Supporting Information

Silylation Efficiency of Chorosilanes, Alkoxysilanes, and Monosilazanes on Periodic Mesoporous Silica

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Experimental Section

General Materials. Tetraethyl orthosilicate (TEOS) from Fluka was used as a silica precursor. Tetramethylammonium hydroxide (25 wt% solution in water, TMAOH), dimethyloctylchlorosilane, octyltriethoxysilane, and cetyltrimethylammonium bromide (CTMABr) were purchased from Aldrich. 1,1,3,3-Tetramethyldisilazane was obtained from ABCR. Triethylamine was purchased from Fluka and concentrated hydrochloric acid (37 wt% in H_2O) was acquired from Riedel-de Haën. The reagents were used as received without further purification if not otherwise noted. Silylation reactions were performed under dry argon using glovebox techniques (MB Braun MB150B-G; <1 ppm O_2, <1 ppm H_2O). Hexane and toluene were purified by using Grubbs columns (MBraun SPS, solvent purification system) and stored in a glovebox. Dimethyloctylchlorosilane, octyltriethoxysilane, and triethylamine were destilled and degassed prior to use. Dimethyloctylsilazane was synthesized from equimolar amounts of dimethyloctylchlorosilane and dimethyllithium amide in a mixture of *n*-hexane and THF at ambient temperature. Octadecyltriethylammonium bromide $[CH_3(CH_2)_{17}NEt_3]^+Br^-$ (C_{18}TEABr) and N-(3-trimethyl-ammoniumpropyl)hexadecylammonium dibromide $[CH_3(CH_2)_{15}NMe_2(CH_2)_3NMe_3]^+2Br^-$ ($C_{16\text{-}3\text{-}1}$) were synthesized according to the literature by reacting octadecylbromide with triethylamine and hexadecyldimethylamine with (3-bromopropyl)trimethylammonium bromide, respectively.[1]

Materials.

The pore-enlarged MCM-41 sample **1** was synthesized according to a procedure described by us previously.[2] The SBA-1 materials **2** and **3** used in this work were synthesized according to recent literature procedures.[3-5] Materials **4** and **5** were synthesized according to a method described by Vinu et *al*, utilizing a prolonged hydrothermal treatment of the SBA-1 synthesis gel, that is, 72 h instead of 1 h at 100 °C.[6] A considerable expansion of the pore system of the latter material was revealed by nitrogen

physisorption data and is further manifested by a shift of the relative angles of the (200) and (211) reflections in the powder XRD pattern to lower angles (see Figure S1).

MCM-41. CTMABr (4.27 g, 11.71 mmol) and 5.51 g C16-3-1 (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 min until a homogenous solution formed. Then TEOS (27.04 g, 129.78 mmol) was added and the resulting solution stirred for 40 min. 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^{-4} Torr, 8 h). The molar composition of the synthesis gel was 0.08:0.08: 120: 0.5:1 CTMABr:$C_{16\text{-}3\text{-}1}$:H_2O:TMAOH:TEOS.

SBA-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 min). 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 heated in a polypropylene bottle to 100 °C and maintained there for n h without stirring (**2** and **3**: n=1; **4** and **5**: n = 72). 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_2O.

Synthesis of the Hybrid Materials

$SiHMe_2$@MCM-41 (1a). Dehydrated MCM-41 (100 mg) is suspended in 5 ml of *n*-hexane. Under stirring, 200 mg of $HN(SiHMe_2)_2$ were added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three hexane washings and subsequent centrifugation. Removal of the remaining solvent by drying under vacuum yielded hybrid material **1a** (89 mg). Analysis found: C, 6.94; H, 1.59; N, 0.05.

$C_8H_{17}SiMe_2NMe_2$@MCM-41 (1b). Dehydrated MCM-41 (198 mg, 0.69 mmol SiOH) was suspended in 5 ml of *n*-hexane and 55 mg (0.26 mmol) of dimethyloctylsilazane in 5 ml *n*-hexane added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three hexane washings and subsequent centrifugation. Removal of the remaining solvent by drying under vacuum yielded hybrid material **1b** (198 mg). Analysis found: C, 11.66; H, 2.84; N, 0.00.

$C_8H_{17}SiMe_2Cl$@MCM-41 (1c). Dehydrated MCM-41 (268 mg, 0.93 mmol SiOH) was suspended in 5 ml of *n*-hexane and 31 mg (0.31 mmol) of triethylamine in 3 ml of *n*-hexane added. The suspension was allowed to stir for 1 h, after which 64 mg (0.31 mmol) of dimethyloctylchlorosilane in 3 ml of *n*-hexane were added and the mixture stirred for additional 18 h at ambient temperature. Nonreacted chlorosilane and triethylamine were separated by three hexane washings and subsequent centrifugation. Removal of the remaining solvent by drying under vacuum and of adduct $NEt_3 \cdot HCl$ via sublimation at 100 °C under vacuum resulted in 238 mg of hybrid material **1c**. Analysis found: C, 14.34; H, 3.34; N, 0.00.

$C_8H_{17}Si(OEt)_3$@MCM-41 (1d). Dehydrated MCM-41 (236 mg, 0.82 mmol SiOH) and 0.28 mmol (78 mg) triethoxyoctylsilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted ethoxysilane, ethanol as a byproduct, and remaining solvent were separated by three hexane washings and centrifugation. Drying under vacuum afforded 207 mg hybrid material **1d**. Analysis found: C, 5.08; H, 2.60; N, 0.00.

$C_8H_{17}SiMe_2NMe_2$@MCM-41 (1e). Dehydrated MCM-41 (153 mg, 0.53 mmol SiOH) is suspended in 5 ml of *n*-hexane and 132 mg (0.61 mmol) of dimethyloctylsilazane in 5 ml *n*-hexane is added. The suspension is stirred for 18 h at ambient temperature. Nonreacted silazane is separated by three times *n*-hexane washings via centrifugation. Subsequently removing the remaining solvent by drying under vacuum, yields the hybrid material (204 mg). Analysis found: C, 22.75; H, 4.35; N, 0.00.

$C_8H_{17}SiMe_2Cl$@MCM-41 (1f). Dehydrated MCM-41 (203 mg, 0.70 mmol SiOH) was suspended in 5 ml of n-hexane and 85 mg (0.84 mmol) of triethylamine in 3 ml of n-hexane added. The suspension was allowed to stir for 1 h, after which 167 mg (0.81 mmol) of dimethyloctylchlorosilane in 3 ml of *n*-hexane was added and the mixture stirred for additional 18 h at ambient temperature. Nonreacted chlorosilane and triethylamine were separated by three hexane washings and subsequent centrifugation. Removal of the remaining solvent by drying under vacuum and of the adduct $NEt_3 \cdot HCl$ by sublimation at 100 °C under vacuum resulted in 227 mg of hybrid material **1f**. Analysis found: C, 20.08; H, 3.60; N, 0.00.

$C_8H_{17}Si(OEt)_3$@MCM-41 (1g). Dehydrated MCM-41 (190 mg, 0.66 mmol SiOH) and 0.81 mmol (223 mg) triethoxyoctylsilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted ethoxysilane, ethanol as a byproduct, and remaining solvent were separated separated by three hexane washings and centrifugation. Drying under vacuum afforded 177 mg of hybrid material **1g**. Analysis found: C, 7.92; H, 2.07; N, 0.00.

$SiHMe_2$@SBA-1 (2a). Dehydrated SBA-1 (100 mg) was suspended in 5 ml of *n*-hexane. Under stirring, 200 mg of $HN(SiHMe_2)_2$ were added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-hexane washings and centrifugation. Removal of the remaining solvent by drying under vacuum yielded hybrid material **2a** (84 mg). Analysis found: C, 8.49; H, 2.28; N, 0.12.

