Supporting Information

Postfunctionalization of periodic mesoporous silica SBA-1 with magnesium and iron(II) silylamides

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Synthesis Procedures

Materials.

**SBA-1 1:** C$_{18}$TEABr (5.70 g, 13.08 mmol), concentrated HCl (37 wt %, 362.9 g, 3.18 mol), and distilled water (598.5 g, 33.23 mol) were combined, and the resulting mixture was vigorously stirred until a homogeneous solution formed (ca. 30 minutes). The solution was cooled to 0 °C in an ice bath and 13.68 g (65.67 mmol) of TEOS was slowly added. Stirring was continued for 4 h at 0 °C, and then the reaction mixture was heated in a polypropylene bottle to 100 °C and maintained there for n hours without stirring (n =1; 6). The solid product was recovered by filtration (without washing) and dried at ambient temperature. The as-synthesized material was calcined at 540 °C (air, 5 h) and dehydrated in vacuo (270 °C, $10^{-4}$ Torr, 8 h). The molar composition of the synthesis gel was 1:5:280:3500 C$_{18}$TEABr:TEOS:HCl:H$_2$O.

Grafting Precursors.

**[Mg(N(SiHMe$_2$)$_2$)$_2$]** (2). To a solution of 1.87 g HN(SiHMe$_2$)$_2$ (14.00 mmol) in 5 mL hexane a 1M Mg(n-Bu)$_2$ solution in heptane (7 ml, 7.00 mmol) was added slowly. The solution was stirred for 4 h at ambient temperature during which gas evolution was observed (n-butane). Afterwards, the solvent was removed in vacuo. Two times subsequent crystallization in n-hexane at –35 °C yielded 1.80 g (6.23 mmol, 89% yield) colourless crystals of the pure compound. Analysis calculated for C$_8$H$_{28}$N$_2$Si$_4$Mg (wt%): C, 33.25; H, 9.77; N, 9.69. Found: C, 33.64; H, 9.04; N, 9.51. DRIFT (KBr, cm$^{-1}$): 2953s, 2897w, 2078s, 2047s, 1781w, 1428w, 1259s, 1247s, 1058s, 889s, 843s, 793s, 775s, 765s, 737w, 709w, 692w, 683w, 634w, 619w, 488m, 408w.

**[Mg(N(SiMe$_3$)$_2$)$_2$]** (3). To a solution of 2.26 g HN(SiMe$_3$)$_2$ (14.00 mmol) in 5 mL hexane a 1M Mg(n-Bu)$_2$ solution in heptane (7 ml, 7.00 mmol) was added slowly. The solution was
stirred for 4 hours at ambient temperature during which gas evolution was observed (n-butane). Afterwards, the solvent was removed in vacuo. Two times subsequent crystallization in n-hexane at -35°C yielded 2.11 g (6.11 mmol, 87% yield) colourless crystals of the pure compound. Analysis calculated for C₁₂H₃₆N₂Si₄Mg (wt%): C, 41.77; H, 10.52; N, 7.04. Found: C, 41.51; H, 11.14; N, 7.77. DRIFT (KBr, KBr, cm⁻¹): 2946s, 2897m, 1462w, 1450w, 1429w, 1391w, 1316w, 1296w, 1251m, 1239s, 1184w, 1025m, 986s, 876s, 841s, 826s, 780m, 747m, 712w, 664m, 621w, 610m, 435w.

[Fe^{II}(N(SiHMe₂)₂)_2]₂ (5). A solution of 4.40 g LiN(SiHMe₂)₂ (31.56 mmol) in 5 mL THF was added slowly (highly exothermic reaction) to a milky solution of 2.04 g FeCl₂ (15.78 mmol) in 5 mL THF. The solution turned dark brown immediately. After one hour of stirring at ambient temperature, the solvent was removed. Centrifugation and three times washing of the remaining solid with n-hexane led to a dark green/black solution. The washing fractions were collected and n-hexane was removed. Extraction with n-hexane and two times subsequent crystallization in n-hexane at -35 °C yielded 3.06 g (9.56 mmol, 61% yield) green crystals of the pure compound. Analysis calculated for C₈H₂₈N₂Si₄Fe (wt%): C, 29.98; H, 8.81; N, 8.74. Found: C, 29.49; H, 9.01; N, 8.46. DRIFT (KBr, KBr, cm⁻¹): 2949s, 2899m, 2116s, 2083s, 1418w, 1250s, 1001m, 889s, 839s, 804m, 788m, 773m, 727w, 628w, 604w 472w.

