The impact of crystal size and temperature on the adsorption-induced flexibility of the Zr-based metal-organic framework DUT-98

Simon Krause1,2*, Volodymyr Bon1, Hongchu Du3,4, Rafal E. Dunin-Borkowski3, Ulrich Stoeck1, Irena Senkovska1, Stefan Kaskel1*

* correspondence to Simon Krause: simon.krause@rug.nl, Stefan Kaskel: Stefan.kaskel@tu-dresden.de

1. Materials and Methods
The following chemicals and methods were applied in the synthesis and analysis of DUT-981: ZrCl₄ (Sigma Aldrich), N,N-dimethylformamide anhydrous (<150 ppm H₂O, Sigma Aldrich), acetic acid (Fisher Scientific) and ethanol (abs.) (VWR Prolabo) were used as received. The Ligand H₃CPCDC was used from a previous study1,2.

Powder X-ray diffraction (PXRD) patterns were collected with a PANALYTICAL X’Pert Pro diffractometer operated at 40 kV and 30 mA with monochromated Cu-Kα₁ (λ = 0.15405 nm) radiation. The samples were placed on a Si sample holder. Variable Temperature PXRD was perform in a closed chamber under dynamic vacuum of 10⁻⁴ mbar on a PANALYTICAL X’PERT PRO with λ = 0.15405 nm in Bragg-Brentano-geometry. The temperature was raised with 5 K min⁻¹ starting at 300 K. For each selected temperatures PXRD patterns in the 2θ-range from 4 up to 22 °, with a step size of 0.028 ° and 40 s per step were recorded. Gas and vapour adsorption experiments were carried out on a Belsorp-max (MicrotracBEL Corp., Japan). High purity gases were used (N₂: 99.999%, He: 99.999%). Water adsorption isotherms were recorded at 298 K using a Hydrosorb of Quantachrome Instruments. Thermogravimetric analyses (TGA) were carried out in air atmosphere using a Netzsch STA 409 thermal analyzer. Scanning electron microscopy (SEM) and Scanning Electron Transmission Microscopy (STEM) images were taken with secondary electrons in a HITACHI SU8020 microscope. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a BRUKER VERTEX 70 spectrometer with 16 scans for each sample and a resolution of 2 cm⁻¹. Prior to the measurement 3 - 5 mg of sample were mixed with 60 mg of dry KBr and pressed in the sample holder. TEM images were recorded with binning 4 at 80 kV accelerating voltage using an FEI Titan G3 50-300 PICO microscope equipped with a 4096 x 4096 pixels Gatan Ultrascan 4000 UHS charge coupled device camera (CCD). The frame exposure time is 0.3 s.
1. Synthesis and activation procedure

General synthesis of DUT-98

Synthesis and activation of DUT-98

Synthesis of DUT-98 samples with varying crystal size was performed as following:

*Synthesis of DUT-98*(1)
The Synthesis was performed according to a previously reported procedure\(^3\).

*Synthesis of DUT-98*(2)
In a 100 ml Schott bottle ZrCl\(_4\) (248 mg, 1.06 mmol) and acetic acid (16 ml, 270 mmol) are dissolved in 30 ml of a 1:1 mixture of DMF and N-methyl-2-pyrrolidon at 80 °C for 3 h. To the solution the ligand H\(_3\)CPCDC (200 mg, 0.53 mmol) is added and dissolved by ultrasonication. The reaction mixture is kept at 120 °C for 2 d to form a white precipitate.

*Synthesis of DUT-98*(3)
In a 100 ml Schott bottle ZrCl\(_4\) (145 mg, 0.6 mmol) and acetic acid (4 ml, 70 mmol) are dissolved in 18 ml of a 1:1 mixture of DMF and N-methyl-2-pyrrolidon at 80 °C for 3 h. To the solution the ligand H\(_3\)CPCDC (120 mg, 0.3 mmol) is added and dissolved by ultrasonication. The reaction mixture is kept at 120 °C for 18 h to form a white gel.