$C_8H_{17}SiMe_2NMe_2$@ SBA-1 (2b). Dehydrated SBA-1 (250 mg, 1.11 mmol SiOH) was suspended in 5 ml of *n*-hexane and 87 mg (0.40 mmol) of dimethyloctylsilazane in 5 ml *n*-hexane added. The

suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-hexane washings and centrifugation. Evaporation of the remaining solvent under vacuum yielded hybrid material **2b** (291 mg). Analysis found: C, 14.78; H, 3.32; N, 0.91. Corrected for 0% $HNMe_2$: C, 13.62; N, 0.00.

$C_8H_{17}SiMe_2Cl$@SBA-1 (2c). Dehydrated SBA-1 (250 mg, 1.11 mmol) and 0.37 mmol (77 mg) dimethyloctylchlorosilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted chlorosilane and remaining solvent were separated by three *n*-hexane washings and centrifugation. Subsequent drying under vacuum afforded 222 mg of hybrid material **2c**. Analysis found: C, 4.47; H, 1.01; N, 0.01.

$C_8H_{17}Si(OEt)_3$@SBA-1 (2d). Dehydrated SBA-1 (250 mg, 1.11 mmol) and 0.38 mmol (106 mg) triethoxyoctylsilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted ethoxysilane, ethanol as a byproduct, and remaining solvent were separated by three *n*-hexane washings and centrifugation. Subsequently drying under vacuum afforded 244 mg of hybrid material **2d**. Analysis found: C, 7.48; H, 1.57; N, 0.00.

$SiHMe_2$@SBA-1 (3a). Dehydrated SBA-1 100 mg was suspended in 5 ml of *n*-hexane. Under stirring, 200 mg of $HN(SiHMe_2)_2$ was added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-hexane washings and centrifugation. Subsequent evaporation of the remaining solvent under vacuum yielded hybrid material **3a** (81 mg). Analysis found: C, 7.36; H, 1.90; N, 0.02.

$C_8H_{17}SiMe_2NMe_2$@ SBA-1 (3b). Dehydrated SBA-1 (100 mg, 0.37 mmol SiOH) was suspended in 5 ml of *n*-hexane and 84 mg (0.39 mmol) of dimethyloctylsilazane in 5 ml *n*-hexane added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-hexane washings and centrifugation. Subsequent evaporation of the remaining solvent under vacuum yielded hybrid material **3b** (122 mg). Analysis found: C, 22.86; H, 4.12; N, 0.04.

$C_8H_{17}SiMe_2Cl$@SBA-1 (3c). Dehydrated SBA-1 (220 mg, 0.82 mmol SiOH) and 1.21 mmol (250 mg) dimethyloctylchlorosilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted chlorosilane and remaining solvent are separated by three *n*-hexane washings and centrifugation. Subsequent drying under vacuum afforded 217 mg of hybrid material **3c**. Analysis found: C, 7.65; H, 1.13; N, 0.03.

$C_8H_{17}SiMe_2Cl$@SBA-1 (3d). Dehydrated SBA-1 (152 mg, 0.57 mmol SiOH) was suspended in 5 ml of *n*-hexane and 63 mg (0.62 mmol) of triethylamine in 3 ml of *n*-hexane added. The suspension was allowed to stir for 1 h, after which 133 mg (0.64 mmol) of dimethyloctylchlorosilane in 3 ml of *n*-hexane were added and the mixture stirred for additional 18 h at ambient temperature. Nonreacted chlorosilane and triethylamine were separated by three *n*-hexane washings and centrifugation. Subsequent evaporation of the remaining solvent under vacuum and removal of the adduct $NEt_3 \cdot HCl$ by sublimation at 100 °C under vacuum resulted in 212 mg of hybrid material **3d**. Analysis found: C, 19.98; H, 3.83; N, 0.00.

$C_8H_{17}Si(OEt)_3$@SBA-1 (3e). Dehydrated SBA-1 (225 mg, 0.84 mmol SiOH) and 1.27 mmol (350 mg) triethoxyoctylsilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted ethoxysilane, ethanol as a byproduct and remaining solvent were separated by three *n*-hexane washings and centrifugation. Subsequent drying under vacuum afforded 218 mg of hybrid material **3e**. Analysis found: C, 12.27; H, 1.90; N, 0.01.

$SiHMe_2$@SBA-1 (4a). Dehydrated SBA-1 (100 mg) was suspended in 5 ml of *n*-hexane. Under stirring, 200 mg of $HN(SiHMe_2)_2$ was added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-hexane washings and centrifugation. Evaporation of the remaining solvent under vacuum yielded the hybrid material **4a** (72 mg). Analysis found: C, 7.07; H, 1.99; N, 0.09.

$C_8H_{17}SiMe_2NMe_2$@ SBA-1 (4b). Dehydrated SBA-1 (250 mg, 0.89 mmol SiOH) was suspended in 5 ml of *n*-hexane and 67 mg (0.31 mmol) of dimethyloctylsilazane in 5 ml *n*-hexane added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-hexane washings and centrifugation. Evaporation of the remaining solvent under vacuum yielded hybrid material **4b** (254 mg). Analysis found: C, 13.33; H, 2.74; N, 0.85. Calculated: C, . N = 0.00

$C_8H_{17}SiMe_2Cl$@SBA-1 (4c). Dehydrated SBA-1 (250 mg, 0.89 mmol) and 0.29 mmol (61 mg) dimethyloctylchlorosilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted chlorosilane and remaining solvent are separated by three *n*-hexane washings and centrifugation. Evaporation under vacuum afforded 219 mg of hybrid material **4c**. Analysis found: C, 4.39; H, 0.97; N, 0.00.

$C_8H_{17}Si(OEt)_3$@SBA-1 (4d). Dehydrated SBA-1 (250 mg, 0.89 mmol) and 0.31 mmol (87 mg) triethoxyoctylsilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted ethoxysilane, ethanol as a byproduct, and remaining solvent were separated by three *n*-hexane washings and centrifugation. Subsequent drying under vacuum afforded 200 mg of hybrid material **4d**. Analysis found: C, 7.99; H, 1.65; N, 0.01.

$SiHMe_2$@SBA-1 (5a). Dehydrated SBA-1 (100 mg) was suspended in 5 ml of *n*-hexane. Under stirring, 200 mg of $HN(SiHMe_2)_2$ was added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-hexane washings and centrifugation. Evaporation of the remaining solvent under vacuum yielded 101 mg of hybrid material **5a**. Analysis found: C, 6.08; H, 3.37; N, 0.00.

$C_8H_{17}SiMe_2NMe_2$@ SBA-1 (5b). Dehydrated SBA-1 (310 mg, 0.92 mmol SiOH) was suspended in 5 ml of *n*-hexane and 66 mg (0.31 mmol) of dimethyloctylsilazane in 5 ml *n*-hexane added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-

hexane washings and centrifugation. Evaporation of the remaining solvent under vacuum yielded 142 mg of hybrid material **5b**. Analysis found: C, 10.28; H, 2.21; N, 0.00.

$C_8H_{17}SiMe_2NMe_2$@SBA-1 (5c). Dehydrated SBA-1 (155 mg, 0.46 mmol SiOH) was suspended in 5 ml of *n*-hexane and 149 mg (0.69 mmol) of dimethyloctylsilazane in 5 ml *n*-hexane added. The suspension was stirred for 18 h at ambient temperature. Nonreacted silazane was separated by three *n*-hexane washings and centrifugation. Evaporation of the remaining solvent under vacuum yielded 211 mg of hybrid material **5c**. Analysis found: C, 22.06; H, 3.91; N, 0.00.

$C_8H_{17}Si(OEt)_3$@SBA-1 (5d). Dehydrated SBA-1 (274 mg, 0.81 mmol) and 0.27 mmol (75 mg) triethoxyoctylsilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted ethoxysilane, ethanol as a byproduct, and remaining solvent were separated by three *n*-hexane washings and centrifugation. Subsequent drying under vacuum afforded 223 mg of hybrid material **5d**. Analysis found: C, 5.43; H, 3.30; N, 0.00.

