Synthesis, transformation, catalysis and gas sorption investigations on the bismuth metal-organic framework CAU-17

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Abstract: Very few microporous bismuth metal-organic frameworks have been discovered to date, and of these no detailed experimental characterization of the synthesis and properties have been reported until now for the only one which can be prepared from inexpensive starting materials: CAU-17 [Bi(BTC)(H_2O)], with H_3BTC = trimesic acid. *In situ* X-ray powder diffraction during solvothermal synthesis of CAU-17 revealed that it crystallizes rapidly within 2 minutes, and if the reaction is not stopped the MOF transforms into a nonporous dense purely inorganic material within one hour, revealing that CAU-17 is a crystalline intermediate phase. Synthesis scale-up employing more concentrated reaction mixtures resulted in another Bi trimesate of composition [Bi(HBTC)(NO_3)(MeOH)]·MeOH, which structurally decomposes upon storage under ambient conditions. Sorption experiments showed that CAU-17 is microporous with a BET surface area of 530 m^2/g. As a potential greenhouse gas sorbent, CAU-17 showed high SF_6/N_2 and CO_2/N_2 selectivity > 31 and 29, respectively. Furthermore, the catalytic activity of CAU-17 was studied in the regioselective ring-opening of styrene oxide by methanol to obtain 2-methoxy-2-phenylethanol, thus demonstrating the existence of coordinatively unsaturated sites in the crystal structure of CAU-17.

Introduction

Metal-organic frameworks[1–6] (MOFs) are a flourishing class of porous materials built of metal cations bridged by organic linker molecules, and have potential applications in gas storage,[7] gas separation,[8] heterogeneous catalysis[9] and medicine.[10] The use of bismuth cations in the formation of MOFs is of interest for their unusual properties for a heavy metal. Despite being the heaviest quasi-stable element ($t_{1/2}(^{209}Bi) = 1.9 \cdot 10^{19}$ a),[11] bismuth and its compounds are generally nontoxic and several are even used as metallodrugs to treat wounds and gastrointestinal disorders.[12–16] Although some MOFs consisting of lighter metal cations have been predesigned and successfully synthesized through prior knowledge of common inorganic building units and concepts of reticular chemistry,[17] the structural behavior of Bi^{3+} ions in solvothermal reactions of MOFs remains highly unpredictable, and most bismuth MOFs have very unique inorganic building units that differ from structure to structure. Also, the large ionic radius of Bi^{3+} ions (r (Bi^{3+}) = 1.31 Å, CN = 8) leads to highly complex and irregular coordination geometries around the Bi^{3+} cations, which are often influenced by the $6s^2$ lone pair of electrons.[18] Characterization of bismuth oxido clusters forming as metastable reaction products is a big challenge, as demonstrated in literature.[19]

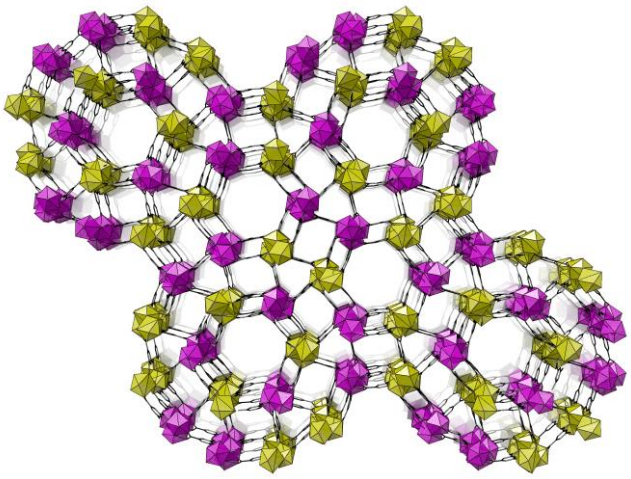

Figure 1. Crystal structure of CAU-17 (view along [001]). Bi-O-helices are shown in yellow (left handed) and purple (right handed).

However, the synthesis of microporous bismuth-based MOFs still remains a challenge today. Only four permanently microporous MOFs (i.e. type I isotherms for N_2) have been successfully synthesized using Bi^{3+} cations, to the best of our knowledge, including CAU-7,[20] NOTT-220,[21] CAU-17[22] and CAU-35.[23] All of these MOFs have only been discovered within the past five years, and relatively few detailed analyses of their properties and their potential applications have been reported. CAU-7 has been described as a mild heterogeneous Lewis acid catalyst as demonstrated for the hydroxymethylation of 2-methylfuran,[20] and high gravimetric uptake of CO_2 and CH_4 was reported for NOTT-

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Supporting information (SI) for this article is given via a link at the end of the document. The crystallographic information for **3** is available in the Cambridge Structural Database (CSD) as CCDC 1579911.

220.[21] Of these four microporous bismuth MOFs, CAU-17 is the only one that is synthesized using an inexpensive reagent for the organic linker: trimesic acid. We recently reported the crystal structure of CAU-17 (**1**, [Bi(BTC)(H_2O)], where BTC^{3-} = 1,3,5-benzenetricarboxylate or trimesate), although without details of its synthesis, transformations, properties, and potential applications.[22] The crystal structure is built of left- and right-handed helices of edge-sharing BiO_9-polyhedra that are linked by BTC^{3-} ions to form a framework with hexagonal, rectangular and triangular channels with pore diameters of 9.6, 3.6 and 3.4 Å, respectively, as obtained by considering the van der Waals radii of the pore wall atoms (Fig. 1).[22] Every Bi^{3+} ion is coordinated by one terminal H_2O molecule, which can be removed reversibly (see H_2O sorption in supporting information (SI)). Regarding its topology, CAU-17 has by far the most complex underlying net among all observed MOF structures to date with 54 unique nodes connected by 135 edges. As CAU-17 is currently the only bismuth MOF that can be synthesized from inexpensive reagents and is one of the more intricate MOF structures known to date, detailed studies on its synthesis, stability and properties are certainly warranted.

