Supporting Information

Functionalization of MCM-41 and SBA-1 with Titanium(IV) (Silyl)Amides

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MCM-41. CTMABr (4.27 g, 11.71 mmol) and 5.51 g C\textsubscript{16,3,1} (10.39 mmol) were combined with distilled water (280.76 g, 15.60 mol) and 23.65 g TMAOH solution (64.88 mmol) and stirred for 30 minutes until a homogenous solution was achieved. Then TEOS (27.04 g, 129.78 mmol) was added and the resulting solution stirred for 40 minutes. The material was filtrated, re-suspended in 350 mL of distilled water, transferred into a Teflon autoclave and treated for 6 D at 100 °C. The solid product was recovered by filtration and dried at ambient temperature. The as-synthesized material was calcined at 540 °C (air, 5 h) and dehydrated in vacuo (270 °C, 10\textsuperscript{−4} Torr, 8 h). The molar composition of the synthesis gel was 0.08:0.08: 120: 0.5:1 CTMABr:C\textsubscript{16,3,1}:H\textsubscript{2}O:TMAOH:TEOS.

SBA-1. C\textsubscript{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 vigorously stirred until a homogeneous solution formed (ca. 30 min). The solution was cooled to 0 °C in an ice bath and 13.68 g (65.67 mmol) of TEOS slowly added. Stirring was continued for 4 h at 0 °C, and then the reaction mixture heated in a polypropylene bottle to 100 °C and maintained there for 1 h without stirring. 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\textsuperscript{−4} Torr, 8 h). The molar composition of the synthesis gel was 1:5:280:3500 C\textsubscript{18}TEABr:TEOS:HCl:H\textsubscript{2}O.
**Figure S1.** Powder XRD patterns of the parent materials: MCM-41 (1) (upper left), MCM-41 (2) (upper right), and SBA-1 (3) (bottom).
**Figure S2.** BJH pore size distribution of SBA-1 (3) (■), SiMePh₂@SBA-1 (3a) (●) and Ti(NMe₂)₄@SiMePh₂@SBA-1 (3b) (▲).

**Figure S3.** BJH pore size distribution of SBA-1 (3) (■), Mg[N(SiHMe₂)₂]₂@SBA-1 (3c) (●) and Ti(NMe₂)₄@Mg[N(SiHMe₂)₂]₂@SBA-1 (3d) (▲).
**Figure S4.** BJH pore size distribution of SBA-1 (3) (■), Ti(NMe₂)₄@SBA-1 (3e) (●) and (R-H₂BINOL)@Ti(NMe₂)₄@SBA-1 (3f) (▲).

**Figure S5.** BJH pore size distribution of SBA-1 (3) (■), Ti(NMe₂)₃[N(SiHMMe₂)₂]@SBA-1 (3g) (●) and Ti(NMe₂)₃[N(SiHMMe₂)₂]@SBA-1 (3h) (▲).
Figure S6. IR spectra (DRIFT) of the hybrid materials SiMePh₂@MCM-41 (1a) and Ti(NMe₂)₄@SiMePh₂@MCM-41 (1b) and precursor Ti(NMe₂)₄ in the range of 400-4000 cm⁻¹.

Figure S7. IR spectra (DRIFT) of the hybrid materials Ti(NMe₂)₃[N(SiHMe₂)₂]@MCM-41 (1c) and precursor Ti(NMe₂)₃[N(SiHMe₂)₂] (4) in the range of 1300-4000 cm⁻¹.
**Figure S8.** IR spectra (DRIFT) of the hybrid materials Ti(NMe$_2$)$_4$@MCM-41 (2a) and (R-H$_2$BINOL)@Ti(NMe$_2$)$_4$@MCM-41 (2b) and precursor Ti(NMe$_2$)$_2$(R-BINOL) (5) in the range of 1300-4000 cm$^{-1}$. 
Figure S9. IR spectra (DRIFT) of the hybrid materials SiMePh$_2$@SBA-1 (3a) and Ti(NMe$_2$)$_4$@SiMePh$_2$@SBA-1 (3b) and precursor Ti(NMe)$_4$ in the range of 400-4000 cm$^{-1}$ and 1300-4000 cm$^{-1}$. 

Figure S10. IR spectra (DRIFT) of the hybrid materials Mg[N(SiHMe$_2$)$_2$]$_2$@SBA-1 (3c) and Ti(NMe$_2$)$_4$@Mg[N(SiHMe$_2$)$_2$]$_2$@SBA-1 (3d) and precursor Ti(NMe$_2$)$_4$ in the range of 400-4000 cm$^{-1}$.

Figure S11. IR spectra (DRIFT) of the hybrid materials Ti(NMe$_2$)$_4$@SBA-1 (3e) and (R-$\text{H}_2$BINOL)@Ti(NMe$_2$)$_4$@SBA-1 (3f) and precursor Ti(NMe$_2$)$_2$(R-BINOL) (5) in the range of 400-4000 cm$^{-1}$.
Figure S12. IR spectra (DRIFT) of the hybrid materials Ti(NMe₂)_3[N(SiHMe₂)_2]@SBA-1 (3g) and Ti(NMe₂)_3[N(SiHMe₂)_2]@SBA-1 (3h) and precursor Ti(NMe₂)_3[N(SiHMe₂)_2] (4) in the range of 400-4000 cm⁻¹.
**Figure S13.** IR spectra (DRIFT) of the parent materials MCM-41 (1), MCM-41 (2) and SBA-1 (3) in the range of 400-4000 cm\(^{-1}\).

**Figure S14.** IR spectrum (DRIFT) of \{Mg[N(SiMe\(_2\)]\(_2\)]\(_2\}\}_2 in the range of 400-4000 cm\(^{-1}\).
Figure S15. $^1$H NMR spectrum (600.13 MHz) of $R$-$H_2$BINOL in C$_6$D$_6$.

Figure S16. $^1$H NMR spectrum (600.13 MHz) of $R$-$H_2$BINOL in C$_6$D$_6$. 
Figure S17. $^1$H NMR spectrum (600.13 MHz) of Ti(NMe$_2$)$_2$(R-BINOL) (5) in C$_6$D$_6$.

Figure S18. $^1$H NMR spectrum (400.13 MHz) of Ti(NMe$_2$)$_3$[N(SiHMe$_2$)$_2$] (4) in C$_6$D$_6$. 
**Figure S19.** $^{13}$C NMR spectrum (100.61 MHz) of Ti(NMe$_2$)$_3$[N(SiHMe$_2$)$_2$] (4) in C$_6$D$_6$.

**Figure S20.** $^1$H NMR spectrum (400.13 MHz) of Ti(NMe$_2$)$_4$ in C$_6$D$_6$. 
**Figure S21.** $^{13}$C NMR spectrum (100.61 MHz) of Ti(NMe$_2$)$_4$ in C$_6$D$_6$.

**Figure S22.** $^1$H NMR spectrum (600.13 MHz) of {Mg[N(SiHMe$_2$)$_2$]$_2$}$_2$ in C$_6$D$_6$. 
Figure S23. $^{13}$C NMR spectrum (100.61 MHz) of {Mg[N(SiMe$_2$)$_2$]}$_2$ in C$_6$D$_6$. 