$C_8H_{17}Si(OEt)_3$@SBA-1 (5e). Dehydrated SBA-1 (128 mg, 0.38 mmol) and 0.59 mmol (162 mg) triethoxyoctylsilane, dissolved in 10 ml of toluene, were transferred into a pressure tube. After having stirred for 30 minutes the pressure tube was heated to 125 °C and stirred at that temperature for 18 h. Nonreacted ethoxysilane, ethanol as a byproduct, and remaining solvent were separated by three *n*-hexane washings and centrifugation. Subsequen drying under vacuum afforded 115 mg of hybrid material **5e**. Analysis found: C, 12.64; H, 3.54; N, 0.00.

$C_8H_{17}SiMe_2Cl$@SBA-1 (5f). Dehydrated SBA-1 (319 mg, 0.95 mmol SiOH) was suspended in 5 ml of *n*-hexane and 35 mg (0.35 mmol) of triethylamine in 3 ml of *n*-hexane added. The suspension was allowed to stir for 1 h, after which 70 mg (0.34 mmol) of dimethyloctylchlorosilane in 3 ml of *n*-hexane were added and the mixture stirred for additional 18 h at ambient temperature. Nonreacted chlorosilane and triethylamine were separated by three *n*-hexane washings and centrifugation. Subsequent removal of the remaining solvent by drying under vacuum and of the adduct $NEt_3 \cdot HCl$ by sublimation at 100 °C under vacuum resulted in 305 mg of hybrid material **5f**. Analysis found: C, 6.97; H, 3.14; N, 0.00.

$C_8H_{17}SiMe_2Cl$@SBA-1 (5g). Dehydrated SBA-1 (129 mg, 0.38 mmol SiOH) was suspended in 5 ml of *n*-hexane and 58 mg (0.57 mmol) of triethylamine in 3 ml of *n*-hexane added. The suspension was allowed to stir for 1 h, after which 122 mg (0.59 mmol) of dimethyloctylchlorosilane in 3 ml of *n*-hexane were added and the mixture stirred for additional 18 h at ambient temperature. Nonreacted chlorosilane and triethylamine were separated by three *n*-hexane washings and centrifugation. Evaporation of the remaining solvent under vacuum and removal of adduct $NEt_3 \cdot HCl$ by sublimation at 100 °C under vacuum gave 101 mg of hybrid material **5g**. Analysis found: C, 22.88; H, 4.30; N, 0.00.

Table S1: Structural Parameters Obtained from the High Resolution α_s-Plot for the Parent and Silylated MCM-41 Materials

Sample	Ratio of silylating reagent and SiOH population[a]	Silylating reagent	Primary Mesopore Surface Area [m^2/g][b]	Pore diameter (w_d, w_{mod}) [nm][c]	Primary Mesopore Volume [cm^3/g][d]	Total Pore Volume [cm^3/g][e]
1			680	4.9	1.06	1.14
1a	excess	$HN(SiHMe_2)_2$	430	4.3	0.66	0.74
1b	1/3	$C_8H_{17}SiMe_2NMe_2$	410	4.2	0.64	0.70
1c	1/3	$C_8H_{17}SiMe_2Cl$[f]	360	4.0	0.56	0.61
1d	1/3	$C_8H_{17}Si(OEt)_3$[g]	520	4.4	0.81	0.88
1e	1.15	$C_8H_{17}SiMe_2NMe_2$	200	3.3	0.32	0.35
1f	1.15	$C_8H_{17}SiMe_2Cl$[f]	270	3.7	0.42	0.46
1g	1.2	$C_8H_{17}Si(OEt)_3$[g]	470	4.3	0.72	0.79

[a] SiOH population calculated from the corrected carbon value of the dimethylsilylated samples. [b] Assessed from the α_s-plot according to Kruk *et al*.[7] [c] Calculated using

$$w_d = \sqrt{\frac{8}{\sqrt{3}\pi}} d \sqrt{\frac{\rho V_p}{1+\rho V_p}}$$

for the parent material[7] and

$$w_{\mathrm{mod}} = w_d \sqrt{\frac{V_p}{V_{p,MCM-41}\left[1-\frac{x_c(M-1.008)}{12.001\cdot n_c}\right]}}$$

for the silylated materials.[8] [d] Assessed from the α_s-plot using the simplified formula $V_p = v_p \cdot c_f$ due to the absence of microporosity. [e] Obtained by $V_{tot} = v_{0.99} \cdot c_f$ at $p/p_0 = 0.99$.[7] [f] Reaction conditions: NEt_3 as a base, stirring at ambient temperature, solvent: *n*-hexane. [g] Reaction conditions: stirring at 125 °C, solvent: toluene.

Table S2: Analytical Data, Surface Area, Pore Volume, and Pore Diameter of Parent and Silylated Largepore SBA-1 Materials

Sample	Ratio of silylating reagent and SiOH population[a]	Silylating reagent	a_S[m^2/g][b]	d_p[nm][c]	D_{me} [nm][d]	V_p[cm/g][e]	SiOH [mmol/g][a]	C [wt%][f]	SE [%][g]
4			1030	3.0	5.2	1.11	3.55		
4a	excess	$HN(SiHMe_2)_2$	740	2.3	4.9	0.70		7.07	100
4b	1/3	$C_8H_{17}SiMe_2NMe_2$	700	2.3	4.8	0.62		12.20	91
4c	1/3	$C_8H_{17}SiMe_2Cl$[h]	970	2.8	5.1	1.01		4.36	33
4d	1/3	$C_8H_{17}Si(OEt)_3$[h]	860	2.8	5.1	0.90		7.99	60
5			900	3.1	5.0	0.98	2.97		
5a	excess	$HN(SiHMe_2)_2$	620	2.4	4.7	0.62		6.08	100
5b	1/3	$C_8H_{17}SiMe_2NMe_2$	800	2.4	4.9	0.77		10.28	87
5c	excess	$C_8H_{17}SiMe_2NMe_2$	600	n.d.	4.4	0.40		22.06	62
5d	1/3	$C_8H_{17}SiMe_2Cl$[i]	700	2.3	4.8	0.64		6.97	54
5e	excess	$C_8H_{17}SiMe_2Cl$[i]	600	1.9	4.5	0.46		22.88	64
5f	1/3	$C_8H_{17}Si(OEt)_3$[h]	850	3.0	5.0	0.91		5.43	38
5g	excess	$C_8H_{17}Si(OEt)_3$[h]	800	2.7	4.9	0.86		12.64	30

[a] SiOH population calculated from the corrected carbon value of the dimethylsilylated samples. [b] Specific BET surface area. [c] Pore diameter according to the maximum of the BJH pore size distribution calculated from the adsorption branch; all samples were pretreated at 250 °C (parent materials) and 100 °C (silylated samples) respectively *in vacuo* until the pressure was < 10^{-3} Torr. [d] Cage diameter according to the "model of spherical cavities" as proposed by Ravikovitch and Neimark.[9] [e] Pore volume determined at the relative preasure $p/p_0 = 0.975$. [f] Elemental analysis obtained after treatment at 100 °C *in vacuo* (<10^{-3} Torr). [g] The silylation efficiency SE was determined by the molar ratio of the grafted species divided by the maximum amount of silanol groups that could be grafted (based on the assumption that the corrected carbon-value of the elemental analysis divided by the amount of carbon atoms present the molar amount of the grafted species). [h] Reaction conditions: stirring at 125 °C, solvent: toluene. [i] Reaction conditions: using NEt_3 as a base, stirring at ambient temperature, solvent: *n*-hexane.