Researchers have been striving to improve their understanding of the synthesis mechanisms of MOFs in order to achieve better control over their particle size, shape, and other physical and chemical properties and also to discover novel short-lived intermediate phases.[24] Since solvothermal reactions are often performed with long reaction times (typically on the order of days or weeks), short-lived crystalline intermediates can easily be overlooked. Intermediates can be more interesting than the products they eventually transform into with prolonged reaction times, since later products tend to form more thermodynamically stable dense crystal structures. *In situ* powder X-ray diffraction (PXRD) has been an invaluable tool for understanding such crystallization processes.[25–27] In an investigation of the synthesis mechanisms of bismuth trimesates hydrothermally synthesized in water *in situ* PXRD revealed rapid formation of the first crystalline product, followed by sequential transformations into a second and third crystalline phase after extended heating time.[28] The evolution of the materials with heating time was elucidated by quenching the reaction to isolate the three individual phases for crystal structure determination.[28] In total, six crystalline bismuth trimesate structures have been reported thus far, and the large number of crystal structures that can be synthesized from the same combination of Bi^{3+} and linker is attributed to the flexible coordination environment of Bi^{3+} ions. However, apart from CAU-17, which is synthesized in methanol, the remaining five crystalline phases are dense nonporous materials.[28–30]

MOFs are widely studied heterogeneous catalysts due to their unique properties, high surface areas and the availability of different active sites.[31–34] Among the various positions of active sites such as in the linkers or in the empty spaces of MOFs,[35] one of the frequently used active sites in MOFs are the metal nodes as Lewis acid sites.[36–39] Ring opening of epoxides is considered as a model reaction to probe the catalytic activity of different solid materials with such active sites.[35,40–46] Obviously, these solids are expected to be beneficial in comparison to their corresponding homogeneous counterpart due to the ability to recover and reuse the catalyst in consecutive cycles.

Storage and separation of gases is another important property of MOFs which has been in the focus of many investigations. Thus *Zhou* and coworkers very recently performed grand canonical Monte Carlo simulations and dispersion-corrected density functional theory to model the sorption of CH_4 and H_2 by CAU-17 which suggest the material has high CH_4/H_2 selectivity compared to several classic MOFs.[47] Due to the pore diameter of the hexagonal pores of CAU-17 (9.6 Å from the crystal structure) this MOF could be of particular interest for adsorption and separation of the greenhouse gas SF_6, which is considered as the most potent greenhouse gas according to an investigation by the Intergovernmental Panel on Climate Change.[48] Other microporous materials with similar pore diameters, such as zeolite Y (10 Å),[49] MOF-74 (11 Å)[50] and porous organic cages[51] have been shown to be suitable for the separation of SF_6 from N_2.

Herein we present the results of our systematic study on the synthesis and transformation of CAU-17 by *in situ* PXRD, thermal and chemical stability, and its application in heterogeneous catalysis and gas separation. In this work we present for the first time *in situ* PXRD studies, utilizing a custom-built reactor, on the formation and transformation of CAU-17 revealing that the material is a crystalline intermediate.

Results and Discussion

Synthesis and transformation of CAU-17

The synthesis of CAU-17 was systematically studied to learn more about the crystallization process and to optimize the synthesis, i.e. to improve the yield. The synthesis was always performed in glass vials, which were either placed in a pre-heated aluminium block or heated by microwave radiation and stirred during the reaction. The vials were utilized with a volume of 2.5 mL or 20 mL solvent respectively. The *in situ* PXRD studies were carried out in the custom-made SynRAC (synchrotron-based reaction cell for the analysis of chemical reactions) set-up.[52] It allows the investigation of solvothermal syntheses in glass vials, which are typically used in research and which have been used in reactions employing the aforementioned custom-made aluminium block. These vials can be heated to the target temperature within only a few minutes (Fig. S3-S9). The set-up can be penetrated by synchrotron X-rays, allowing *in situ* PXRD data to be collected during formation and transformation of crystalline products without disturbing the solvothermal reaction. The *in situ* PXRD studies of the crystallization of CAU-17 revealed that it already forms during the heat-up process even before the reaction mixture reaches the target temperature (Fig. 2). After a short reaction time, porous CAU-17 transforms into an unknown purely inorganic dense phase of composition $Bi_2O(OH)_3(NO_3)\cdot xH_2O$ (**2**) (Fig. S11), which could not be structurally characterized due to poor crystallinity. Increasing the reaction temperature also increases the rate of transformation. Bragg reflections of **2** appear after 31 min (120 °C), 18 min (130 °C) and 11 min (140 °C) of reaction time (Fig. S2). These observations are consistent with the fact that products with denser (non-porous) crystal structures are generally

thermodynamically more stable and tend to form after longer reaction times.

