Supporting Information (SI)

Engineering new defects in MIL-100(Fe) via a mixed-ligand approach to effect enhanced volatile organic compounds adsorption capacity

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Experimental section

Conventional solvothermal method synthesis of MIL-100(Fe) at 160 °C

Conventional MIL-100(Fe) was prepared following a reported procedure with a minor modification. † Firstly, 0.56 g of iron powder, 1.4 g of H$_3$BTC, 0.42 mL of HNO$_3$ and 0.89 mL of HF were dispersed in 50 mL deionized water, and then stirred for 15 min. Next, the obtained gel mixture was transferred into a stainless steel vessel and heated at 160 °C for 24 h. After cooling naturally to room temperature, the solid product was filtered and then mixed with 25 mL DMF under vigorous stirring for 2 h. Next, the mixture was filtered and the precipitate (fine orange powder) was dried in an oven at 150 °C for 12 h. After that, the product was filtered and immersed with ethanol at 60 °C for 24 h, and then stirred with NH$_4$F aqueous solution (10 mM, 80 mL) at 60 °C for 24 h. Finally, the product was filtered and washed with hot deionized water (60 °C, three times), and then
dried in an oven at 150 °C for 12 h. The resultant product is denoted as MIL-100(Fe)_D2.

**Synthesis of MIL-100(Fe) with only p-benzoquinone at room temperature**

In a typical synthesis, Solution I was prepared by adding 0.28 g of iron powder and 0.21 mL of HNO₃ to 25 mL of deionized water. After sonication for 15 min, 0.7 g of H₃BTC and 5.4 mg of p-benzoquinone were added to Solution I under fast magnetic stirring (Solution II), and then the Solution II was continually stirred at room temperature and pressure. After stirring for 12 h, Solution II was filtered and the obtained product was immersed in N,N-dimethylmethanamide (30 mL) for 30 min (Solution III), and then the product was filtered and dried. To fully remove the recrystallized H₃BTC and solvents trapped in the pore channels, the solid product was immersed in ethanol solution twice at 60 °C for 24 h, then stirred with NH₄F aqueous solution (10 mM, 80 mL) at 60 °C for 24 h. Subsequently, the product was filtered and washed with hot deionized water (60 °C, three times), and then dried in an oven at 150 °C for 12 h. The resultant product is denoted as MIL-100(Fe)_E2.

**Synthesis of MIL-100(Fe) with only TPA at room temperature**

The procedure used to synthesize MIL-100(Fe)_F2 was similar to the procedure used to prepare MIL-100(Fe)_A2, except that the p-benzoquinone was removed. The resultant product is denoted as MIL-100(Fe)_F2.

![Figure S1. FTIR spectra of the as-synthesized MIL-100(Fe)_An (n = 1, 2, 3) and C-MIL-100(Fe) samples in the narrow region of 2000–1600 cm⁻¹.](image-url)
Figure S2. N₂ adsorption–desorption isotherms of MIL-100(Fe)_An (n = 1, 2, 3) samples.

Figure S3. TEM images of MIL-100(Fe) samples: (a) C-MIL-100(Fe); (b) MIL-100(Fe)_A1; (c) MIL-100(Fe)_A2; (d) MIL-100(Fe)_A3.

Figure S4. TGA of hierarchically porous MIL-100(Fe)_An (n = 1, 2, 3) and C-MIL-100(Fe).
Figure S5. Powder XRD patterns of MIL-100(Fe) samples synthesized with different reaction times.

Figure S6. N\textsubscript{2} adsorption–desorption isotherms and (b) PSDs of hierarchically porous MIL-100(Fe) samples synthesized with different reaction times.

Figure S7. Powder XRD patterns of MIL-100(Fe) samples synthesized with different pH conditions.
Figure S8. (a) N₂ adsorption–desorption isotherms and (b) PSDs of hierarchically porous MIL-100(Fe) samples synthesized with different pH conditions.

Figure S9. PXRD patterns of the obtained products synthesized with different iron sources.

Figure S10. (a) N₂ adsorption–desorption isotherms and (b) PSDs of hierarchically porous MIL-100(Fe) samples synthesized with different iron sources.

Figure S11. PSDs of MIL-100(Fe)_D2 sample synthesized with conventional solvothermal method.
**Figure S12.** PXRD patterns of the obtained MIL-100(Fe)$_2$F$_2$ sample.

**Figure S13.** Powder XRD patterns of MIL-100(Fe)$_2$C$_2$ and the simulated MIL-100(Fe) pattern.

**Figure S14.** SEM image of hierarchically porous MIL-100(Fe)$_2$C$_2$ sample.
Figure S15. TGA of hierarchically porous MIL-100(Fe)\textsubscript{C2} and C-MIL-100(Fe) samples.

Table S1. Porosity properties of MIL-100(Fe)\textsubscript{A2} and MIL-100(Fe)\textsubscript{C2}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}^a$ [m\textsuperscript{2}·g\textsuperscript{-1}]</th>
<th>$S_{\text{micro}}^b$ [m\textsuperscript{2}·g\textsuperscript{-1}]</th>
<th>$S_{\text{meso}}^c$ [m\textsuperscript{2}·g\textsuperscript{-1}]</th>
<th>$V_t^d$ [cm\textsuperscript{3}·g\textsuperscript{-1}]</th>
<th>$V_{\text{micro}}^e$ [cm\textsuperscript{3}·g\textsuperscript{-1}]</th>
<th>$V_{\text{meso}}^e$ [cm\textsuperscript{3}·g\textsuperscript{-1}]</th>
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</thead>
<tbody>
<tr>
<td>MIL-100(Fe)\textsubscript{A2}</td>
<td>1011</td>
<td>504</td>
<td>507</td>
<td>0.57</td>
<td>0.24</td>
<td>0.33</td>
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<tr>
<td>MIL-100(Fe)\textsubscript{C2}</td>
<td>682</td>
<td>354</td>
<td>328</td>
<td>0.46</td>
<td>0.17</td>
<td>0.29</td>
</tr>
</tbody>
</table>

$S_{\text{BET}}$: Brunauer–Emmett–Teller (BET) surface area; $S_{\text{micro}}$: micropore surface area; $S_{\text{meso}}$: mesopore surface area; $V_t$: total pore volume; $V_{\text{micro}}$: micropore volume; $V_{\text{meso}}$: mesopore volume.

References