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The Surface Chemistry of Hydrophobic Silica Aerogels

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ABSTRACT: The properties of silica aerogels, and the ability to prepare them by ambient pressure drying, hinge on their chemical surface modification. Until now, quantitative analysis of the surface chemistry has not been possible by state-of-the-art analytical methods. Here, we determine the surface chemistry of six archetypal, ambient pressure dried, hydrophobic silica aerogels and open-porous foams with quantitative ^1H , ^{13}C and ^{29}Si and ^1H - ^{29}Si heteronuclear solid-state NMR spectroscopy. The quality of the external calibration, the validation by elemental analysis and the consistency between the ^1H , ^{13}C and ^{29}Si MAS NMR data, enable us to robustly quantify the surface chemistry of these classical silica materials. Four aerogels were derived from tetraethoxysilane (TEOS), polyethoxydisiloxane (PEDS) or waterglass precursors and hydrophobized with trimethylsilyl (TMS) groups through immersion in hexamethyldisilazane (HMDZ) in heptane, trimethylchlorosilane (TMCS) in heptane, or hexamethyldisiloxane (HMDSO) in ethanol. The resulting aerogels display remarkably similar chemistries despite their very different precursors (alkoxides, waterglass), hydrophobization agents (HMDZ, TMCS, HMDSO) and gelation and hydrophobization solvents (water, ethanol, heptane). The TMS content is nearly the same (22-27 wt%), the ethoxy content is low (<4 wt%) and the silica speciation displays a narrow range for all four aerogels. The ^1H - ^{29}Si heteronuclear correlation spectra provide unambiguous evidence for the grafting of the TMS groups on the silica surfaces. Remarkably, the NMR data enables the prediction of the silica particle size to within 1 to 2 nm of that derived by TEM analysis. Two additional, inherently hydrophobic, ambient pressure dried, open-porous silica foams were synthesized from methyltrimethoxysilane (MTMS) and from a MTMS-dimethyldimethoxysilane (DMDMS) mixture, respectively. The reduction in the number of bridging oxygen per Si atom, from 3.76-3.90 for TEOS, PEDS or waterglass based aerogels, to 2.86 for the MTMS based open-porous foam and to 1.90 for the MTMS-DMDMS derived open-porous foam, results in a brittle to super-flexible transition. Our results highlight the importance of the chemical treatment of the wet gels (hydrophobization and solvent exchange) on the final surface chemistry of silica aerogels.

1. INTRODUCTION

Since their first realization in 1932 by Kistler¹, silica aerogels have been used for thermal insulation^{2,3}, catalyst support⁴, selective gas sorption (CO₂)⁵⁻⁷, drug delivery⁸ and oil spill clean-up⁹. These applications depend on the exceptional properties of silica aerogel, most notably their high volume fraction of mesopores and large surface area. However, it is difficult to maintain the porosity during solvent removal because of the strong capillary forces and the condensation reactions between surface silanol groups that occur during drying. To circumvent these problems, silica aerogels traditionally have been prepared by super-critical drying, often after a solvent exchange into CO₂^{10,11}. Following the demonstration that the solvent can be removed by evaporative drying at ambient pressure if the surfaces have been hydrophobized, a wide range of synthesis routes have been developed to prepare hydrophobic silica aerogel by ambient pressure drying¹²⁻¹⁵. Classical mesoporous silica aerogels are prepared from waterglass, tetra(m)ethoxysilane (TMOS/TEOS) or polyethoxydisiloxane (PEDS – a pre-polymerized form of TEOS) precursors^{14, 16-20}. Acid-base catalyzed sol-gel processes²¹ produce gels that, when dried without surface modification, are inherently hydrophilic. In order to allow for drying at ambient pressure, and to improve the long-term stability of the final product, the surface can be hydrophobized prior to drying by immersing them in a modification solution where surface silanol groups are replaced by hydrophobic groups, typically trimethylsilyl (TMS). The TMS groups are most often introduced through trimethylchlorosilane (TMCS), hexamethyldisilazane (HMDZ) or hexamethyldisiloxane (HMDSO) hydrophobization agents. An alternative, more direct route to synthesize open-porous, inherently hydrophobic silica materials is to use precursors that already contain chemically bound hydrophobic groups, for example methyltri(m)ethoxysilane (MTMS/MTES)^{12, 22} or dimethyldimethoxysilane (DMDMS)²³ with three or two Si-O bonds and one or two Si-C bonds, respectively. The resulting materials are super-hydrophobic and flexible^{12, 22, 23}, but the ambient pressure dried flexible foams do not possess the exceptionally low thermal conductivities of classical silica aerogels due to their larger pore sizes.