The synthesis of CAU-17 is generally sensitive to changes of the reaction conditions. Especially at lower temperatures (<120 °C), the reaction mixture tends to form unknown impurities at short reaction times. To synthesize phase pure CAU-17, the synthesis conditions were optimized to a reaction time of 20 min and a temperature of 120 °C. Since *in situ* PXRD revealed that the crystallization of CAU-17 occurs spontaneously during the initial heat-up process, a kinetic study of the crystallization process was not possible.

Structural characterization of **2** was not successful. Continuous rotation electron diffraction[53] was employed to determine the structure of **2**, or at least the lattice parameters, but due to diffuse scattering along the c* axis (Fig. S10) this could not be accomplished despite numerous attempts. However, the two well-ordered axes indicate that the lattice parameters are approximately: a = 10 Å, b = 10 Å, c = X, α = 90°, β = 90°, γ = 120° (X could not be established due to diffuse scattering). Elemental and TG analysis revealed the formation of a purely inorganic compound with the composition $Bi_2O(OH)_3(NO_3)\cdot xH_2O$ (Tab. S1 and Fig. S13). Thus, this transformation can only take place in a nitrate ion containing medium, such as the reaction mixture.

During the synthesis optimization of CAU-17 a new crystalline phase, [Bi(HBTC)(NO_3)(MeOH)]·MeOH (**3**), was discovered throughout the synthesis scale up, when the concentration of starting materials was increased (crystallographic and refinement details are provided in the SI). The open-framework structure of **3** is built of corner sharing BiO_9 polyhedra that are interconnected by NO_3^- ions to form chains along the *a*-axis. Three chains are connected by a $HBTC^{2-}$ ion resulting in a one-dimensional channel system along the *a*-axis. The –COOH group only coordinates with one oxygen atom to the Bi^{3+} ion, while in contrast the $–COO^-$ groups coordinate as bidentate ligands. Every Bi^{3+} ion has a terminally coordinating methanol molecule in its coordination sphere, and additionally there is one methanol molecule per formula unit in the pores as a guest (Fig. 3 and Fig. S33-S35). Upon storage under ambient conditions the compound rapidly loses its crystallinity due to the removal of methanol.

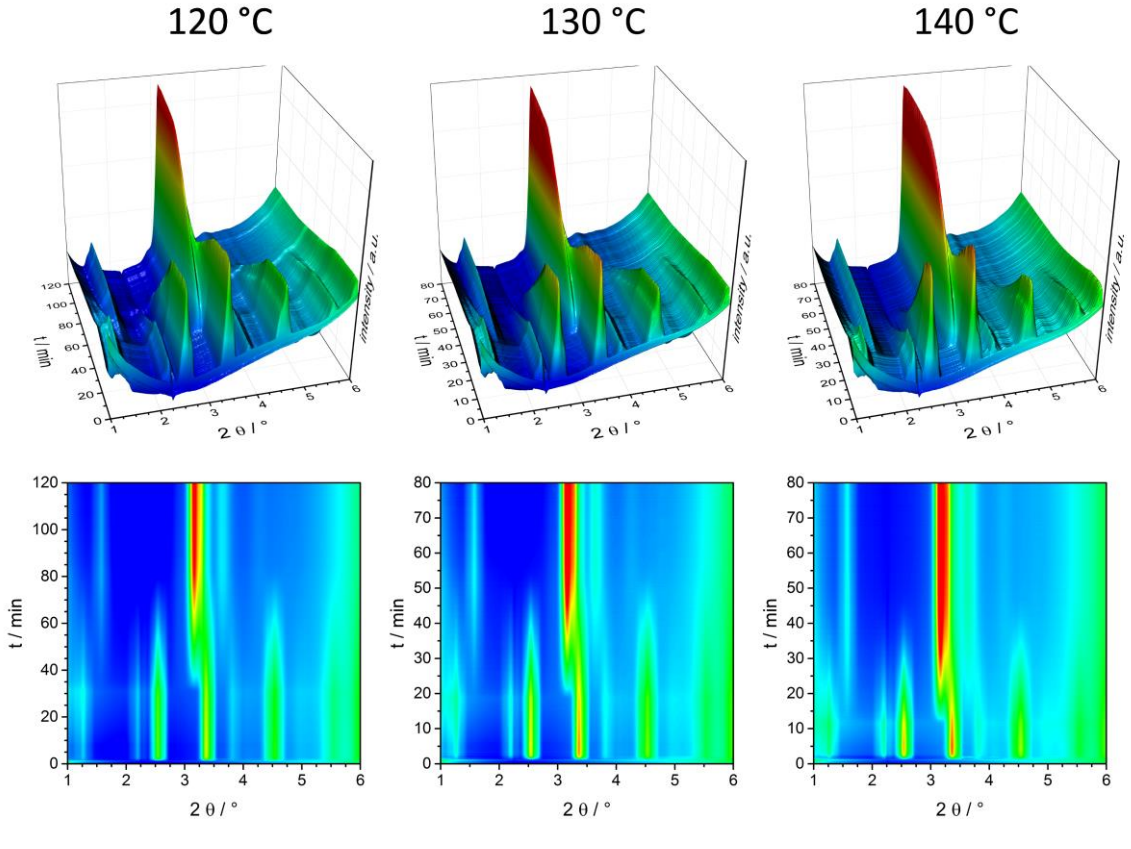


Figure 2. *In situ* PXRD datasets collected during the reaction of Bi^{3+} with H_3BTC in methanol employing synchrotron radiation at beamline P09, PETRA III, Hamburg, Germany (λ = 0.539 Å). (Top) 3D projection, (bottom) 2D projection. The conversion of CAU-17 into **2** is noticeably faster at higher temperatures.