PXRD Patterns

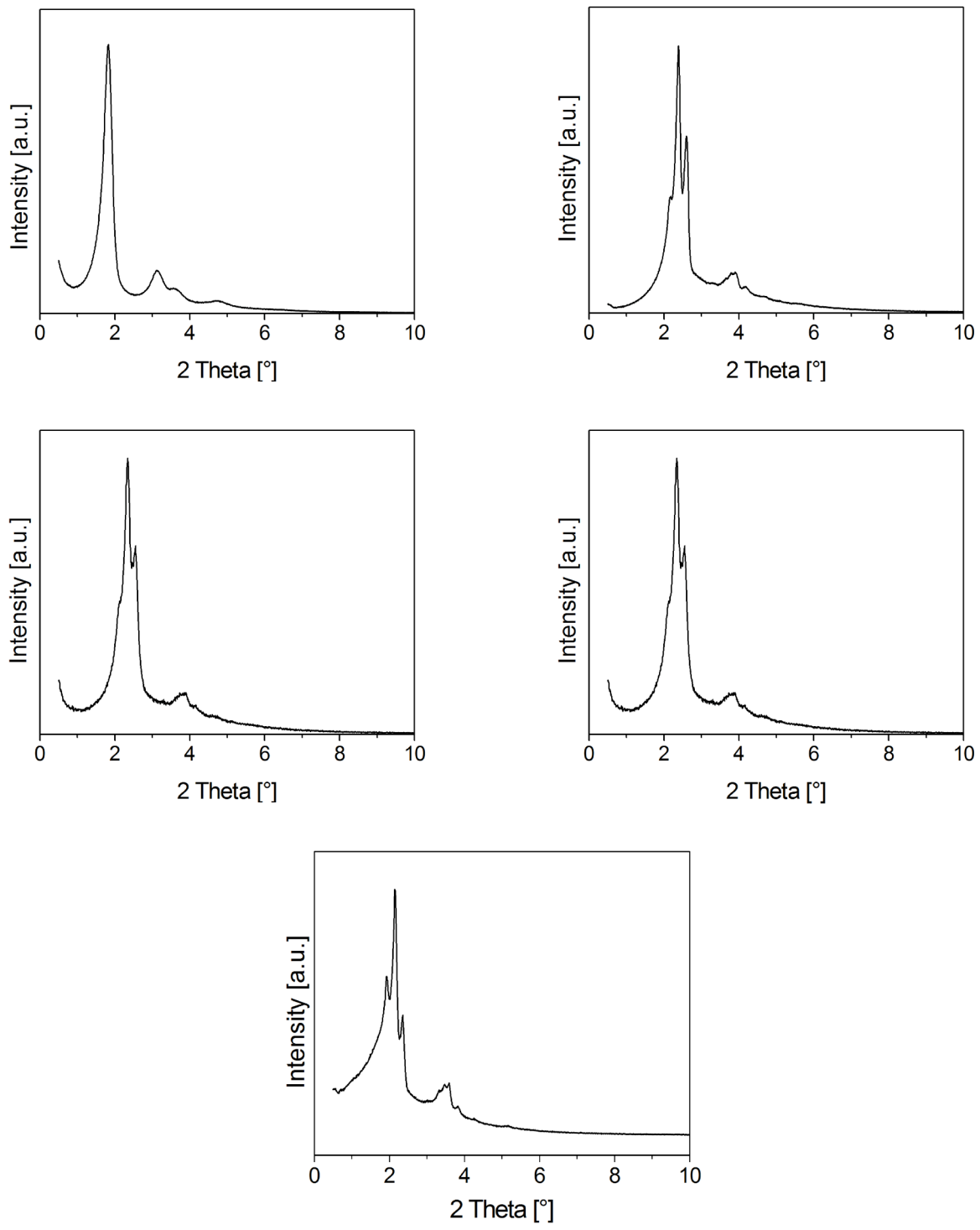


Figure S1. Powder XRD patterns of the parent materials: MCM-41 **1** (upper left), SBA-1 **2** (upper right), SBA-1 **3** (middle left),SBA-1 **4** (middle right) and SBA-1 **5** (bottom).

Nitrogen Physisorption Data

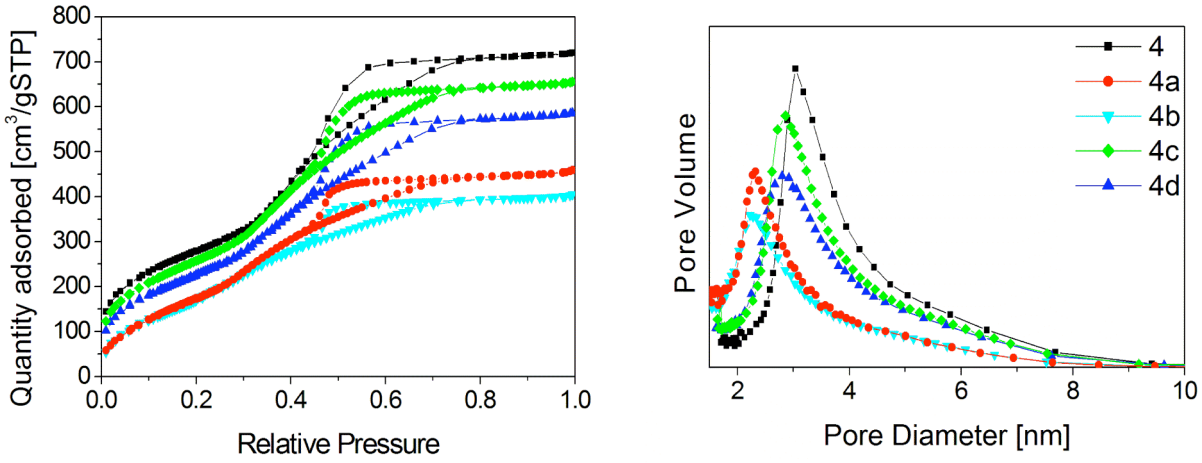


Figure S2. Nitrogen physisorption isotherms and pore size distributions of the parent and silylated materials addressing 1/3 of the silanol groups of largepore SBA-1 **4**.

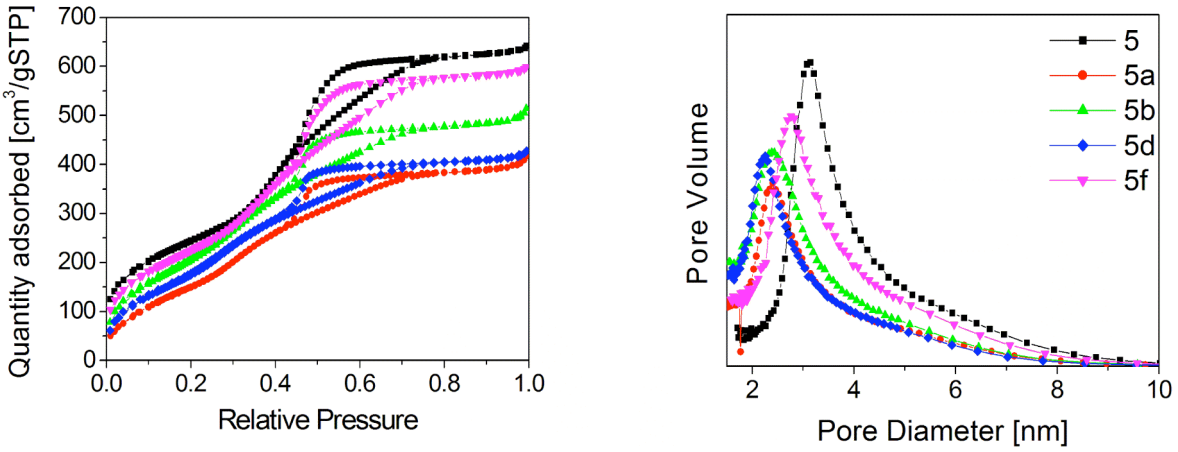


Figure S3. Nitrogen physisorption isotherms and pore size distributions of the parent and silylated materials addressing 1/3 of the silanol groups of largepore SBA-1 **5**.