Although ambient pressure drying of hydrophobic silica aerogels is a scientifically and industrially well-established process today, the surface modification process has so far eluded quantitative analysis. Solid-state NMR spectroscopy provides element specific and potentially quantitative insights into the speciation and surface chemistry of silica nanomaterials²⁴⁻³². ^1H , ^{13}C and ^{29}Si are all spin-1/2 nuclei with well resolved spectra and speciation data can be readily obtained for all major constituents of silica aerogel, apart from oxygen. Recently, we established ^1H , ^{13}C and ^{29}Si solid-state MAS NMR spectroscopy as an accurate, quantitative method to determine the surface density of various functional groups, e.g. TMS and ethoxy³³. Here, we use this protocol to compare the surface chemistry and microstructure of six archetypal, ambient-pressure dried, hydrophobic silica aerogels and open-porous foams derived from TEOS, PEDS, waterglass, MTMS and DMDMS precursors and quantify the surface composition and spatial density of the different functional groups. In addition, we probe the connectivity of these functional groups to the silica network by ^1H - ^{29}Si Heteronuclear Correlation (HETCOR) spectroscopy.

2. EXPERIMENTAL

2.1 Sample Synthesis. Six silica aerogel samples have been prepared according to classical synthesis procedures from the literature (Table 1). A typical two-step TEOS based silica aerogel was hydrophobized with HMDZ in heptane (1)¹⁴. A PEDS based aerogel was hydrophobized with HMDSO in ethanol (2)³³. Two waterglass based aerogels were hydrophobized in heptane with TMCS, either without (3) or with (4) a previous solvent exchange from water to ethanol¹⁸. Inherently superhydrophobic MTMS (5) and MTMS+DMDMS (6) open-porous foams did not require an additional hydrophobization step¹². All samples were prepared by ambient pressure drying according to the conditions listed in Table 1 and the detailed description in the Supplementary Information.

Table 1. Synthesis conditions and physical properties of silica aerogels (1-4) and open-porous foams (5-6).

Sample number	Silica aerogels				Open-porous silica foams	
	1	2	3	4	5	6
Sample name	TEOS/HMDZ	PEDS/HMDSO	WG/TMCS	WG/SE/TMCS	MTMS	MTMS+DMDMS
Reference	Rao et al. 2001, 2005	Pajonk et al. 1995	Wang et al. 2009	Wang et al. 2009	Bhagat et al. 2007	Hayase et al. 2011
Precursors	TEOS in ethanol	PEDS in EtOH	Waterglass	Waterglass	MTMS	MTMS+DMDMS
Washing	EtOH (2x), n-heptane (4x)	-	-	EtOH (3x), n-heptane (4x)	-	H ₂ O (2x), EtOH (2x)
Hydrophobe	HMDZ in n-heptane	HMDSO in EtOH	TMCS in EtOH/n-heptane	TMCS in n-heptane	-	-
Washing	n-heptane (4x)	-	-	-	-	-
Density ρ (g/cm ³)	0.203	0.113	0.135	0.136	0.171	0.105
Particle diameter (nm)						
- TEM	6.1	6.7	5.0	5.6	-	-
- NMR (without TMS correction)	4.6	4.5	3.7	3.0	-	-
- NMR (with TMS correction)	5.3	5.2	4.4	3.7	-	-
Surface area (m ² /g)						
- S_{BET}	602	733	637	773	385	^b
- S_{NMR} (see text)	593	606	737	909	-	-
Pore volume (cm ³ /g)						
- from density ($V=1/\rho-1/\rho_0$) ^a	4.5	8.4	7.0	6.9	5.3	9.0
- BJH adsorption (1.7-300 nm)	3.7	3.8	4.0	3.6	0.2	^b
Average pore diameter (nm)						
- from $4V/S_{\text{BET}}$	30	46	44	36	55	^b

