Synthesis of Ordered Mesoporous Carbon Materials by Dry Etching


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Experimental Section

Synthesis of OM-KC (DUT-118):

2.0 g of KIT-6 were mixed with 10 ml aqueous solution of 2.5 g sucrose and 0.28 g 96% sulfuric acid. To polymerize the hydrocarbon, the mixture was heated up to 100 °C for 6 h and to 160 °C for another 6 h. To fill the entire pore system of KIT-6, the procedure was repeated with 10 ml aqueous solution of 1.6 g sucrose and 0.18 g 96% sulfuric acid, followed by heating to 100 °C and 160 °C. For carbonization and template removal, 1.0 g composite was transferred in a quartz boat and placed in a quartz tube inside a horizontal furnace. After flushing the furnace with an argon flow of 150 ml min⁻¹ for half an hour, the sample was heated up to 900 °C with a heating rate of 300 K h⁻¹. After half an hour of carbonization the gas flow was changed to a mixture of 80 ml min⁻¹ chlorine and 70 ml min⁻¹ argon. After three hours of chlorination the furnace was cooled down to 600 °C under an argon flow of 150 ml min⁻¹. At that temperature, the gas flow was changed to 80 ml min⁻¹ hydrogen to remove chlorine and silicon chloride species adsorbed in the pores of OM-KC (DUT-118). Afterwards, the furnace was cooled down to room temperature under an argon flow.

Characterization:

N₂ and CO₂ physisorption experiments were carried out using an Autosorb-1 (Quantachrome, USA) at -196 °C and 0 °C, respectively. N₂ physisorption isotherms before and after n-nonane preadsorption were carried out in a homemade manometric equipment developed at the Advanced Materials Group (LMA). Preadsorption of n-nonane was performed in the manometric equipment described above as follows: After degassing the samples at 250 °C for 4 h, the sample was exposed to n-nonane (Aldrich, 99%) for 30 min at -196 °C and subsequently left in contact with the liquid for 3 h at room temperature. After the preadsorption, the samples were degassed at 25 °C overnight prior to the second measurement of the nitrogen physisorption isotherm. The total pore volumes were determined at a relative pressure of 0.95 p/p₀ and 0.03 p/p₀ for CO₂ physisorption, respectively. PSDs were calculated using a QSDFT kernel for nitrogen (-196 °C) on carbon assuming slit/cylindrical pore geometries (adsorption branch kernel) Specific surface areas were estimated with BET equation in a relative pressure range of 0.05-0.2 p/p₀. TEM images were recorded using a Cs-corrected JEOL JEM-2010F microscope (JEOL, Japan). Low angle XRD measurements were performed using a Nanostar (Bruker) with Cu-Kα radiation. Unit cell size was calculated using the (211) peak and the quadratic bragg equation for cubic systems. Energy dispersive X-ray spectroscopy was carried out with a DSM-982 Gemini,(Zeiss). Raman spectra were recorded with a RM-2000 (Renishaw) using an 532 nm-
Laser (Gem532, Laser Quantum). Thermogravimetric analysis was performed using a STA-409 (Netzsch), with synthetic air as carrier gas. IR, TG-MS

Characterization:

![Graph](image)

Figure S1: Nitrogen adsorption/desorption (filled symbols/empty symbols) isotherm (-196 °C) of KIT-6.
Figure S2: Thermogravimetric analysis of DUT-118 under synthetic air with a heating rate of 2 °C min⁻¹.
Figure S3: FT-IR spectra of DUT-118 (black) and CMK-8 (grey).
Figure S4: TG-MS analysis of DUT-118 under argon.
Figure S5: Nitrogen adsorption/desorption (filled symbols/empty symbols) isotherm (-196 °C) of CMK-8 and related pore size distribution.

Figure S6: Nitrogen adsorption isotherms (-196 °C) in semi-logarithmic scale of DUT-118 (black) and CMK-8 (grey).
Figure S7: Nitrogen adsorption/desorption isotherms (-196 °C) of DUT-118 prepared at 900°C (black) and 1000°C (grey). Inset: Nitrogen adsorption/desorption isotherms in semi-logarithmic scale.
Figure S8: Nitrogen adsorption/desorption isotherms (-196 °C) of DUT-118 (squares) and CMK-8 (circles) before (black) and after (grey) n-nonane adsorption. Isotherms of DUT-118 are vertically offset by 400 cm³ g⁻¹.

Figure S9: Carbon dioxide adsorption/desorption isotherms (0 °C) of DUT-118 (black) and CMK-8 (grey).
Figure S10: Comparison of QS-DFT fit (straight line) and experimental N$_2$-physisorption (-196 °C) data of DUT-118 (squares).

Figure S11: Pore size distribution of DUT-118 obtained by QS-DFT analysis using the adsorption branch-(black) and equilibrium kernel (grey).
Figure S12: Low angle X-ray diffraction pattern of DUT-118 (top) and CMK-8 (bottom).
Figure S13: Nitrogen adsorption/desorption isotherms (-196 °C) of a carbon derived from SBA-15 as template using the carbochlorination approach.
Figure S14: Low angle X-ray diffraction pattern a carbon derived from SBA-15 as template using the carbochlorination approach.

Table S1. Textural properties of DUT-118 and CMK-8 before and after n-nonane loading

<table>
<thead>
<tr>
<th>Material</th>
<th>SSA\textsubscript{BET}[a]</th>
<th>TPV[b]</th>
<th>MPV (DR)[c]</th>
<th>MesoPV[d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUT-118</td>
<td>1551</td>
<td>2.26</td>
<td>0.60</td>
<td>1.66</td>
</tr>
<tr>
<td>DUT-118-nonane</td>
<td>933</td>
<td>1.75</td>
<td>0.29</td>
<td>1.46</td>
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<tr>
<td>CMK-8</td>
<td>1225</td>
<td>1.62</td>
<td>0.47</td>
<td>1.15</td>
</tr>
<tr>
<td>CMK-8-nonane</td>
<td>608</td>
<td>1.02</td>
<td>0.20</td>
<td>0.82</td>
</tr>
</tbody>
</table>

[a] SSA: Specific surface area obtained using the BET equation in the relative pressure range 0.05 - 0.2 p/p\textsubscript{0} in m\textsuperscript{2} g\textsuperscript{-1}  
[b] TPV: Total pore volume in cm\textsuperscript{3} g\textsuperscript{-1}, obtained at p/p\textsubscript{0}=0.95  
[c] MPV: Micropore volume (pore diameter < 2 nm) in cm\textsuperscript{3} g\textsuperscript{-1}, obtained by Dubinin-Radushkevich  
[d] Mesopore Volume in cm\textsuperscript{3} g\textsuperscript{-1}, obtained by subtraction of MPV (DR) from TPV