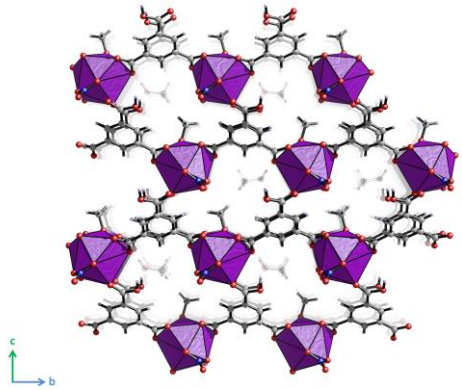


Figure 3. Crystal structure of [Bi(HBTC)(NO_3)(MeOH)]·MeOH (**3**). Bismuth cations are represented as purple polyhedra. Carbon, nitrogen and hydrogen atoms are colored grey, blue and pink respectively. Guest molecules (MeOH) in the pores are translucent.

Thermal and chemical stability

Temperature-dependent PXRD performed in an open capillary revealed changes to the unit cell parameters of CAU-17 at elevated temperatures, which could be recognized by small shifts of the reflections (Fig. 4). A sequential Le Bail fit of the PXRD patterns was performed to analyze the temperature dependency of the unit cell parameters (with error bars see, Fig. S14). The unit cell volume as well as the cell parameters *a* and *b* increase from room temperature up to 100 °C while the parameter *c* decreases, indicating a contraction of the inorganic helices. Up to ca. 120 °C, as determined by thermogravimetric (TG) measurement (Fig. S27), the coordinated H_2O molecules are removed. Although the sample temperature is further increased a shrinking of all unit cell parameters and the unit cell volume up to a temperature of T=270 °C is observed. This qualifies CAU-17 for further investigations of the phenomenon negative thermal expansion (NTE), which has already been reported for other metal-organic frameworks, but a detailed investigation of this property is outside the scope of this publication.[54] Finally, framework decomposition was observed at ~370 °C.

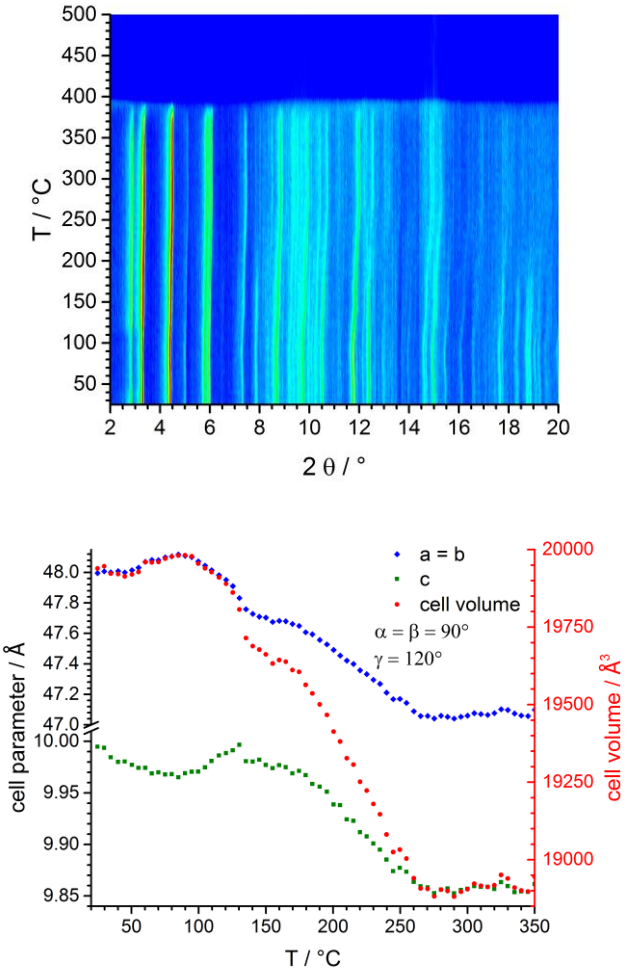


Figure 4. Temperature-dependent PXRD data (top, λ = 0.7093 Å) and results of a sequential Le Bail fit of the cell parameters of CAU-17 (bottom).

To investigate the chemical stability of CAU-17, 20 mg of the MOF were each stirred in different solvents for 24 h at room temperature, filtered and washed with methanol. The exposure to water and aqueous HCl/NaOH at different pH led to a (partial) structural transformation of CAU-17 ([Bi(BTC)(H_2O)]) into the dense pseudo-polymorph [Bi(BTC)(H_2O)]·H_2O[28] (**4**) or resulted in the full degradation of the CAU-17 structure. However, in organic solvents, the structure was maintained in most stability tests. The PXRD patterns of these products and their analysis are given in the SI (Fig. S15-S17).

In order to attain insight into the stability of CAU-17 in water at elevated temperatures, 15 mg of CAU-17 was stirred in 2.5 ml H_2O, while simultaneously recording *in situ* PXRD data of the mixture. In order to accelerate the expected transformation from CAU-17 into **4**, the temperature of the mixture was first set to 120 °C and kept for 90 min. Surprisingly, no immediate structural change was observed. Hence the temperature was stepwise increased by 10 °C every 30 min. Finally at 160 °C/180 min (Fig. 5, right, blue dashed line) a decrease in the intensities of the

reflections takes place and at 170 °C (Fig. 5, right, red dashed line), a sudden change in the powder pattern occurs and CAU-17 transforms to a product with low crystallinity which is different from **2** (Fig. S18). This experiment indicates that CAU-17 can be exposed to water for a rather short time, even at elevated temperatures up 150 °C without losing its crystallinity, while an exposure to aqueous solutions for 24 h at room temperature leads to a partial degradation of CAU-17. However, storing CAU-17 under ambient conditions does not cause degradation of the crystal structure which was proven by PXRD of a ~2 year old sample, Fig. S29).