Estimated uncertainties: density: 5% relative; particle diameter TEM: 1-1.5 nm (1 S.D.); S_{BET} : around 50 m²/g; Pore volume from density: 10% relative

^a ρ_0 =skeleton density, approximated by the density SiO₂ glass (2.20 g/cm³) for samples 1-4, and by 1.80 g/cm³ for samples 5-6.

^b Sample had insufficient nitrogen sorption for meaningful BET analysis due to very low surface area and large pore sizes.

2.2 Basic Characterization. The envelope density was determined from the mass and the volume measured by powder pycnometry (Micromeritics, GeoPyc 1360) for samples 1-4, and by its dimensions for samples 5-6 as these latter materials are too compressible to be measured by the powder displacement method. The specific surface area and volume fraction of mesopores were determined from the nitrogen sorption data (Micromeritics, TriFlex) using Brunauer-Emmet-Teller (BET) analysis³⁴ and Barrett-Joyner-Halenda (BJH) analysis³⁵. The average pore diameter was calculated from the pore volume and surface area rather than the BJH analysis as the latter is known to be affected by the sample deformation during nitrogen sorption experiments³⁶. The C and H content were determined by standard elemental analysis (combustion and subsequent gas-phase FTIR analysis) at the Laboratory for Organic Chemistry of ETH Zurich.

2.3 Electron Microscopy. Transmission electron microscopy (TEM) images were recorded with a JEOL-2200FS microscope operated at an accelerating voltage of 200 kV. The samples were crushed and dispersed in methanol and the resulting dispersion was then dropped onto thin carbon grids and allowed to evaporate at room temperature. Care has been taken to avoid beam-induced modification

of the aerogel morphology by using short exposure times with a low electron dose. Scanning Electron Microscopy (SEM) images of all samples were acquired with a FEI Nova NanoSEM 230 instrument (FEI, Hillsboro, Oregon, USA) at an accelerating voltage of 10 kV and a working distance of 5 mm. The silica aerogels were fixed on the sample holder using a carbon pad and subsequently coated with 10-15 nm of platinum for SEM analysis.

2.4 Solid-State NMR spectroscopy. The NMR procedures closely follow those established in our previous NMR study on silica aerogel³³ and all spectra were processed with matNMR³⁷. Quantitative Magic Angle Spinning (MAS) solid-state ^1H , ^{13}C and ^{29}Si NMR spectra were recorded with wide-bore 9.4 T magnets, corresponding to Larmor frequencies of 400.2, 100.6 and 79.5 MHz for ^1H , ^{13}C and ^{29}Si , respectively. We employed spectral widths and acquisition times of 249.9 ppm and 328 ms, 219.2 ppm and 93 ms, and 349.3 ppm and 74 ms, for ^1H , ^{13}C and ^{29}Si , respectively. The ^1H NMR spectra were recorded on an Avance III system applying a 24 kHz MAS rate in 2.5 mm zirconia rotors to minimize line-widths. The ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker Avance III HD system with a MAS rate of 4 kHz in 7 mm zirconia rotors to maximize signal to noise. All spectra were collected with a recycle delay of at least $5 \cdot T_1$, as determined by saturation recovery experiments, to ensure their quantitative nature. Fully relaxed spectra were also collected for adamantane (^1H and ^{13}C), octakis(trimethylsiloxy)silsesquioxane (Q8M8) (^1H , ^{13}C , ^{29}Si) and tetrakis(trimethylsilyl)silane (^1H , ^{13}C , ^{29}Si) to calibrate the absolute NMR signal intensities. All samples and standards were measured on completely filled rotors to ensure that potential inhomogeneity in sensitivity due to gradients in the radio-frequency (RF) field strength cancel out during the intensity calibration and with sufficiently strong pulses to ensure uniform excitation: 83, 45 and 21 kHz for ^1H , ^{13}C and ^{29}Si , respectively³³. No background contributions were detected for ^{13}C and ^{29}Si . The ^1H background signal from an empty rotor was subtracted.