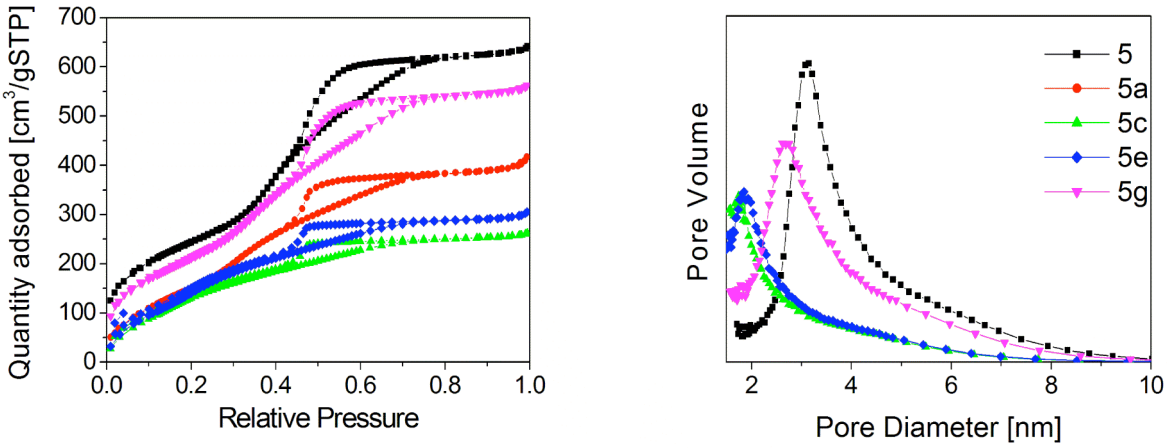


Figure S4. Nitrogen physisorption isotherms and pore size distributions of the parent and silylated materials addressing all of the silanol groups of largepore SBA-1 **5**.

IR Spectra

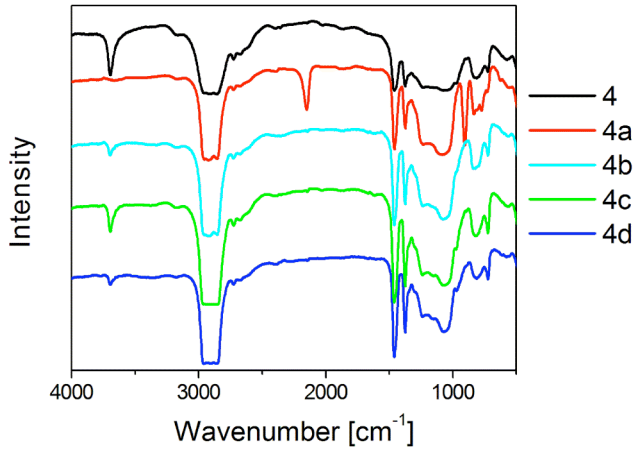


Figure S5. Infrared spectra of the parent and silylated materials addressing 1/3 of the silanol groups of largepore SBA-1 **4**.

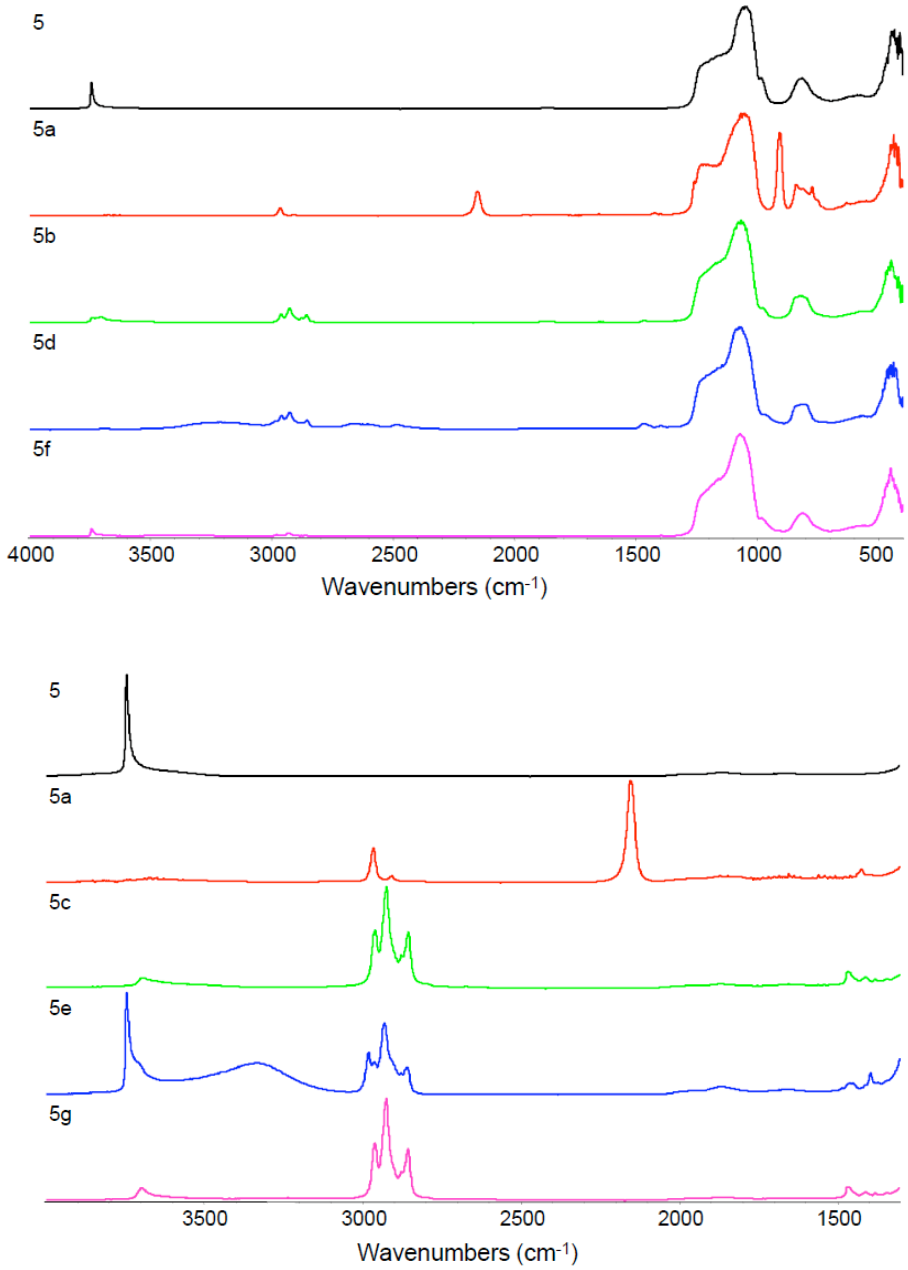


Figure S6. DRIFT spectra of the parent and silylated materials addressing 1/3 of the silanol groups of largepore SBA-1 **5**.