**Hybrid Materials.**

**SiHMe₂@SBA-1** (1a). Dehydrated SBA-1 (1) (100 mg) was suspended in 5 ml of n-hexane. Under stirring, 200 mg (1.50 mmol) of HN(SiHMe₂)₂ was added. The suspension was stirred for 18 h at ambient temperature and nonreacted silazane separated via combined n-hexane washings–centrifugations (3×). Subsequently removing the remaining solvent by drying under vacuum yielded the hybrid material (81 mg). Analysis found (wt%): C, 7.36; H, 1.90; N, 0.02.
**Si(vinyl)Me$_2$@[Mg(N(SiHMe$_2$)$_2$)$_2$]$_2$@SBA-1 (1j).** A suspension of 56 mg of the hybrid material 1i in 5 ml $n$-hexane was prepared. Under stirring, 200 mg (1.08 mmol) of HN[Si(vinyl)Me$_2$]$_2$ was added. After stirring the suspension overnight at ambient temperature, nonreacted silazane was separated via combined $n$-hexane washings–centrifugations (3×). Subsequently removing the remaining solvent by drying under vacuum yielded a slightly yellowish hybrid material (65 mg). Analysis found (wt%): C, 8.99; H, 2.08; N, 0.19; Mg, n.d..

**Si(vinyl)Me$_2$@SBA-1 (1k).** A suspension of 96 mg of the SBA-1 material (1) in 5 ml $n$-hexane was prepared. Under stirring, 500 mg (2.70 mmol) of HN[Si(vinyl)Me$_2$]$_2$ was added. After stirring the suspension overnight at ambient temperature, nonreacted silazane was separated via combined $n$-hexane washings–centrifugations (3×). Subsequently removing the remaining solvent by drying under vacuum yielded a white hybrid material (80.7 mg). Analysis found (wt%): C, 12.65; H, 2.57; N, 0.01.
**Figure S1.** PXRD of SBA-1 1.

**Figure S2.** Nitrogen adsorption/desorption isotherms and corresponding BJH pore size distribution of SBA-1 (1) ( ), SiHMe₂@SBA-1 (1a) ( ), [Mg{N(SiHMe₂)₂}₂]₂@SBA-1 (1b) ( ) after 18 h grafting and [Mg{N(SiHMe₂)₂}₂]₂@SBA-1 (1e) ( ) after 4d grafting.
Figure S3. BJH pore size distribution of SBA-1 (1) ( ), SiHMe₂@SBA-1 (1a) ( ), [Mg{N(SiMe₃)₂}₂]₂@SBA-1 (1c) ( ) after 18 h grafting and [Mg{N(SiMe₃)₂}₂]₂@SBA-1 (1f) ( ) after 4 d grafting.

Figure S4. BJH pore size distribution of SBA-1 (1) ( ), SiHMe₂@SBA-1 (1a) ( ), Mg[N(SiPhMe₂)₂]₂@SBA-1 (1d) ( ) after 18 h grafting and Mg[N(SiPhMe₂)₂]₂@SBA-1 (1g) ( ) after 4 d grafting.
**Figure S5.** Nitrogen adsorption/desorption isotherms and corresponding BJH pore size distribution of SBA-1 (1) ( ), SiHMe₂@SBA-1 (1a) ( ), [Mg{N(SiHMe₂)₂}₂]₂@SBA-1 (1b) ( ) after 18 h grafting and [Fe^{II}{N(SiHMe₂)₂}₂]₂[Mg{N(SiHMe₂)₂}₂]₂@SBA-1 (1h) ( ) after 4 d grafting.

**Figure S6.** BJH pore size distribution of SBA-1 (1) ( ), SiHMe₂@SBA-1 (1a) ( ), [Mg{N(SiHMe₂)₂}₂]₂@SBA-1 (1e) ( ) after 4 d grafting and [Fe^{II}{N(SiHMe₂)₂}₂][Mg{N(SiHMe₂)₂}₂]₂@SBA-1 (1i) ( ) after 4 d grafting.
Figure S7. Nitrogen adsorption/desorption isotherms and corresponding BJH pore size distribution of SBA-1 (1), SiHMe₂@SBA-1 (1a), Si(vinyl)Me₂@[Mg{N(SiHMe₂)₂}₂]@SBA-1 (1j) and Si(vinyl)Me₂@SBA-1 (1k).