The high ^1H NMR sensitivity results in acquisition times of just a few minutes and establishes ^1H NMR as a tool to screen large numbers of samples if the spectra are sufficiently resolved. Despite the

inherently low ^{13}C and ^{29}Si NMR sensitivity and the further loss of sensitivity due to the low sample density, quantitative ^{13}C and ^{29}Si NMR spectra with acceptable signal to noise ratios can be collected within around 2 and 10 hours, respectively. These relatively short acquisition times are mainly due to the relatively short T_1 relaxation times of 2-25 s for ^{13}C and 30-180 s for ^{29}Si , enabling relatively high repetition rates, even for recycle delays $>5 \cdot T_1$. For comparison, ^{29}Si T_1 relaxation times in bulk silica glass can be as long as 7 hours, i.e. two to three orders of magnitude longer³⁸. The high surface area of nanoscale materials and the resulting high concentrations of surface groups further increase sensitivity.

In addition to the quantitative NMR spectra, two-dimensional ^1H - ^{29}Si HETCOR spectra have been acquired to investigate the connectivity between the different sites³⁹. The HETCOR spectra were collected on a Bruker Avance III HD spectrometer with a wide-bore 16.4 T magnet, corresponding to Larmor frequencies of 700 and 139.1 MHz for ^1H and ^{29}Si , respectively. We selected 4 mm zirconia rotors with a spinning rate of 10 kHz as a compromise between sensitivity and spectral resolution in the ^1H dimension. Homonuclear dipolar decoupling using continuous phase modulation (DUMBO) was applied to improve the spectral resolution in the ^1H dimension⁴⁰.

3. RESULTS AND DISCUSSION

3.1 Basic characterization. The density, BET surface area, porosity, pore size and other physical properties are summarized in Table 1. The nitrogen sorption curves are plotted in Fig. S2. The silica aerogels *senso stricto* (based on silica precursors with 4 oxygen neighbors per Si atom, samples 1-4) are brittle materials with densities between 0.113 and 0.205 g/cm³ and surface areas between 602 and 773 m²/g. The MTMS-based open-porous foam (5) has a density of 0.171 g/cm³ and a surface area of 385 m²/g and is somewhat flexible. The MTMS+DMDMS based open-porous foam (6) has a density of 0.105 g/cm³, a surface area too small to be determined by BET and is super-flexible. Aerogels 1-4

display the typical blue hue from the Rayleigh scattering originating from the silica aerogel mesopores (Fig. S1). In contrast, the milky appearance of open-porous foams 5 and 6 is indicative of the presence of larger macropores, as confirmed by SEM microscopy (see below) and the inability of nitrogen sorption to adequately probe the pore sizes of both samples (Table 1, Fig. S2).

3.2 Electron microscopy. The TEM images of the silylated silica aerogel samples demonstrate the typical pearl-necklace morphology with silica particles linked by inter-particle necks (Fig. 1). The particle sizes are somewhat larger for the alkoxide (1-2) than for the waterglass (3-4) based aerogels (Table 1). The SEM images for the silylated samples (1-4) display the typical silica aerogel morphologies with mesopores enclosed by secondary particle aggregates of ca. 20-50 nm in diameter (Fig. 2). Secondary particle in this size range were observed previously by SEM and SAXS for silica and silica-polymer hybrid aerogels ⁴¹. The MTMS and DMDMS based open-porous foams (samples 5-6) display radically different morphologies with much larger pore sizes, particularly for sample 6.

