Mesoporous MCM-22 Zeolites Prepared through Organic Amine-assisted Reversible Structural Change and Protective Desilication for Bulky Molecules Catalysis

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Scheme S1. Product distribution for 1,3,5-TIPB cracking

\[
\text{1,3,5-TIPB} \rightarrow \text{DIPB} + \text{IPB} + \text{BZ}
\]

Scheme S2. Main product in the alkylation of benzene with isopropanol

\[
\text{[Scheme S1. Product distribution for 1,3,5-TIPB cracking]}
\]

\[
\text{[Scheme S2. Main product in the alkylation of benzene with isopropanol]}
\]
Table S1.

The content of organic species and weight loss of MCM-22 precursor (Si/Al = 30) and the samples as-treated with NaOH in the presence of PI or HMI\(^a\)

<table>
<thead>
<tr>
<th>Samples</th>
<th>SDA amount(^a)</th>
<th>C/N ratio(^a)</th>
<th>Weight loss (wt%(^b))</th>
<th>&lt;473 K</th>
<th>473-643 K</th>
<th>643-873K</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-22 precursor</td>
<td>14.5</td>
<td>5.8</td>
<td>0.5</td>
<td>9.3</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>Meso-MCM-22(PI)</td>
<td>10.4</td>
<td>4.9</td>
<td>0.5</td>
<td>7.3</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Meso-MCM-22(HMI)</td>
<td>9.8</td>
<td>5.7</td>
<td>0.2</td>
<td>5.8</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Given by elemental analysis. \(^b\) Given by TGA analysis.
**Figure S1.** XRD patterns of directly calcined MCM-22 (Si/Al = 30) (a), and the samples obtained by treating calcined MCM-22 in 0.1 M NaOH and PI solution (PI/SiO$_2$ = 1.0) at 338 K (b), 358 K (c), 373 K (d), 393 K (e), 423 K (f), and 443 K (g). The NaOH-treated samples were further calcined at 823 K.

**Figure S2.** XRD patterns of calcined MCM-22 (Si/Al = 30) (a), the samples obtained by treating calcined MCM-22 in 0.1 M NaOH solution at PI/SiO$_2$ of 1.0 and at 443 K for 15 min (b), 40 min (c), 1 h (d), 2 h (e), 8 h (f), and 24 (f). The NaOH-treated samples were further calcined at 823 K.
Figure S3. The dependence of relative crystallinity of NaOH-treated MCM-22 samples on the PI/SiO$_2$ ratio at 443 K for 2 h. The crystallinity was measured from the calcined samples at 823 K.

Figure S4. XRD patterns of calcined MCM-22 (Si/Al = 30) (a), and after treatment in 0.1 M NaOH solution at 443 K for 2 h in the presence of PI (b), HMI (c), pyridine (d), piperazine (e), TPAOH (f), and TEAOH (g). The added amount of amine or quaternary ammonium hydroxide corresponded to 1.0 molar ratio relative to SiO$_2$ in zeolite. The NaOH-treated samples were uncalcined (A) and further calcined at 823 K (B).
Figure S5. $\text{N}_2$ adsorption and desorption isotherms (A) and pore size distribution (B) of parent MCM-22 (a), Meso-MCM-22 (2 h) (b), and Meso-MCM-22 (24 h) (c).

Figure S6. SEM images of the samples by treating MCM-22 in 0.1 M NaOH solution at 443 K for 2 h in the presence of TPAOH (a) and TEAOH (b). The amount of quaternary ammonium hydroxide corresponded to 1.0 molar ratio relative to the SiO$_2$ in zeolite.
Figure S7. IR spectra of proton-type parent MCM-22 (a) and Meso-MCM-22 (b) after pyridine was adsorbed and desorbed at 423 K for 1 h.

Figure S8. NH$_3$-TPD profiles of proton-type parent MCM-22 (a) and Meso-MCM-22 (b).
Figure S9. TGA (A) and DTG (B) curves of as-synthesized MCM-22 (Si/Al = 30) (c), as-treated with NaOH in the presence of PI (a) or HMI (b). The samples were dried at 373 K but without calcination.