystal growth for MW heating and a rather phase-boundary-controlled reaction for conventional heating. The findings are in accordance with studies on the formation of manganese thioantimonates.\textsuperscript{[43]} The high concentration of nucleation sites using MW heating leads to a depletion of the reactants in the reaction mixture. Thus, the rate of reaction depends on how fast the reagents diffuse to the place of crystallization. In the case of conventional heating, the formation of nucleation sites is the most important step and determines the overall rate of crystallization. The rate constants at different temperatures allow for the determination of the Arrhenius activation energy for the crystal growth of CAU-1-(OH)\textsubscript{2}, as well as the pre-exponential factors ($A$) for both heating methods (Table S3). Applying the Arrhenius equation and plotting $\ln(k)$ versus $1/T$, the activation energies ($E_a$) using microwave as well as conventional heating are found in the range of 131–136 kJ (Figure 5). Up to now, no activation energies for the formation of Al-based MOFs have been reported in the literature. For comparison, an activation energy of 53 kJ for phase-boundary-controlled crystallization of layered manganese thioantimonates(III) under conventional conditions was determined.\textsuperscript{[43]} For the diffusion-controlled crystallization of lanthanide phosphonatobutanesulfonates, an activation of 128 kJ was recently published.\textsuperscript{[51]} There are only few studies that compare the influence of microwave-assisted and conventional heating on the crystallization rate, and the described data is not consistent. In ex situ quenching experiments on the crystallization of Fe-MIL-53\textsuperscript{[45]} and AlPO-11,\textsuperscript{[50]} higher activation energies under MW conditions were reported. Nevertheless, MW heating led to an acceleration of the crystallization. This was explained to be due to a large increase of the pre-exponential factor by 6 and 8 orders of magnitude for Fe-MIL-53 and AlPO-11, respectively. In our case, the activation energies do not depend on the heating method and the pre-exponential factor increases by a factor of 15 for microwave-assisted synthesis (Table S3). Possible explanations are the increase of the concentration of reaction sites (number of nuclei) and a higher mobility of the reactants in the microwave field that could lead to an increase of the collision frequency.\textsuperscript{[49,52,53]}

**Conclusion**

The chemically and thermally stable MOF CAU-1-(OH)\textsubscript{2}, that contains two -C-OH groups that protrude into the pores has been synthesized by applying our high-throughput methodology. CAU-1-(OH)\textsubscript{2} exhibits high porosity and is stable against water. The influence of the reaction temperature and heating method—that is, conventional versus MW heating—on the crystallization of CAU-1-(OH)\textsubscript{2} has been investigated by employing in situ EDXRD measurements. Hence, a microwave setup was implemented at beamline F3, HASYLAB, Hamburg. In all crystallization experiments, the induction periods as well as the reaction times are shorter when microwave-assisted heating is employed. Both heating methods yield almost identical activation energies around 135 kJ. The Avrami exponents indicate a phase-boundary-controlled reaction when using conventional heating methods and a diffusion-controlled reaction for the microwave syntheses.

**Experimental Section**

**Chemicals:** AlCl\textsubscript{3}·6H\textsubscript{2}O (Riedel-de Haen, ≥ 99%), 2,5-dihydroxyterephthalic acid (H\textsubscript{2}BDC(OH)\textsubscript{2}; Aldrich, 98%), methanol (BASF, purum), and NaOH (Merck, ≥ 99%) were used as purchased. **Synthesis:** Pure-phase CAU-1-(OH)\textsubscript{2} was formed in the temperature range from 110 to 150°C without any crystalline byproducts. For the optimized synthesis in the 24-reactor system,\textsuperscript{[45]} a mixture of AlCl\textsubscript{3}·6H\textsubscript{2}O (104.8 mg, 0.433 mmol), H\textsubscript{2}BDC(OH)\textsubscript{2} (29.9 mg, 0.151 mmol), and 2 mL methanolic NaOH (45 µL, 0.09 mmol) was heated at 125°C in methanol (1000 µL) for 5 h. After filtration, a yellow microcrystalline product was obtained. Scale up of the reaction was performed in a 27 mL Teflon-lined steel bomb using tenfold the amount of the optimized synthesis procedure. The in situ investigations were carried out under stirring in glass vessels with twice the amount of the optimized synthesis. The as-synthesized product of CAU-1-(OH)\textsubscript{2} contained large amounts of NaCl. To remove these, the dry yellow microcrystalline raw product was washed on the filter paper several times with water. The sample was dried in air overnight or in an oven at 60°C for 20 min. After the washing process a yield of 50% based on the amount of dihydroxyterephthalic acid was obtained (elemental analysis of dehydrated CAU-1-(OH)\textsubscript{2} ([Al\textsubscript{10}O\textsubscript{2}H\textsubscript{10}O\textsubscript{4}](OCH\textsubscript{3})\textsubscript{8}(BDC(OH)\textsubscript{2})\textsubscript{6}]; obsd: C 39.63, H 3.71; calcd: C 39.35, H 3.07). Dehydration was carried out for 3 h at 130°C and 1 × 10\textsuperscript{-2} bar. The absence of chloride and sodium ions was confirmed by EDX analyses. The IR spectrum of CAU-1-(OH)\textsubscript{2} (Figure S14 in the Supporting Information) shows the symmetric and asymmetric stretching modes of the bridging carboxylate group at 1598 and 1470 cm\textsuperscript{-1}. The aliphatic C–H stretching vibrations of the methoxy group occurs around 2900 cm\textsuperscript{-1}. The typical