Figure 1. TEM images of four archetypal silica aerogels.

Figure 2. SEM images of six archetypal silica aerogels and open-porous foams. Samples 1-4 are true aerogels with mesopores in the 10-40 nm range. The MTMS, and particularly the MTMS+DMDMS samples (5-6), are open-porous foams with much larger pores.

3.3 Quantitative NMR spectra. The quantitative ^{29}Si NMR spectra display all the peaks expected for hydrophobic silica aerogel materials (Fig. 3c) ^{25, 31-33}. Aerogels 1-4 consist of silica with 76 to 90% Q^4 and 10 to 24% Q^3 , where Q^n denotes a tetrahedral Si with n bridging oxygen (BO) and $(n-1)$ non-bridging oxygen (NBO) (Table S1, Fig. 3c, Fig. S3). These samples also display a clear ^{29}Si NMR peak for TMS. The MTMS derived open-porous foam (5) consists of T^3 and T^2 sites, where T^n stands for a tetrahedral Si with 1 C, n BO and $(3-n)$ NBO neighbors in a molar 86:14 T^3 : T^2 ratio (Table S2, Fig. 3c) ²⁵. The MTMS+DMDMS derived open-porous foam (6) contains T^3 : T^2 : D^2 : D^1 in a 52:6:38:4 molar proportion, where D^n is a Si tetrahedron with 2 neighbouring C atoms as well as n BO and $(2-n)$ NBO (Table S2, Fig. 3c). The quantitative ^1H and ^{13}C spectra (Fig. 3a,b) give further insight into the silica chemistry. They confirm the presence of TMS groups for the silylated samples (1-4) in addition to a

minor fraction of ethoxy groups ($\equiv\text{Si}(\text{Q}^3)\text{-O-CH}_2\text{-CH}_3$, see HETCOR data below) and in the case of sample 3, a small fraction of $\equiv\text{Si-OH}$ (see HETCOR data below). Samples 3 and 4 also contain minor peaks related to impurities from the exchange resin. The quantitative ^1H and ^{13}C spectra of the MTMS derived sample (5) confirm the presence of methyl groups linked to the T sites, $\equiv\text{Si}(\text{T})\text{-CH}_3$ (see HETCOR data below) and a minor peak associated with methoxy groups ($\equiv\text{Si}(\text{T}^2)\text{-O-CH}_3$). The quantitative ^{13}C spectrum of the MTMS+DMDMS derived sample (6) confirms the presence of both T and D groups. Unlike the ^{13}C spectrum, the ^1H spectrum is unable to resolve both types of methyl groups, but the ^1H NMR is sensitive enough to detect a very minor peak associated with methoxy groups. Note that the detection of minor amounts of silanol ($\equiv\text{Si-OH}$) is difficult with NMR because this species contains only a single H atom (compared to 3, 5 and 9 for methoxy, ethoxy and TMS groups, respectively) and because silanol groups are characterized by broad ^1H NMR lines that shift depending on the strength of the hydrogen bonding ⁴². The silanol content can be estimated indirectly from the difference in Q^3 and ethoxy content, assuming that each Q^3 species is linked to either an ethoxy or a hydroxyl group (Table 2).

Fig. 3. Quantitative ^1H (a), ^{13}C (b) and ^{29}Si (c) NMR spectra of six archetypal silica materials. The round markers denote spinning sidebands; the squares denote peaks due to an unidentified impurity in the waterglass based samples, presumably from the exchange resin.

