Electronic Supplementary Information (ESI)

Solvent-free synthesis of hierarchical zeolite Y by carbochlorination

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S.1 Chlorination temperature ................................................................. 2
S.2 Carbon Content in Composite .......................................................... 3
S.3 Reaction time ....................................................................................... 7
S.4 Chlorine concentration ........................................................................ 9
S.5 Si/Al ratio .......................................................................................... 11
S.6 References ........................................................................................ 13
S.1 Chlorination temperature

Fig. S1 $^{29}$Si CP-MAS NMR spectra of the parent zeolite and composite 2 prepared at 400 and 500 °C. Si(nAl) species have been assigned according to [S1]

Fig. S2 $^{27}$Al CP-MAS NMR spectra of the parent zeolite and composite 2 prepared at 400 and 500 °C. Al species have been assigned according to [S2]
S.2 Carbon Content in Composite

Fig. S3  TG/MS of parent material and all 3 composites with different carbon loadings under synthetic air from 25 to 1250 °C (heating rate 5 K min⁻¹)

Fig. S4  N2-Isotherms at -196 °C of samples at 500 °C from different zeolite-carbon composite red (C1-500-4-10/70), blue (C2-500-4-10/70), green (C3-500-4-10/70)
**Fig. S5**  \( \text{N}_2 \)-adsorption isotherms of parent material and samples with different carbon loadings carbochlorinated at 400 °C

**Fig. S6**  \( \text{N}_2 \)-adsorption isotherms of parent material and samples with different carbon loadings carbochlorinated at 600 °C
Fig. S7  Powder XRD of carbochlorinated samples with different carbon loadings at 400 °C, 500 °C and 600 °C. Diffractograms are normalized on the main reflex [111] at 6 ° 2θ.

Fig. S8  TPAD of parent material and samples with different carbon loadings carbochlorinated at 400 °C after calcination under air for 6 h at 550 °C.
Fig. S9 TPAD of parent material and samples with different carbon loadings carbochlorinated at 600 °C after calcination under air for 6 h at 550 °C.
S.3 Reaction time

Fig. S10  \( \text{N}_2 \)-isotherms at -196 °C from composite 2 samples at 400 °C and 500 °C with different reaction time

Fig. S11  \( \text{N}_2 \)-adsorption isotherms of parent material and samples carbochlorinated at 500 °C and 600 °C over 2 h, 4 h or 8 h, respectively
Fig. S12  TPAD of parent material and samples carbochlorinated at 500°C and 600 °C over 2h, 4 h or 8 h, respectively. Samples were calcinated under air for 6 h at 550 °C.

Fig. S13  Powder XRD of parent material and samples carbochlorinated at 500°C and 600 °C over 2h, 4 h or 8 h, respectively. Diffractograms are normalized on the main reflex [111] at 6 ° 2θ.
S.4 Chlorine concentration

Fig. S14  
N$_2$-adsorption isotherms of parent material and samples carbochlorinated at 600 °C for 4 h with different chlorine concentrations.

Fig. S15  
Powder XRD of parent material and samples carbochlorinated at 600 °C for 4 h with different chlorine concentrations. Diffractograms are normalized on the main reflex [111] at 6 ° 2θ.
Fig. S16  TPAD of parent material and samples carbochlorinated at 600 °C for 4 h with different chlorine concentrations. Samples were calcinated under air for 6 h at 550 °C.

Table S1  characterization data of samples synthesized at 600 °C for different chlorine concentrations. Physisorption data derived from N₂-isotherms measured at -196 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al b</th>
<th>SSA BET c / m² g⁻¹</th>
<th>PV total d / m³ g⁻¹</th>
<th>PV micro e / m³ g⁻¹</th>
<th>PV meso f / m³ g⁻¹</th>
<th>HF g</th>
<th>C sample h / %</th>
<th>Total acidity i / mmol g⁻¹</th>
<th>C res j / w%</th>
<th>Yield k / w%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Y 5 pure</td>
<td>3.0</td>
<td>751</td>
<td>0.43</td>
<td>0.29</td>
<td>0.12</td>
<td>0.08</td>
<td>100</td>
<td>0.995</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C2-600-4-10/110</td>
<td>16.0</td>
<td>287</td>
<td>0.40</td>
<td>0.06</td>
<td>0.34</td>
<td>0.08</td>
<td>28</td>
<td>0.412</td>
<td>1.09</td>
<td>70.6</td>
</tr>
<tr>
<td>C2-600-4-10/70</td>
<td>18.3</td>
<td>275</td>
<td>0.42</td>
<td>0.05</td>
<td>0.37</td>
<td>0.07</td>
<td>26</td>
<td>0.227</td>
<td>0.71</td>
<td>72.2</td>
</tr>
</tbody>
</table>

a sample description given in experimental section
b ICP-OES elemental analysis
c Multi-point BET-method
d Total pore volume at p/p₀ = 0.95
e t-plot method p/p₀ from 0.2 to 0.5
f PV meso = PV total - PV micro
g hierarchy factor HF = (PV micro/PV total) x (SSA/BET)⁰
h % XRD intensity/HY after ASTM 3906-03⁹
i total acidity determined by TPAD
j residual carbon (C sample) analyzed by TG; C res = C sample - C H-Y 5 pure
k calculated by weighing before and after carbochlorination
S.5 Si/Al ratio

Fig. S17  N$_2$-adsorption isotherms of parent material and composite 5 carbochlorinated at different temperatures for 4 h respectively

Fig. S18  XRD from composite 5 samples carbochlorinated at different temperatures. Diffractograms are normalized on the main reflex [111] at 6° 2θ.
Fig. S19 TG/MS of parent material and all 3 composites with different carbon loadings under synthetic air from 25 to 1250 °C (heating rate 5 K min⁻¹)

Fig. S20 TPAD of parent material and samples with different carbon loadings carbochlorinated at 800 °C after calcination under air for 6 h at 550 °C.

- total acidity
  - 0.094 mmol g⁻¹; H-Y 80 pure
  - 0.057 mmol g⁻¹; C4-800-4-10/70-C
  - 0.078 mmol g⁻¹; C5-800-4-10/70-C
  - 0.055 mmol g⁻¹; C6-800-4-10/70-C
S.6 References