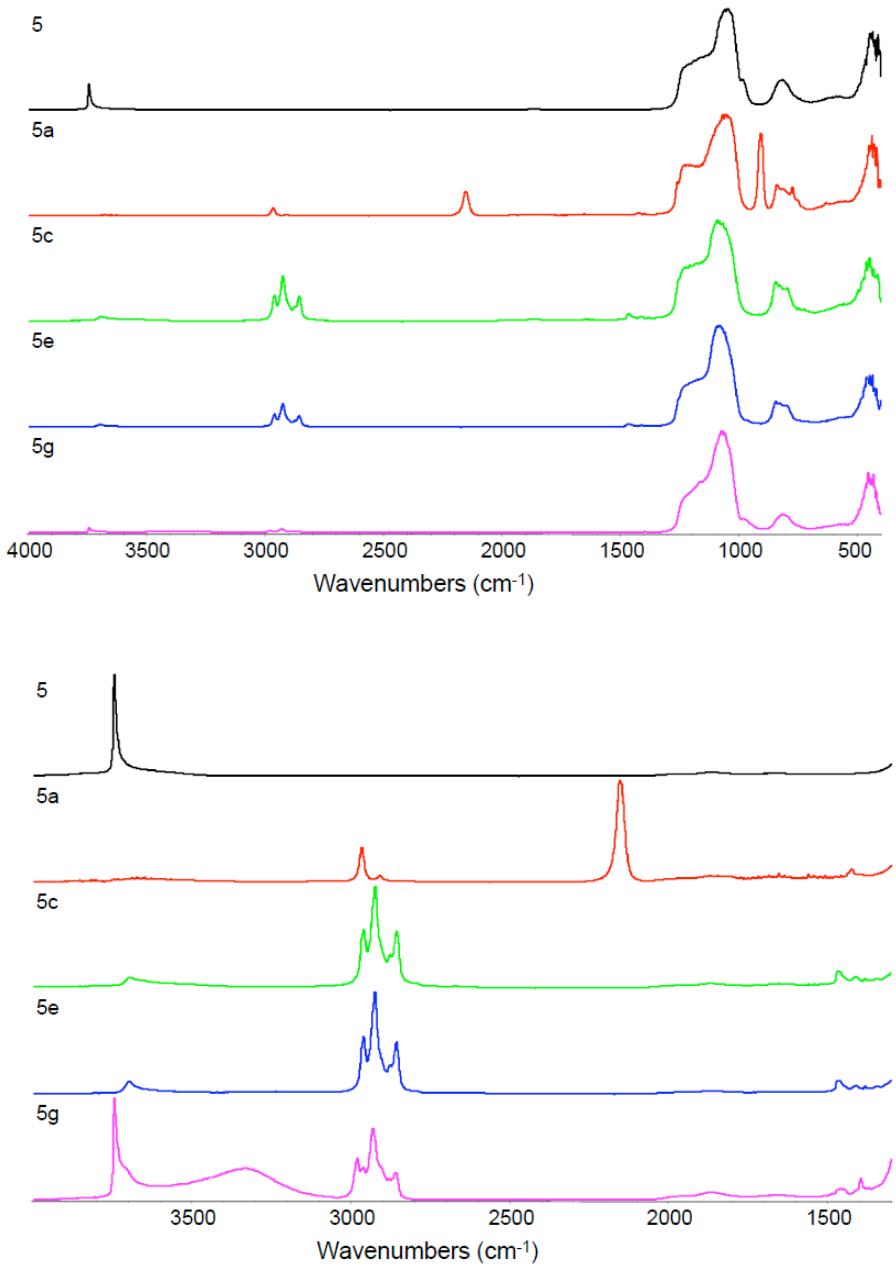
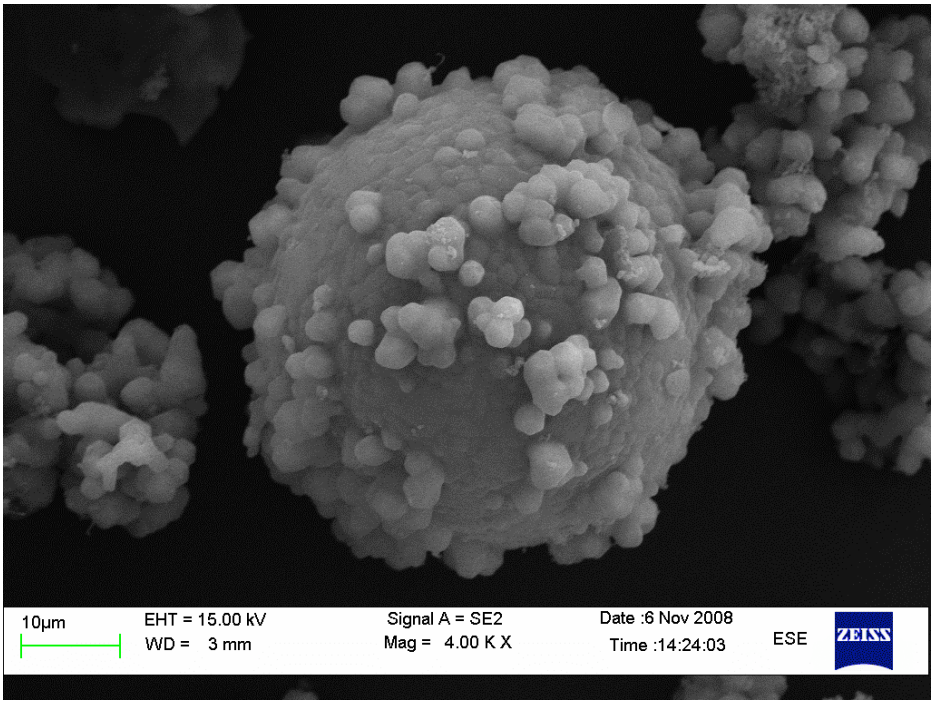


Figure S7. DRIFT spectra of the parent and silylated largepore SBA-1 **5**; excess of the silylation reagent has been used.

SEM Images



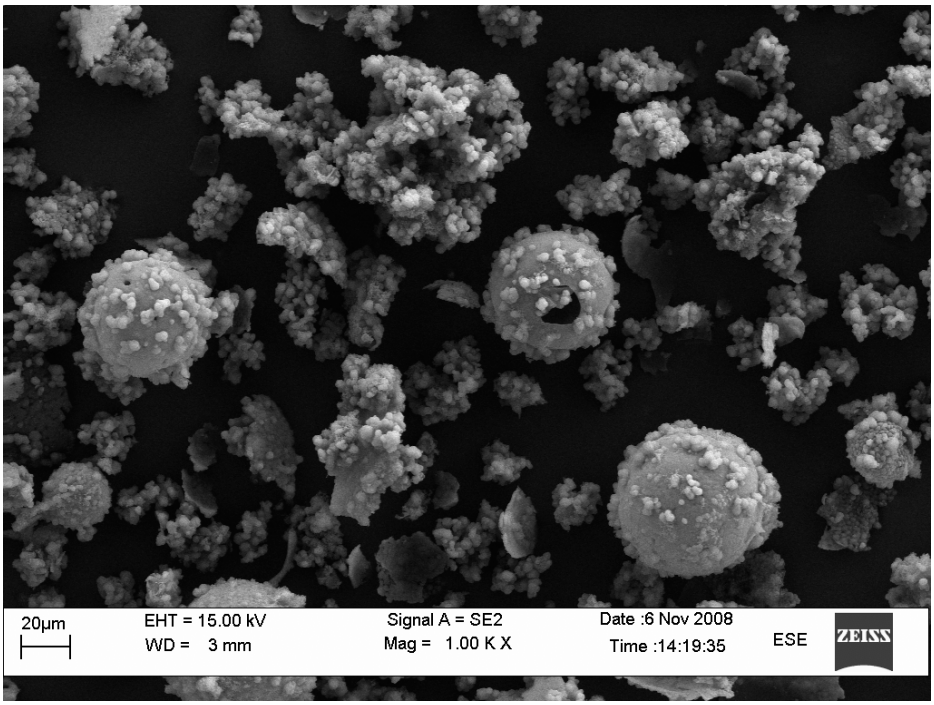


Figure S8. SEM images of parent material **2** (SBA-1).