3.4 Calibration and validation. Without calibration, only ratios of different chemical species can be quantified from fully relaxed NMR spectra (Fig. 3). In a recent study, we demonstrated that it is possible to calibrate the absolute spectral intensities by external calibration with standard samples³³. Such an external calibration allows one to determine the absolute content of specific sites in a sample and to correlate the NMR data from different nuclei. The slopes of the ^1H , ^{13}C and ^{29}Si calibration curves (Fig. 4a-c, Table S5) enable the estimation of the absolute amount of each nucleus and species in the sample. The H, C and Si content can be derived directly from the NMR spectra and the O content can be calculated from the ^{29}Si NMR data according to $[\text{O}_{\text{total}}] = 2[\text{Q}^4] + 2.5[\text{Q}^3] + 0.5[\text{TMS}]$ (in moles). Thus, the total weight of sample in the rotor can be estimated from the NMR data alone and this provides a first validation of the quantification procedure (Table S3, Fig. 4d). A second validation is provided by comparing the H and C content derived by NMR with those derived by elemental analysis

(Fig. 4e, Table S4). A final validation is provided by the consistency between the different measurements: the ^1H , ^{13}C and ^{29}Si data give consistent estimates for the content of the various molecular groups (T and D sites, TMS and ethoxy groups) (Table 2, Fig. 4f).

Fig. 4. Calibration (a-c) and validation (d-f) of the ^1H , ^{13}C and ^{29}Si MAS NMR data. a) ^1H calibration, b) ^{13}C calibration, c) ^{29}Si calibration, d) validation by total mass in rotor, e) validation by elemental analysis, f) internal consistency; red: ^1H , blue: ^{29}Si , black: nominal composition, squares: TMS, triangle: D sites, circles: T sites, star: ethoxy groups.

3.5 The composition of silica aerogels and open-porous foams. The silylated aerogels (1-4) display remarkably similar NMR spectra (Fig. 3) and bulk and surface chemistries (Table 2) despite their very different precursors (alkoxide, waterglass), hydrophobization agents (HMDZ, HMDSO and TMCS) and

gelation and hydrophobization solvents (water, ethanol, n-heptane): the TMS content is nearly constant between 22-27 wt%, the amount of ethoxy groups ranges from 0 to 4 wt% and also the silica speciation displays a narrow range: $0.10 \leq Q^3/(Q^3+Q^4) \leq 0.24$. These similarities in chemistry result in aerogels with near-identical morphology (Figs. 1, 2) and properties for samples prepared from different precursors⁴³. The surface chemistry of silylated silica aerogels and its dependence on the processing conditions will be discussed in more detail in Section 3.8.

The MTMS and MTMS/DMDMS based silica open-porous foams (5-6) display completely different chemistries compared to the silylated aerogel samples (1-4). The Si is present as Tⁿ and Dⁿ species, whose concentrations directly correspond to the MTMS/DMDMS ratio of the precursors (Table 2). Note that, contrary to sample 4, no ethoxy groups can be detected in the spectra of the MTMS+DMDMS open-porous foam (6), indicating that the alcoholysis is not efficient for this sample even though it was washed in ethanol multiple times. The reduction in BO/Si from 3.76-3.89 for aerogels (1-4) to 2.86 for the MTMS (5) and 2.48 for the MTMS+DMDMS (6) derived open-porous foams (Table S1, Table S2) results in a drastic change of the microstructural and physical properties from predominantly mesoporous to predominantly macroporous (Table 1) and from brittle to super-flexible, particularly in combination with ambient drying processes^{12, 22, 23}.

Table 2. Concentrations of functional groups (mmol/g)