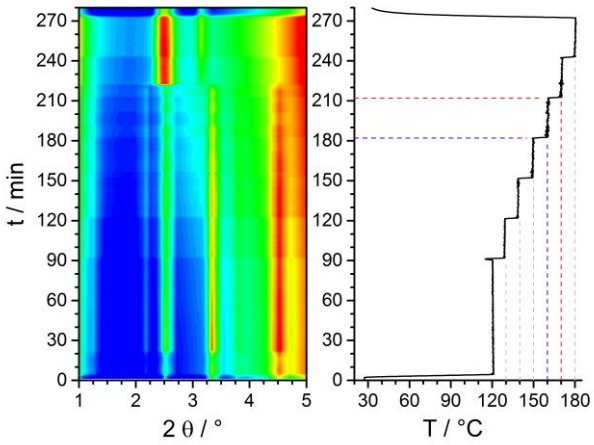


Figure 5. (Left) *In situ* PXRD datasets collected during the stirring of CAU-17 in water at elevated temperatures (λ = 0.539 Å). (Right) Reaction time and temperature corresponding to the *in situ* PXRD data shown left.

Greenhouse gas separation and adsorption

The sorption properties of CAU-17 were also investigated in detail. The Langmuir ($S_{Langmuir}$) and BET (S_{BET}) surface areas were determined by N_2 sorption as 650 m^2/g and 530 m^2/g, respectively. The total micropore volume was 0.24 cm^3/g, calculated using the adsorption point at $p/p_0 = 0.98$.

In order to examine the performance of CAU-17 as an adsorbent, sorption experiments with N_2, SF_6, as well as CO_2 were performed at different temperatures (0-55 °C) between 0 and 1 bar (Fig. S21). The CO_2 and SF_6 uptakes were significantly higher than the N_2 uptake at all tested temperatures (0, 20, 40, 55 °C). The uptake of CO_2 at 0°C, 1 bar reached 3.36 mmol/g. Under the same conditions, the SF_6 and the N_2 uptakes were 1.61 mmol/g and 0.36 mmol/g, respectively (Fig. 6). The performance of CAU-17 to separate gas mixtures was estimated using the ideal adsorbed solution theory (IAST). In the case of CO_2/N_2 mixtures, a temperature dependency was observed. The selectivity dropped from ~29 at 0 °C to 15 at 55°C (at 100 kPa). Simulations performed by *Zhou et al.* on CAU-17 suggested a CO_2/N_2 selectivity (at 25°C 1 bar) lower than that calculated here using IAST based on our experimental data across the entire tested temperature range.[47] The selectivity for SF_6/N_2 mixtures was higher in general, and fairly constant (~31) at all tested temperatures. The high selectivity was expected due to the diameter of the hexagonal pores, i.e. 9.6 and 9.3 Å as determined from the crystal structure and DFT calculations using the N_2 adsorption isotherms, respectively. The SF_6/N_2 selectivity and total uptake values of ~31 and 1.61 mmol/g for CAU-17, respectively, are not quite as high as reported for the benchmark materials Zn-MOF-74 (46.1) and Co-MOF-74 (1.96 mmol/g), calculated for a 10% SF_6/90% N_2 mixture.[50] A detailed analysis of all sorption related results, including water adsorption experiments performed at 20°C and the calculated heat of adsorption for CO_2 and SF_6, can be found in the SI.

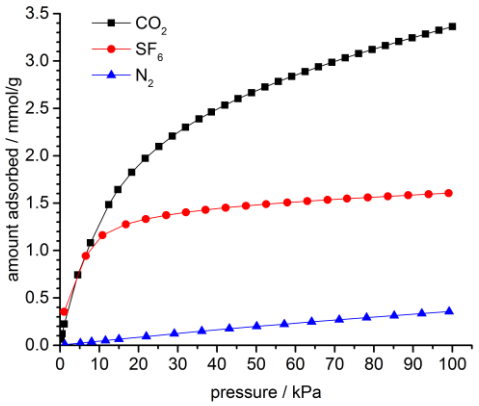
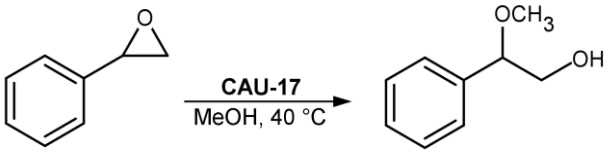


Figure 6. Adsorption isotherms of CAU-17 with CO_2, SF_6 and N_2 recorded at 0°C.

Heterogeneous catalysis

The catalytic activity of CAU-17 was investigated in the ring opening of styrene oxide to 2-methoxy-2-phenylethanol using methanol as solvent and nucleophile under mild reaction conditions (Scheme 1). Compounds **2** and **3** were not investigated due to their low crystallinity and stability, respectively.



Scheme 1. Regioselective ring opening reaction of styrene oxide catalyzed by CAU-17 in methanol.