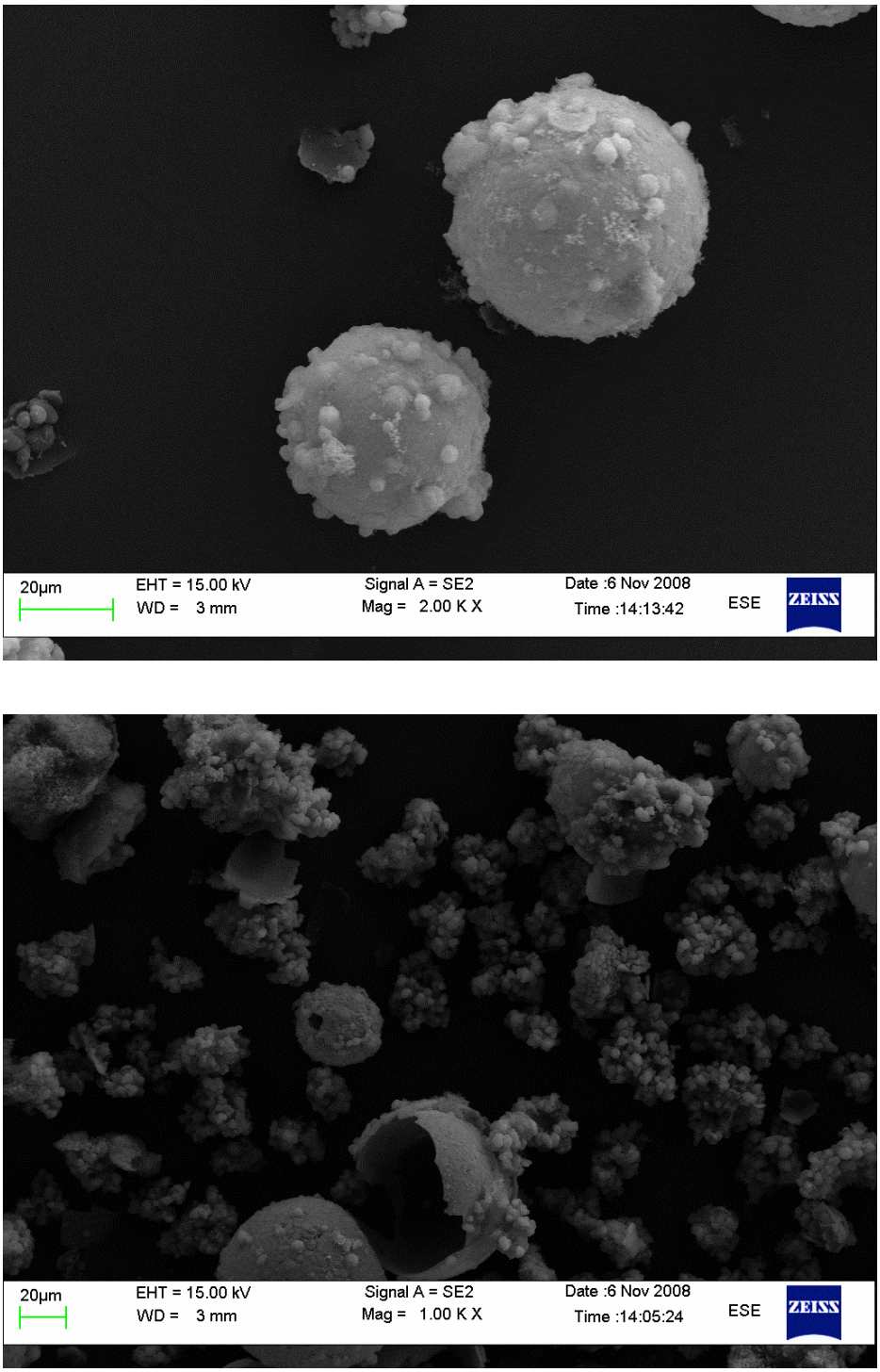
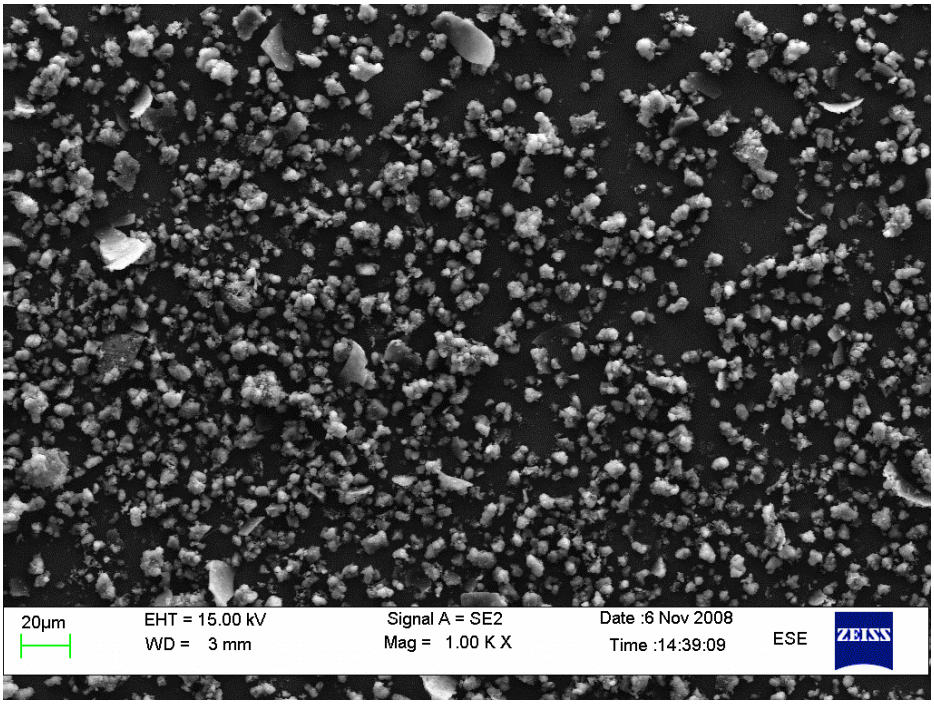


Figure S9. SEM images of parent material **5** (SBA-1 LP).



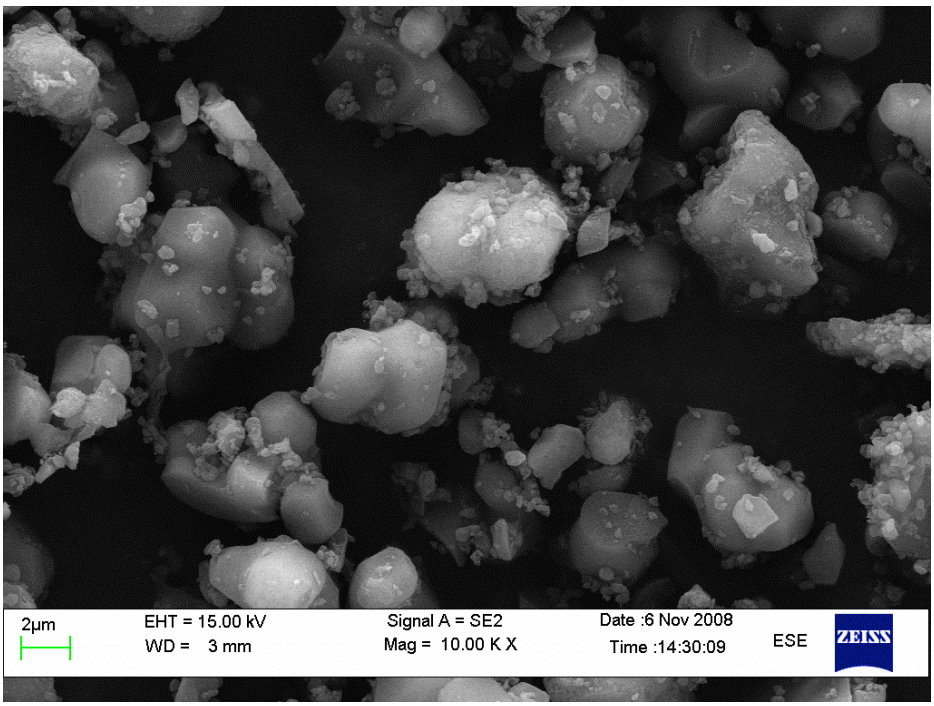


Figure S10. SEM images of silylated SBA-1 **2b** (functionalized with $C_8H_{17}SiMe_2NMe_2$, **A**).