			TEOS/HMDZ	PEDS/HMDSO	WG/TMCS	WG/SE/TMCS	MTMS	MTMS+DMDMS
			1	2	3	4	5	6
Q ⁴	SiO ₂	²⁹ Si	10.8 ± 0.7	10.5 ± 0.7	8.4 ± 0.6	8.6 ± 0.6		
Q ³	≡Si-O _{NBO}	²⁹ Si	1.3 ± 0.1	1.5 ± 0.1	1.7 ± 0.1	2.7 ± 0.2		
TMS	≡Si-O-Si(CH ₃) ₃	¹ H	3.8 ± 0.2	2.9 ± 0.2	3.1 ± 0.2	3.0 ± 0.2		
		¹³ C	2.6 ± 0.2	2.8 ± 0.2	2.5 ± 0.2	2.5 ± 0.2		
		²⁹ Si	3.1 ± 0.3	2.9 ± 0.3	2.7 ± 0.3	3.2 ± 0.3		
Ethoxy	≡Si-O-CH ₂ -CH ₃	¹ H (CH ₃)	0.3 ± 0.1	0.6 ± 0.1	< LOD	0.9 ± 0.1		
		¹ H (CH ₂)	0.3 ± 0.1	0.5 ± 0.1	< LOD	0.8 ± 0.1		
		¹³ C (CH ₃)	< LOD	< LOD	< LOD	1.6 ± 0.8		
		¹³ C (CH ₂)	< LOD	< LOD	< LOD	1.2 ± 0.6		
Silanol ^b	≡Si-OH	Q ³ -Ethoxy	1.0 ± 0.1	1.0 ± 0.1	1.7 ± 0.1	1.8 ± 0.2		
T sites	≡Si(T)-CH ₃	¹ H					13.6 ± 0.7	not resolved
		¹³ C					13.7 ± 0.9	7.3 ± 0.6
		²⁹ Si					15.4 ± 0.9	8.2 ± 0.6
		nominal ^a					14.4 ± 0.3	8.4 ± 0.2
D sites	≡Si(D)-CH ₃	¹ H						not resolved
		¹³ C						5.0 ± 0.4
		²⁹ Si						6.0 ± 0.5
		nominal ^a						5.6 ± 0.2

^a Calculated from starting materials and Tⁿ and Dⁿ speciation derived from the ²⁹Si NMR spectra.

^b Determined indirectly assuming each Q³ has either an ethoxy or a silanol neighbor.

LOD: Limit of detection

3.6 Site connectivity. The ¹H-²⁹Si HETCOR spectra (Fig. 5) inform on the connectivity between the various silica sites and functional groups. These spectra rely on the dipolar coupling and give information about the spatial proximity between the ¹H and ²⁹Si, but not a priori about chemical bonding. For all silylated samples (Fig. 5a-d), the TMS protons strongly correlate not only to TMS Si, but also to Q⁴, indicating the successful chemical grafting of TMS groups during hydrophobization where a Q³-OH is converted into a Q⁴-TMS connection. Additional weak peaks are interpreted as Q³-OCH₂CH₃ (Fig. 5b,d) and Q³-OH (Fig. 5c). The ethoxy CH₃ to TMS Si correlation (Fig. 5d) indicates that TMS and ethoxy groups are interspersed to some extent on the silica surface, i.e. TMS and ethoxy form a non-phase-separated monolayer on the silica surface. The spectra for the MTMS and MTMS+DMDMS based samples (Fig. 5e,f) show strong correlations of the methyl protons to all silica sites (T³, T², D², D¹) as expected since all these Si sites are connected to at least one methyl group. Note that the DUMBO sequence suppresses most of the dipolar broadening, with narrower peaks in the ¹H projection of the HETCOR spectra than in the quantitative ¹H spectra, even though the latter

were collected at a higher MAS rate (24 kHz versus 10 kHz). Nevertheless, the suppression of the dipolar broadening by DUMBO is incomplete, resulting in residual vertical tails to the peaks. The spectrum of the MTMS based sample displays two minor cross peaks between the methoxy protons and the T^2 and T^3 sites. This methoxy can either be residual from the MTMS precursor or originate from the methanol solvent through alcoholysis reactions such as $=Si(CH_3)(OH) + CH_3OH \leftrightarrow =Si(CH_3)(OCH_3) + H_2O$. The intensity of the correlation to T^2 is enhanced compared to the T^2/T^3 ratio: a T site linked to a methoxy group inevitably has a NBO and is a T^2 site, whereas T^3 sites by definition cannot be connected to a methoxy group.