*Synthesis of DUT-98*(4)
In a 100 ml Schott bottle ZrCl\(_4\) (370 mg, 1.6 mmol) and acetic acid (10 ml, 175 mmol) are dissolved in 45 ml of DMF. To the solution the ligand H\(_3\)CPCDC (300 mg, 0.8 mmol) and water (5 ml, 280 mmol) are added and dissolved by ultrasonication. The reaction mixture is kept at 120 °C for 16 h to form a white gel.

Synthesis of DUT-98(Hf)
In a 20 ml Pyrex tube 256 mg (0.8 mmol) HfCl\(_4\) and acetic acid (0.5 ml, 8.75 mmol) are dissolved in 5 ml of DMF. To the solution the ligand H\(_3\)CPCDC (60 mg, 0.16 mmol) and water (0.2 ml, 11.2 mmol) are added and dissolved by ultrasonication. The reaction mixture is kept at 120 °C for 24 h to form a white gel.
An overview of the synthesis parameter is provided in the following table:

**Supplementary Table 1. Reaction conditions**

<table>
<thead>
<tr>
<th>Material ID</th>
<th>solvent</th>
<th>eq. water(a)</th>
<th>eq. acetic acid(a)</th>
<th>Reaction time</th>
<th>Yield (%) (a)</th>
<th>Crystal size(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUT-98(1)(4)</td>
<td>DMF</td>
<td>&lt;0.01</td>
<td>1625</td>
<td>14 d</td>
<td>46</td>
<td>120 µm</td>
</tr>
<tr>
<td>DUT-98(2)</td>
<td>DMF:NMP (1:1)</td>
<td>&lt;0.02</td>
<td>509</td>
<td>2 d</td>
<td>49</td>
<td>10 µm</td>
</tr>
<tr>
<td>DUT-98(3)</td>
<td>DMF:NMP (1:1)</td>
<td>&lt;0.02</td>
<td>233</td>
<td>18 h</td>
<td>52</td>
<td>500 nm</td>
</tr>
<tr>
<td>DUT-98(4)</td>
<td>DMF</td>
<td>350</td>
<td>219</td>
<td>16 h</td>
<td>51</td>
<td>50 nm</td>
</tr>
<tr>
<td>DUT-98(Hf)</td>
<td>DMF:NMP (1:1)</td>
<td>70</td>
<td>55</td>
<td>24 h</td>
<td>55</td>
<td>130 nm</td>
</tr>
</tbody>
</table>

(a) Based on linker H₃CPCDC, (b) Estimated from SEM images, size refers to length of the rod-shaped crystals due to crystal intergrowth no distribution could be determined by the error is estimated to be 200%.

After solvothermal synthesis the powders were with fresh DMF 4 times over a period of 2 days, and suspended in ethanol which was exchanged 6 times for 4 days. A Jumbo Critical Point Dryer 13200J AB (SPI Supplies) was used for supercritical drying. The sample was purged 20 times with liquid CO₂ (purity: 99.995%) at ~ 15 °C over 96 hours before raising the temperature and pressure beyond the critical point and releasing CO₂.

**Supplementary Table 2. BET surfac area, specific pore volume and uptake of nitrogen of the series of investigated DUT-98 samples.**