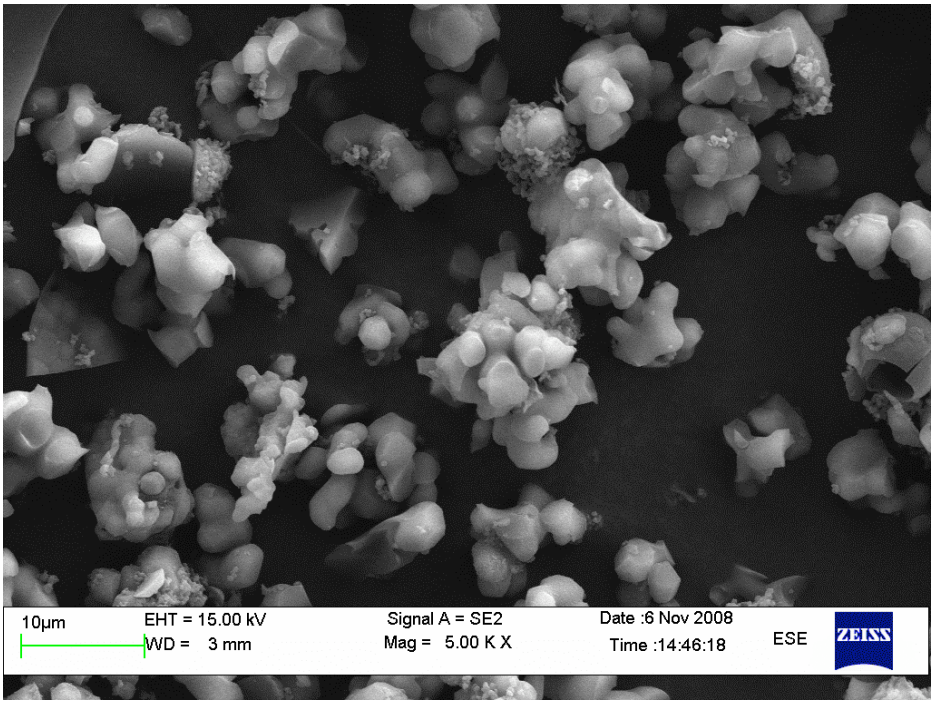


Figure S11. SEM image of silylated SBA-1 **3b** (functionalized with excess $C_8H_{17}SiMe_2NMe_2$, **A**).

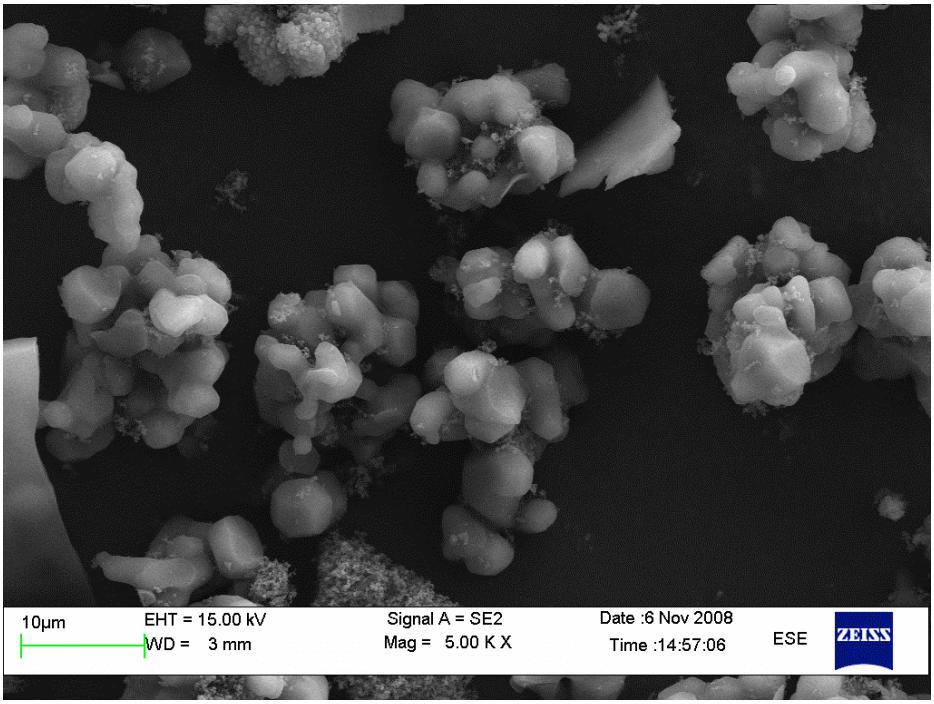


Figure S12. SEM image of silylated SBA-1 **5b** (functionalized with $C_8H_{17}SiMe_2NMe_2$, **A**).

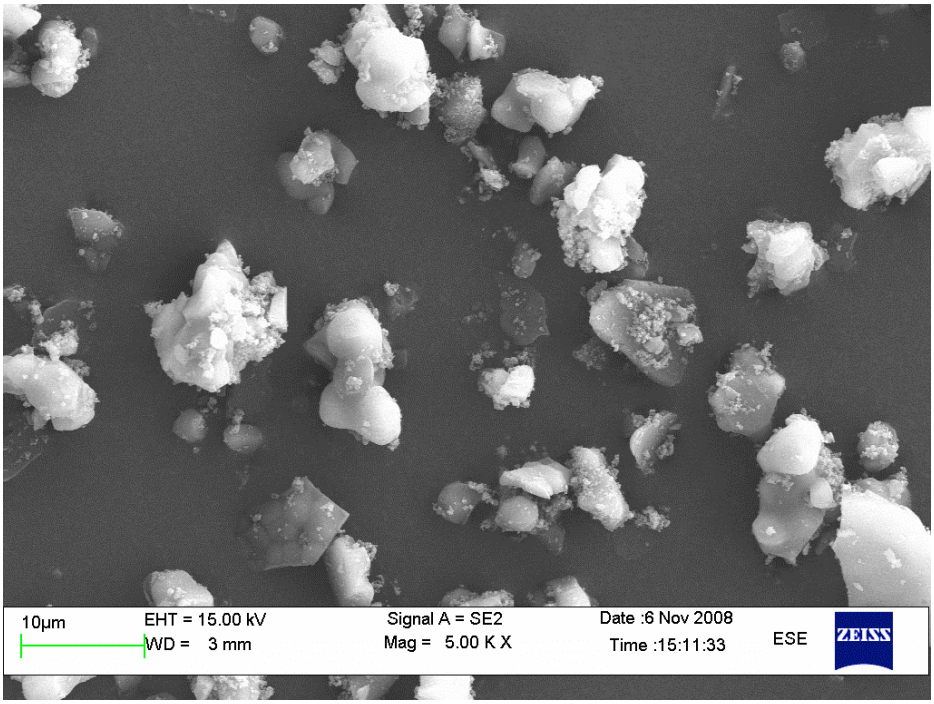


Figure S13. SEM image of silylated SBA-1 **5c** (functionalized with excess $C_8H_{17}SiMe_2NMe_2$, **A**).

TEM Images

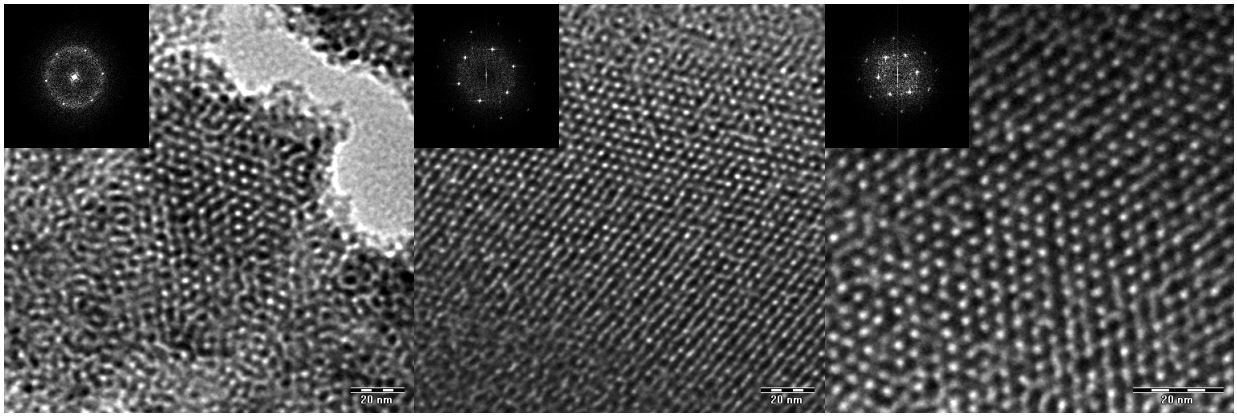


Figure S14. TEM images of SBA-1 materials **5** (left), **5b** (middle), and **5c** (right) from [111] direction.

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