The blank control experiment showed no product formation, thus indicating the need of a catalyst to promote this reaction. In contrast, the ring opening of styrene oxide in the presence of activated CAU-17 (120 °C, 3 h under reduced pressure) resulted in complete conversion with 100% regioselectivity to 2-methoxy-2-phenylethanol. The time-conversion plot for this conversion with the formation of desired product is given in Figure 7. This behavior can be easily understood from the fact that the water molecules

coordinating to Bi^{3+} ions in the framework can be removed, thus, creating free coordinatively unsaturated sites which in turn act as catalytic Lewis acid sites. In order to test this hypothesis, a control experiment was performed using the as-synthesized CAU-17 without any activation and the observed result clearly show a lower activity compared to the activated CAU-17 under identical reaction conditions. A filtration test was carried out to verify the stability of the CAU-17 catalyst. Thus, the catalyst was removed by filtration after 21 h and the reaction was continued. No further product is formed which infers that catalysis is truly heterogeneous. Furthermore, no noticeable changes are observed by PXRD (Fig. S30) and the activity of CAU-17 was retained in two consecutive catalytic reactions. These results clearly indicate that CAU-17 is a stable, recyclable catalyst for this reaction.

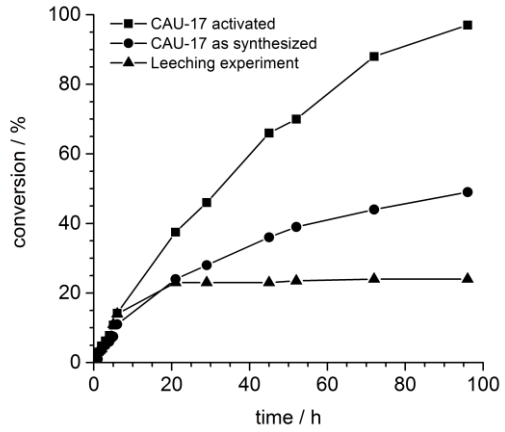


Figure 7. Time conversion plot for the ring opening of styrene oxide catalyzed by activated or as-synthesized CAU-17 and filtration test (leaching experiment). Reaction conditions: styrene oxide (1 mmol), catalyst (50 mg), methanol (3 mL), 40 °C.

These encouraging results observed with CAU-17 prompted us to compare its activity with the ones of its dense pseudo-polymorph $[Bi(BTC)(H_2O)]\cdot H_2O$[28] (**4**) and the MOF CAU-7[20] under identical reaction conditions. The crystal structure of CAU-7 ([Bi(BTB)], where BTB^{3-} = 1,3,5-benzenetrisbenzoate) is built of linear chains of face sharing BiO_9 polyhedra that are interconnected by BTB^{3-} ions to form slightly distorted hexagonal channels arranged in a honeycomb net. The observed results are presented in Figure 8. The overall conversion rate increases with time for all three catalysts. Compound **4** displayed a linear relationship between conversion rate and time, which was not observed for the other two catalysts. The initial reaction rate depends on the catalyst used (CAU-17 > CAU-7 > **4**). This suggests that CAU-17 is a superior catalyst for this reaction compared with **4** and CAU-7. The differences in activity between CAU-7 and **4** can be explained in terms of stability. PXRD of the different catalysts after the activation and after the reaction (Fig. S31-S32) revealed that the catalyst **4** structurally degrades during the activation.

The catalytic activity of CAU-17 in the regioselective ring opening reaction of styrene oxide is inferior to those reported for other MOFs[42,44,55] but there are also studies that reports the necessity of long reaction times.[56,57] Nevertheless the study clearly demonstrates the existence of coordinatively unsaturated sites in the crystal structure of CAU-17.

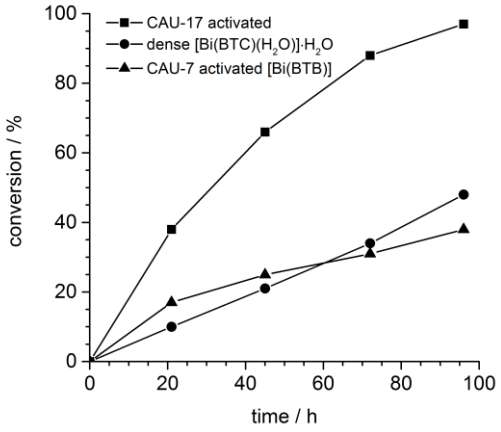


Figure 8. Time conversion plot for the ring opening of styrene oxide by CAU-17, dense phase **4** and CAU-7 as catalysts. These catalysts were activated before catalytic reaction at 120 °C for 3 h under vacuum.

Conclusions

In summary, a detailed analysis of the synthesis of CAU-17 was presented displaying not only its fast formation but also its transformation into a dense phase upon prolonged reaction times as well as the formation of another bismuth trimesate $Bi(HBTC)(NO_3)(MeOH)]\cdot MeOH$ (**3**) upon increase of the reactant concentrations. The *in situ* PXRD results exemplify the possible importance of short reaction times in MOF synthesis. The reaction of bismuth nitrate and trimesic acid depends strongly on the solvent employed. As observed for water as solvent multiple crystalline phases are also obtained in methanol. The crystal structure exhibits some interesting features. Thus the thermal stability (~350 °C) and the possibility to remove coordinating water molecules render this compound as a heterogeneous catalyst in the 100 % regioselective conversion of styrene oxide into 2-methoxy-2-phenylethanol. The size of the hexagonal one-dimensional pores allows for a high adsorption capacity and selectively for greenhouse gases such as CO_2 and SF_6 over N_2. Last not least the temperature-dependent PXRD study of CAU-17 has revealed interesting structural behavior, which needs to be explained in detail in the future.