<table>
<thead>
<tr>
<th></th>
<th>BET Surface area (m² g⁻¹)</th>
<th>N₂-uptake at p/p₀ = 0.1 (cm³ g⁻¹)</th>
<th>N₂-uptake at p/p₀ = 0.98 (cm³ g⁻¹)</th>
<th>Specific pore volume at p/p₀ = 0.98 (cm³ g⁻¹)</th>
<th>Specific micropore volume at p/p₀ = 0.1 (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUT-98(1)</td>
<td>21</td>
<td>21</td>
<td>257</td>
<td>0.4</td>
<td>0.005</td>
</tr>
<tr>
<td>DUT-98(2)</td>
<td>954</td>
<td>232</td>
<td>258</td>
<td>0.41</td>
<td>0.37</td>
</tr>
<tr>
<td>DUT-98(3)</td>
<td>1303</td>
<td>324</td>
<td>442</td>
<td>0.95</td>
<td>0.53</td>
</tr>
<tr>
<td>DUT-98(4)</td>
<td>1161</td>
<td>289</td>
<td>1088</td>
<td>1.66</td>
<td>0.49</td>
</tr>
<tr>
<td>Simulated</td>
<td>1665</td>
<td>464</td>
<td>464</td>
<td>n. V.</td>
<td>0.72</td>
</tr>
<tr>
<td>DUT-98(Hf)</td>
<td>1004</td>
<td>209</td>
<td>674</td>
<td>1.31</td>
<td>0.41</td>
</tr>
</tbody>
</table>

(a) calculated on the basis of DUT-98(Zr)op crystal structure and software POREBLAZER
A change in crystal morphology was observed upon performing multiple adsorption-desorption experiments on the same DUT-98(1) sample. Isotherms of these experiments can be obtained from reference 1 and were performed in the following order: nitrogen 77 K, CO$_2$ 195 K, $n$-butane 273 K, and vapors of methanol, ethanol, 2-propanol, toluene, heptane, acetone, and water all at 298 K.

Supplementary Figure 1. SEM images of DUT-98(1) at different magnifications after supercritical activation before adsorption cycling.
Supplementary Figure 2. SEM images of DUT-98(1) at different magnifications after adsorption cycling

Supplementary Figure 3. PXRD patterns of a) DUT-98 after supercritical activation, b) after adsorption cycling, c) suspended in methanol at 298 K with sample placed in sealed glass capillary. Simulated patterns for DUT-98_{op} and \textit{cp} are given for comparison.
Supplementary Figure 4. SEM images of supercritically activated DUT-98(1). Scale bars a) 500 µm, b) 200 µm, c) 100 µm.

Supplementary Figure 5. SEM images of supercritically activated DUT-98(2). Scale bars a) 200 µm, b) 50 µm, c) 5 µm.

Supplementary Figure 6. a-d) SEM images of supercritically activated DUT-98(3). E-f) STEM images of supercritically activated DUT-98(3). Scale bars a) 3 µm, b) 1 µm, c) 500 nm, d) 3 µm, e) 3 µm and f) 1 µm.
Supplementary Figure 7. SEM images of supercritically activated DUT-98(4). Scale bars a) 3 µm, b) 1 µm, c) 500 nm.

Supplementary Figure 8. TEM images of DUT-98(Hf). Scale bars a) 100 nm, b) 20 nm, c) 20 nm. These images were recorded with focus and spherical aberrations both negative, therefore the lattice planes comprising the Hf clusters show dark contrast in the images. Image shown in b) was filtered using a nonlinear algorithm for noise reduction. The averaged lattice space observed in HRTEM images shown in b) and c) is about 1.5 nm as revealed in d) by the line profile across the nanocrystal indicated by the red arrow in b).
Supplementary Figure 9. PXRD patterns of DUT-98(Hf) a) after supercritical activation, and b) suspended in Ethanol. Simulated patterns derived from single crystal structure for DUT-98(Zr) op and cp are given for comparison.

Supplementary Figure 10. Nitrogen adsorption isotherm at 77 K of DUT-98(Hf). Closed symbols adsorption, open symbols desorption.
Supplementary Figure 11. TGA analysis of DUT-98(1) (red), DUT-98(2) (organe), DUT-98(3) (green), DUT-98(4) (red) with 5 °C offset.

Supplementary Figure 12. a) DRIFT Spectra of DUT-98 and b) Magnified section of water-relevant wavenumbers.
Supplementary Figure 13. a) DRIFT Spectra of DUT-98(1) and DUT-98(1)-ht after treatment at 80 °C in vacuum.
b) Magnified section of water-relevant wavenumbers.

Supplementary References: