Electronic Supplementary Information for:

Improving the performance of a poorly adsorbing porous material: Template mediated addition of microporosity to a crystalline submicroporous MOF

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S.1. General information

All chemical were of reagent grade and were used as commercially obtained. Thermal analyses (TG/DTA) were performed on a TA Instruments SDT 2960 thermal analyser from room temperature to 800 °C in a synthetic air atmosphere (79% N₂ / 21% O₂) with a heating rate of 5 °C/min.

The X-ray powder diffraction (XRPD) patterns for samples 1a-d and 1d' were collected on a Phillips XPERT powder diffractometer with Cu-Kα radiation (λ = 1.54060 Å) over the range 1 < 2θ < 38° with a step size of 0.02° and an acquisition time of 2 s per step at 25 °C. Indexation of the diffraction profiles were made by means of the FULLPROF program (pattern-matching analysis) on the basis of the space group and the cell parameters found for compound 1a by single crystal X-ray diffraction. Variable-temperature powder X-ray diffraction measurements were run under ambient atmosphere in the range 5 < 2θ < 38° with a step size of 0.03° and an acquisition time of 2 s per step. The samples were heated up to 50 °C and after that the diagrams were collected every 50 °C up to 400 °C.

Nitrogen physisorption data were recorded with a Quantachrome QUADRASORB-SI-MP at 77 K. The specific surface area was calculated from the adsorption branch in the relative pressure interval from 0.01 to 0.05 using the Brunauer-Emmett-Teller (BET) method. The total pore volume was estimated from the quantity of gas adsorbed at a relative pressure of 0.93 (P₀ being 1 bar).
S.2. **Synthesis**

**Synthesis of sample 1a:**
An aqueous-methanolic suspension (25 mL, 15:10) of the butyric acid (2.5 mmol) was added dropwise to an aqueous solution (125 mL) of Cu(NO₃)₂·3H₂O (2.5 mmol) and adenine (2.5 mmol). The mixture was left with continuous stirring and maintaining at room temperature until a light green polycrystalline precipitate was achieved.

**Synthesis of samples 1b-1d:**
An aqueous suspension (25 mL) of the butyric acid (12.5 mmol, 25 mmol and 50 mmol, for 1b, 1c and 1d respectively ) was added dropwise to an aqueous solution (125 mL) of Cu(NO₃)₂·3H₂O (2.5 mmol) and adenine (2.5 mmol). The mixtures were left with continuous stirring and maintaining the temperature around 4 ºC until a light green polycrystalline precipitate was achieved.

**Synthesis of sample 1d’**
An aqueous suspension (25 mL) of the butyric acid (50 mmol) and 1,3,5-trimethybenzene (5 mmol) was added dropwise to an aqueous solution (125 mL) of Cu(NO₃)₂·3H₂O (2.5 mmol) and adenine (2.5 mmol). The mixture was left with continuous stirring and maintaining the temperature around 4 ºC until a light green polycrystalline precipitate was achieved.

All the precipitates were filtered and thoroughly washed with water and methanol, respectively, and they were left drying at room temperature under a continuous air flow.
S.3. **Conductivity measurements**

This method is applied to measure the Critical Micelle Concentration (CMC) of ionic surfactants. The CMC can be estimated from the change in the trend of the conductivity (sudden slope change or a maximum). [J. N. Phillips, *Trans. Faraday Soc.*, **1955**, *51*, 561.] It deserves to note that the addition of an aqueous Cu(NO$_3$)$_2$ solution gives rise to a pronounced decrease of the critical micelle concentration. The butanoic acid concentrations used to obtain the templated samples are well above this last value (CMC = 0.05M).

![Electrical conductivity data](image)

**Figure S3.** Electrical conductivity data as a function of: (a) [HBut] at 4°C and (b) [HBut] with constant $C_{\text{Cu(NO}_3\text{)}_2} = 5 \cdot 10^{-2}$ M at 4°C.
S.4. Dynamic light scattering
The size distribution of micelles was determined at 25°C by dynamic light scattering (DLS) using a Vasco\textsuperscript{γ} DLS particle size analyzer from Micromeritics Instrument Corporation. These measurements showed a hydrodynamic radius of \(~8\) nm, and taking into account that the value obtained by this technique includes a layer of solvent molecules surrounding the micelle, the obtained results are in agreement with the presence of small sized butanoic acid micelles.

**Figure S4.** Size distribution of micelles measured by dynamic light scattering.
S.5. Thermogravimetric and Mass spectrometry/Infrared spectroscopy coupled measurements

The loss of water molecules takes place mainly at temperatures below 100 °C. After this first process, the untemplated sample 1a (Cu:But in 1:1) does not show any meaningful weight change according to the TG curve, and its thermal decomposition starts slightly above 200 °C. However, in samples 1b-1d as the butanoic acid ratio is increased, once water molecules have been lost, the subsequent loss of the embedded aggregates of butanoic acid molecules starts at temperatures close to 100 °C, and it extends until 200 °C.

Figure S5.1. Thermogravimetric analysis of samples 1a-1d and 1d'.
The analysis of mass spectrometry of the prepared samples has allowed the tracking of the most characteristic peaks of water, butyric acid and 1,3,5-trimethylbenzene. In concordance with TG curves, in sample 1a the water release takes place at temperatures below 150 °C, followed by loss of structural butanoate coming from the framework collapse (250 °C). However, samples 1d and 1d' show the release of the butanoic acid excess after reaching a temperature of ca. 140 °C. Additionally, sample 1d' exhibits the loss of embedded TMB molecules over the 140-250 °C range.