Experimental Section

The chemicals were purchased from Aldrich, Alfa Aesar or Walter CMP and used without further purification. HPLC grade methanol was used as

the solvent in catalytic reactions. Syntheses were carried out under solvothermal conditions in a Biotage Initiator microwave oven employing 10 or 30 mL vials or in a custom-made aluminum block placed on a heating stirrer plate using DURAN culture tubes 12x100 mm D50 GL 14M.KAP. PXRD measurements were carried out with $CuK_{\alpha1}$ and $MoK_{\alpha1}$ radiation on a Stoe Stadi P Combi diffractometer in transmission geometry, equipped with a MYTHEN detector. Temperature-dependent PXRD was performed in a Stoe capillary furnace in a 0.5 mm quartz capillary. Gas Chromatography 6890N network Agilent Technologies was used for determining the conversion and selectivity using a FID detector and the product was confirmed by Hewlett Packard 5971A GC-MS instrument in catalytic reactions. The sequential LeBail-fit was performed in TOPAS Academic 4.[58] Thermogravimetric measurements were performed on a NETZSCH STA-409CD under air flow of 75 ml/min with a heating rate of 4 K/min. IR spectra were measured on a Bruker ALPHA-P spectrometer using an ATR unit.

***In situ* PXRD crystallization experiment:** The *in situ* PXRD crystallization experiments were carried out at PETRA III, beamline P09 at DESY, Hamburg (Germany). Diffraction data were collected on a Perkin Elmer Digital X-ray Flat Panel Detector (λ = 0.53905 Å). The sample-detector distance was set to 592 mm to measure a 2θ-range of approximately 0.7-36°. The custom-made SynRAC set-up was used to heat the reaction mixture.[52] The reaction mixture was cooled after the reaction with compressed air. Detailed full temperature profiles of the reactions are provided in the SI (Fig. S4, S7, S9). The data was normalized to the Al-reflection of the reactor window in order to eliminate absorption problems, caused by particles in the beam, which lead to fluctuating intensity.

Preparation of the *in situ* PXRD experiment $Bi(NO_3)_3$/trimesic acid/MeOH: A mixture of trimesic acid (H_3BTC, 50.0 mg, 238 µmol) and ground $Bi(NO_3)_3{\cdot}5\,H_2O$ (100 mg, 207 µmol) in 2.5 mL MeOH was dissolved at room temperature by shaking for 1 min, waiting 1 min and shaking for 1 min again. The sealed glass vial was heated in a custom-made reactor system to 120-140 °C under stirring.

Synthesis of $[Bi(BTC)(H_2O)]$ (CAU-17, 1): To a mixture of trimesic acid (H_3BTC, 250 mg, 1.19 mmol) and ground $Bi(NO_3)_3{\cdot}5\,H_2O$ (502 mg, 1.04 mmol) in a 30 mL glass vial, 20 mL MeOH were added carefully. The sealed vial was heated in the microwave oven to 120 °C and kept at this temperature for 20 min under stirring with 600 rpm. After cooling the solid product was filtered off and washed with MeOH. A white powder was obtained in a yield of 239.5 mg (46% based on H_3BTC). Phase purity was confirmed by PXRD (Fig. S29-S30) and elemental analysis (calculated (%) for $Bi(C_9O_6H_3)(H_2O)_4$: C 22.1 H 2.27; measured (%): C 21.7 H 1.49).

Synthesis of the final product of the *in situ* experiments ($Bi_2O(OH)_3(NO_3){\cdot}xH_2O$, 2): To obtain a suitable amount of **2** for characterization, the following procedure was used: A mixture of trimesic acid (H_3BTC, 250 mg, 1.19 mmol) and ground $Bi(NO_3)_3{\cdot}5\,H_2O$ (502 mg, 1.04 mmol) was dissolved in 20 mL MeOH at room temperature by shaking for 1 min, waiting 1 min and shaking for 1 min again in a 30 mL glass vial. The sealed vial was heated in the microwave oven to 120 °C and kept at this temperature for 3 h under stirring with 600 rpm. After cooling the solid product was filtered off and washed with MeOH. A white powder was obtained in a yield of 240 mg. Further details are given in the SI.

Synthesis of $[Bi(HBTC)(NO_3)(MeOH)]{\cdot}MeOH$ (3): To a mixture of trimesic acid (H_3BTC, 300 mg, 1.43 mmol) and ground $Bi(NO_3)_3{\cdot}5\,H_2O$ (603 mg, 1.24 mmol), 2 mL MeOH were added. The sealed glass vial (DURAN culture tubes 12x100 mm D50 GL 14M.KAP) was placed in a pre-heated aluminium block for 50 min at 50 °C without stirring. The solid product was filtrated and washed with 10 mL MeOH. A white powder was obtained by centrifugation in a yield of 438 mg (69% based on H_3BTC). Phase purity was confirmed by PXRD (Fig. S36) and elemental analysis (calculated (%) for $Bi(C_9O_6H_4)(NO_3)(CH_3OH)(H_2O)$: C 22.7 H 1.90 N 2.65; measured (%): C 21.7 H 1.61 N 2.92). The sample was stored at 4 °C to avoid evaporation of the MeOH, which leads to degradation of the structure. Suitable single crystals could be obtained by mixing trimesic acid (H_3BTC, 125 mg, 595 µmol) and ground $Bi(NO_3)_3{\cdot}5\,H_2O$ (251 mg, 517 µmol) with 5 mL MeOH at room temperature by shaking. The sealed glass vial was heated in the microwave oven to 120 °C and kept at this temperature for 18 min without stirring. The obtained white single crystals were collected by filtration and washed with MeOH.