![Figure 5. Arrhenius plots to calculate the activation energies for crystal growth of CAU-1-(OH)\textsubscript{2} by means of conventional (●) and MW (○) heating.](image-url)
stretching band for the OH groups were not observed due to the presence of water molecules that are involved in O-H-O hydrogen bonding. The band of the C-O stretching vibration of the hydroxyl groups of the incorporated linker molecules appears at 1240 cm⁻¹.

**Methods**

X-ray powder diffraction patterns were recorded using a STOE STADI P diffractometer equipped with a linear position-sensitive detector using monochromated CuKα radiation. Lattice parameters were determined using the DICVOL program[40] and refined using the STOE software package WinXpow.[41] Temperature-dependent X-ray diffraction experiments were performed under air using a STOE STADI P diffractometer equipped with an image plate detector and a STOE capillary furnace (version 0.65.1) using monochromated CuKα radiation. Each powder pattern was recorded in the 4–20° range (2θ) at intervals of 10°/C up to 300°C with a duration of 20 min per scan. The temperature ramp between two patterns was 5°C min⁻¹. Thermogravimetric (TG) analysis was carried out in air (75 mL min⁻¹, 25–800°C, 1°C min⁻¹) using a Netzsch STA-409CD. Carbon, hydrogen, and nitrogen contents were determined by elemental chemical analysis using an Eurovector EuroEA elemental analyzer. IR spectra were recorded using an ATI Matheson Genesis in the spectral range 4000–400 cm⁻¹ using the KBr disk method. The hydrodynamic diameter of the CAU-1-(OH)₂ particles were measured by dynamic light scattering using a DelsaNano C apparatus (Beckman & Coulter). EDX analysis was performed using a Philips SEM XL 30. Several types of adsorption experiments were carried out at three different institutes. Based on the TG data, activation at 130°C up to 500°C was carried out in air (75 mL min⁻¹) for all measurements. The specific surface area of the dehydrated CAU-1-(OH)₂, was determined measuring the N₂ sorption isotherms at 77 K. Several tests showed that the reaction mixture reached the critical energy of 16.6 keV and gave a positron beam energy of 5.4 GeV. The energy range from 6 to 57 keV exhibits a maximum at a critical energy of 16.6 keV and gives a positron beam energy of 5.4 GeV. The beamline receives white synchrotron radiation from a bending magnet with a critical energy of 16.6 keV and gives a positron beam energy of 4.5 GeV. The energy range from 6 to 77 keV exhibits a maximum at about 25 keV. A liquid-nitrogen-cooled solid-state germanium detector with a resolution of about 1% was used in situ investigations were carried out using conventional as well as MW heating. For conventional heating, the reactions were performed in glass tubes in special autoclaves within the copper block next to the autoclave and regulated to an accuracy of ±1 K. Several tests showed that the reaction mixture reached the reaction temperature within two minutes.[10] For the microwave reactions, a slightly modified version of the commercially available Biotage Initiator microwave synthesizer was used. The reaction temperature attained within 1 min corresponded to ramp rates of 2–5°C/s. Reactor vials with an internal diameter of 14 mm and a volume of 10 mL were used throughout the study. Temperatures were measured using an internal IR sensor. To increase beam intensity on the detector, two holes were drilled into the microwave reaction chamber to assure an unhindered synchrotron beam path through the reaction vessel. With this setup, we are able to record time-resolved X-ray powder patterns with acceptable counting statistics within acquisition times of 30 to 120 s. The resulting spectra were evaluated with the tool “calif,” which can be obtained for free at beamline F3. For the data evaluation, the intensive 011 reflection was used. The data are background-corrected and the peaks were fit with Gaussian functions.

**Acknowledgements**

We thank DESY for the beamtime (project no. II-2008002SEC), Andre Rothkirch for the software support, and Mark Feyand for his assistance during the data evaluation. The State of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft (DFG, SPP 1362 “Porous Metal-Organic Frameworks” under the grant STO 643/5-1 and STA 428/17-1) are gratefully acknowledged for the financial support. The research that led to these results has received funding from the European Community’s Seventh Framework Programme (FP7/2007–2013) under grant agreement no. 228062.

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Received: December 22, 2010
Published online: April 27, 2011