Figure S5.2. Mass spectrometry analysis for samples 1a, 1d and 1d' of (a) water, (b) butyric acid and (c) 1,3,5-trimethylbenzene.
TG-FTIR data allow to infer the same results as the ones expounded for TG-MS. Herein, peaks corresponding to water ($\nu_{\text{OH}}$), butanoic acid ($\nu_{\text{C-H}}, \nu_{\text{O-C-O}}$) and TMB ($\nu_{\text{C-H}}$) release were monitored with the increasing temperature ($\nu_{\text{OH}}$ (3500-3400 cm$^{-1}$), $\nu_{\text{C-H}}$ (3100-2900 cm$^{-1}$) and $\nu_{\text{O-C-O}}$ (1750-1650 cm$^{-1}$)).

Figure S5.3. TG-FTIR coupled.
S.6. Powder X-ray diffraction patterns

Figure S6. Powder X-ray diffraction patterns of samples 1a-1d and 1d'.
S.7. Variable temperature powder X-ray diffraction measurement for samples

All the samples show the same behaviour within the analyzed temperature range. Figure S5 shows variable temperature PXRD patterns for 1a. The crystal structure seems to retain its integrity until 200 °C. At 250 °C the collapse of the structure becomes evident, leading to an amorphous phase at higher temperatures (300-400 °C).

Figure S7. Powder X-ray diffraction patterns for sample 1a collected from room temperature to 400 °C.
S.8. Outgassing conditions

All samples were outgassed at a pressure close to 0.1 torr during 20 h. Taking into account the TG-MS-FTIR measurements and temperature variable PXRD data (sections S5 and S3), different temperatures were tested to select the optimum outgassing conditions. The integrity of the outgassed samples was analyzed after the N₂ isotherms measurements by PXRD and SEM (section S7). When non butanoic excess was present (1a), the surface area is close to the expected one for the pristine compound,¹ and only a slight increase of the surface area is observed between samples outgassed at temperatures of 130 and 140 ºC. On the other hand in the samples 1b-1d, a notorious increase of the surface area values is observed at the outgassing temperature of 140 ºC, but negligible adsorption is achieved for smaller outgassing temperatures. As it can be inferred, to evacuate the excess of the embedded butanoic acid molecules, a minimum temperature of 140 ºC is required when the samples are outgassed at 0.1 torr during 20 h. Non significant increase in the surface area values were detected at temperatures greater than 140 ºC, thus a temperature of 140 ºC was established as optimum for the comparative study. Moreover, longer outgassing times did not significantly increase the adsorption capacity and times shorter than 10 h showed a reduced area due to an incomplete removal of the guest molecules.

Table S8. Results of different outgassing conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Outgass temperature (ºC)</th>
<th>Weight loss (%)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>130</td>
<td>7</td>
<td>170</td>
</tr>
<tr>
<td>1a</td>
<td>140</td>
<td>10</td>
<td>210</td>
</tr>
<tr>
<td>1b</td>
<td>120</td>
<td>17</td>
<td>14</td>
</tr>
<tr>
<td>1b</td>
<td>140</td>
<td>29</td>
<td>251</td>
</tr>
<tr>
<td>1c</td>
<td>130</td>
<td>16</td>
<td>50</td>
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<tr>
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<td>140</td>
<td>29</td>
<td>377</td>
</tr>
<tr>
<td>1d</td>
<td>130</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td>1d</td>
<td>140</td>
<td>35</td>
<td>428</td>
</tr>
<tr>
<td>1d'</td>
<td>140</td>
<td>24</td>
<td>250</td>
</tr>
</tbody>
</table>

S.9. SEM and XRPD analysis on outgassed samples

The analysis of SEM and PXRD data allows to state that the integrity and the crystallinity of the samples are retained after the outgassing process at 140 °C.

Figure S9. (a) SEM image and (b) plot PXRD data for sample 1d outgassed at 140°C and 1.10^{-4} atm during 20 h.
S.10. \( \text{N}_2 \) adsorption isotherms for samples

All adsorption curves resemble a type I isotherm, however in samples 1b, 1c and 1d the more obtuse knee following by a progressive increase of the uptake seems to be indicative of greater pore sizes than the ones present in sample 1a.

![N2 adsorption isotherms](image)

**Figure S10.** \( \text{N}_2 \) adsorption isotherms at 77 K for (a) 1a-d and (b) 1d'.

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S.11. \( \text{H}_2 \) adsorption isotherms

The \( \text{H}_2 \) uptake increases, in a similar way as described for \( \text{N}_2 \), from a weight percentage of 0.49\% for the untemplated sample (1a) to a 0.54\% for the templated sample (1b).

Figure S11. \( \text{H}_2 \) adsorption isotherms at 77 K for 1a and 1b.
S.12. TEM images of sample 1d

Microcrystalline powders were transferred to holey carbon/copper grids for high resolution transmission electron microscopy, HRTEM (Phillips CM200, LaB6 cathode, 200 kV, point-resolution = 0.235 nm, line-resolution = 0.144 nm). Well shaped crystals (Figure S12) were found with sizes ranging from 100 to 400 nm and, at high magnification, some kind of nanotexture can be observed probably coming from the added porosity.

In order to get better details of the crystals, crystalline powders of the sample were embedded in an epoxy resin and then cut with a Leica Ultracut UCT to obtain ultra-thin sections (30 nm) for TEM observation. The TEM images show a random distribution of voids with size values below 2 nm.

![Figure S12. TEM images on microcrystalline powders (scale bar: 80 nm).](image)
Figure S13. TEM images on microcrystalline powders (scale bar: 80 and 10 nm, respectively).
Figure S14. TEM images of microcrystalline powders embedded in a thin cut of epoxy resin (scale bar: 30 and 7 nm, respectively).