Figure S8. IR spectra (DRIFT) of mesoporous silica SBA-1 (1) and hybrid materials SiHMe₂@SBA-1 (1a), [Mg{N(SiHMe₂)₂}₂]@SBA-1 (1b) and [Mg{N(SiHMe₂)₂}₂]@SBA-1 (1e) and precursor [Mg{N(SiHMe₂)₂}₂] (2) in the range of 400-4000 cm⁻¹.
**Figure S9.** IR spectra (DRIFT) of mesoporous silica SBA-1 (1) and hybrid materials SiHMe$_2$@SBA-1 (1a), [Mg{N(SiMe$_3$)$_2$}]$_2$@SBA-1 (1c) and [Mg{N(SiHMe$_2$)$_2$}]$_2$@SBA-1 (1f) and precursor [Mg{N(SiMe$_3$)$_2$}]$_2$ (3) in the range of 400-4000 cm$^{-1}$.

**Figure S10.** IR spectra (DRIFT) of mesoporous silica SBA-1 (1) and hybrid materials SiHMe$_2$@SBA-1 (1a), Mg[N(SiPhMe$_2$)$_2$]$_2$@SBA-1 (1d) and Mg[N(SiPhMe$_2$)$_2$]$_2$@SBA-1 (1g) and precursor Mg[N(SiPhMe$_2$)$_2$]$_2$ (4) in the range of 400-4000 cm$^{-1}$.
Figure S11. IR spectra (DRIFT) of mesoporous silica SBA-1 (1) and hybrid materials \([\text{Mg}\{\text{N(SiHMe}_2\}_2\}_2]_2@\text{SBA}-1~(1\text{b}),~[\text{Fe}^{II}\{\text{N(SiHMe}_2\}_2\}_2]_2@[\text{Mg}\{\text{N(SiHMe}_2\}_2\}_2]_2@\text{SBA}-1~(1\text{h}),~[\text{Mg}\{\text{N(SiHMe}_2\}_2\}_2]_2@\text{SBA}-1~(1\text{e})\) and \([\text{Fe}^{II}\{\text{N(SiHMe}_2\}_2\}_2]_2@[\text{Mg}\{\text{N(SiHMe}_2\}_2\}_2]_2@\text{SBA}-1~(1\text{i})\) and precursor \([\text{Fe}^{II}\{\text{N(SiHMe}_2\}_2\}_2]_2\) (5) in the range of 400-4000 cm\(^{-1}\).
**Figure S12.** IR spectra (DRIFT) of the silazane HN[Si(vinyl)Me$_2$]$_2$ and the hybrid materials Si(vinyl)Me$_2$@[Mg{N(SiHMe$_2$)$_2$}]$_2$@SBA-1 (1j), Si(vinyl)Me$_2$@SBA-1 (1k).
Table S1. Analytical data of the vinyl-functionalized materials

<table>
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<tr>
<th>Sample/Precursor</th>
<th>$a_b$ [m$^2$/g]$^a$</th>
<th>$D_{max}$ [nm]$^b$</th>
<th>$V_p$ [cm$^3$/g]$^c$</th>
<th>C [wt%]$^d$</th>
<th>N [wt%]$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 SBA-1 (a = 8.50 nm)</td>
<td>1320</td>
<td>4.5</td>
<td>0.82</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1a SiHMe$_2$@SBA-1</td>
<td>1110</td>
<td>4.2</td>
<td>0.51</td>
<td>6.61</td>
<td>0.11</td>
</tr>
<tr>
<td>1j Si(vinyl)Me$_2$@Mg[N(SiHMe$_2$)$_2$]$_x$@SBA-1</td>
<td>960</td>
<td>4.2</td>
<td>0.46</td>
<td>8.99</td>
<td>0.19</td>
</tr>
<tr>
<td>1k Si(vinyl)Me$_2$@SBA-1</td>
<td>950</td>
<td>4.2</td>
<td>0.45</td>
<td>12.65</td>
<td>0.01</td>
</tr>
</tbody>
</table>

$^a$ Specific BET surface area. $^b$ Pore diameter calculated according to Ravikovich and Neimark; $^c$ all samples were pretreated at 250 °C (parent materials), 100 °C (silylated samples) and 25 °C (grafted samples) respectively in vacuo until the pressure was <10$^{-3}$ Torr. $^c$ Pore volume determined at the relative pressure p/p$_0$ = 0.975. $^d$ Elemental analysis obtained after treatment at 100 °C in vacuo (<10$^{-3}$ Torr).