Synthesis of CAU-7: Synthesis was performed following a previously described procedure.[20]

Synthesis of $[Bi(BTC)(H_2O)]{\cdot}H_2O$ (4, dense phase): The synthesis has been derived from the literature known synthesis.[28] To a mixture of trimesic acid (H_3BTC, 300 mg, 1.43 mmol) and ground $Bi(NO_3)_3{\cdot}5\,H_2O$ (693 mg, 1.43 mmol), 20 mL distilled water were added. The sealed glass vial was heated in the microwave oven to 130 °C and kept at this temperature for 5 min under stirring with 600 rpm. After cooling the product was filtered off and washed with DMF and water. A white powder was obtained in a yield of 636.6 mg (99% based on H_3BTC). Phase purity was confirmed by PXRD (Fig. S32) and elemental analysis (calculated (%) for $Bi(C_9O_6H_3)(H_2O)_2$: C 23.9 H 1.56; measured (%): C 22.9 H 1.96).

Chemical stability experiments: The chemical stability was investigated by using the following procedure: A defined amount of 2 mL (4 mL in case of solutions at different pH) were added to 20 mg of **1** in a 5 mL glass vial with a stir bar. The mixture was stirred for 24 h at room temperature and then filtered off and washed with 2 mL of methanol. The water stability experiment was carried out similar to the *in situ* experiments. For this, 15 mg of **1** was stirred in 2.5 ml H_2O while recording PXRD patterns of the mixture and subsequently elevating the temperature (compare: *In situ* PXRD crystallization experiment).

Gas adsorption experiments: Prior to the gas adsorption measurements, the samples were first pretreated under dynamic vacuum at 120 °C for 6 hours, then at 300 °C for further 6 hours. The pretreatment steps were carried out using a Micromeritics SmartVacPrep sample preparation device. Gas adsorption measurements were carried out using a Micromeritics ASAP2020 analyzer. Specific surface area (BET and Langmuir), DFT pore size distribution and total pore volume were calculated using the nitrogen sorption isotherm recorded at liquid nitrogen temperature (-196 °C) for p/p_0 = 0 to 0.99. N_2, SF_6 and CO_2 adsorption isotherms were recorded at 0-55 °C for a pressure range between 0 and 1 bar. A water adsorption isotherm was recorded on the same instrument using the vapor sorption module at 20 °C for $0 \leq p/p_0 \leq 0.95$. Adsorption equilibrium was defined as when the pressure change of the system drops below 0.01% during a 10 s interval (with a minimum 100 s delay). The selectivity calculations were carried out using MATLAB R2014a running with a set of self-written codes.

Procedure for catalytic reactions: A 25 mL round-bottomed flask was charged with the catalyst and styrene oxide (1 mmol) in methanol (3 mL). The ratio between styrene oxide to Bi in the activated CAU-17 was about 10:1. The reaction mixture was stirred for the required time. The reaction was monitored periodically by analyzing the sample by GC until the completion of reaction. The percentage conversion and selectivity was determined by GC analysis. The product was confirmed by GC-MS analysis. Whenever required, the catalyst was activated at 120 °C for 3 h under vacuum.

Crystal structure determination of [Bi(HBTC)(NO_3)(MeOH)]·MeOH (3): Single crystal X-ray diffraction data were collected on a Bruker D8 Venture at 150 K (λ = 0. 71073 Å). Data reduction was performed with SAINT and absorption corrections were applied using the multi-scan method (SADABS). Structure determination was performed in ShelXS.[59] Atoms were refined using a full-matrix least squares technique on F^2 in ShelXL. All non-hydrogen atoms were refined with anisotropic displacement parameters. A riding model was used to constrain the coordinates of hydrogen atoms bonded to parent carbon atoms. Distant restraints were applied to O-H bonds in COOH in trimesate ligands and OH groups of methanol.

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Keywords: bismuth • metal-organic framework • porous material • *in situ* • PXRD • SF_6 sorption • styrene oxide • heterogeneous catalysis

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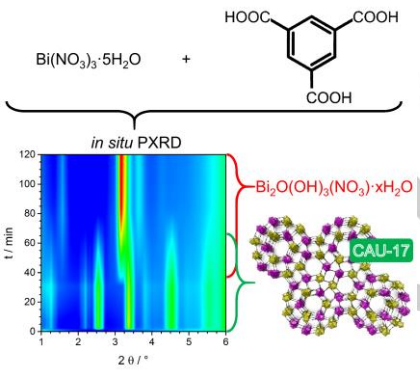
Entry for the Table of Contents

FULL PAPER

The metal-organic framework CAU-17 is the first bismuth MOF synthesized from cheap starting materials. Its properties were investigated with *in situ* PXRD (fast crystallization), thermodiffraction (shrinking unit cell upon heating), $N_2/CO_2/SF_6$ sorption (high selectivity) and by using CAU-17 as catalyst in the ring opening reaction of styrene oxide.



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Synthesis, transformation, catalysis and gas sorption investigations on the bismuth metal-organic framework CAU-17