a)
TEOS/HMDZ
(1)

b)
PEDS/HMDSO
(2)

c)
WG/TMCS
(3)

d)
WG/SE/TMCS
(4)

e)
MTMS
(5)

f)
MTMS+DMDMS
(6)

Fig. 5. ^1H - ^{29}Si heteronuclear solid state NMR spectra of classical silica aerogels and open-porous foams together with their ^1H and ^{29}Si projections and quantitative ^1H and ^{29}Si spectra. Lowest intensity contours at a) 20%, b) 25%, c) 12%, d) 20%, e) 2.5% and f) 5% of the maximum intensity.

3.7 Particle size and surface area. The silica speciation data can be used to estimate the primary particle size of the silylated silica aerogels by comparing the NMR derived internal versus surface Si ratio to a theoretical prediction of that ratio as a function of particle size (Fig. 6). This estimate depends on a number of approximations. 1) The silica particle interior consists entirely of fully cross-linked silica, i.e. Q^4 groups only, and the particle surface layer consist entirely of Q^3 species (with either a hydroxyl or ethoxy group linked to the NBO) or Q^4 linked to a TMS group. The latter species represents a Q^3 species that was converted into a Q^4 during hydrophobization. Under this assumption, the internal/surface Si ratio equals $([\text{Q}^4]-[\text{TMS}])/([\text{Q}^3]+[\text{TMS}])$. 2) The thickness of the surface layer is assumed to be 0.357 nm, the edge length of a cube with a volume that contains a single Si atom, for a density approximated by that of bulk silica glass, 2.20 g/cm^3 , i.e. 0.0454 nm^3 . 3) The silica particles are assumed to be spherical and the loss of surface area at inter-particle necks is not taken into account. Under these approximations, the estimated particle sizes are around 3-3.5 nm for the waterglass (3-4) and 4.5 nm for the alkoxide based aerogels (1-2) (Fig. 6, Table 1). Note that these predicted diameters are for the bare particles without their surface coverage and they need to be corrected for the surface layer of TMS and ethoxy groups (+ ~0.7 nm). For comparison, the particle sizes as determined from the TEM images (Fig. 1, Table 1) are around 5.0 to 5.6 for the waterglass based aerogels and around 6.0 to 6.7 for the alkoxide based aerogels. Thus, the indirect NMR approach accurately predicts relative differences in particle size, with smaller particle diameters for the waterglass based aerogels, but systematically underestimates the absolute particle sizes by about 1 to 2 nm (Table 1, Fig. S4).

The surface area can be estimated from the particle sizes assuming a particle density of 2.20 g/cm^3 and without considering the surface loss at inter-particle necks or the contributions of the TMS, ethoxy and silanol groups to the surface area. This approach results in estimated surface areas on the order of

750-900 m²/g for the waterglass and 600 m²/g for the alkoxide based aerogels (Table 1). This indirect NMR approach reproduces the surface area as determined by BET analysis to within 20% (Table 1, Fig. S5).

Fig. 6. Particle size derived from NMR data. a) Schematic illustration of a nanoparticle: our calculations assume that the surface layer consists of Q³ (with either hydroxyl or ethoxy groups) and Q⁴ attached to TMS groups; the inside of the particle consists exclusively of Q⁴ with four siloxane neighbors. b) Theoretical internal/surface Si ratio as a function of particle diameter (solid line): combined with our NMR data, this curve results in estimated particle diameters of ca. 3-3.5 nm and ca. 4.5 nm for the waterglass and alkoxide based aerogels, respectively (see text for model approximations).

3.8 Surface chemistry of silica aerogels. Before silylation, the surfaces of silica (aero)gels consist predominantly of Q³, i.e. Si tetrahedra with three ≡Si-O-Si≡ bonds and one ≡Si-OR group. The nature of the functional group attached to the non-bridging oxygen depends on the precursor, solvent system and solvent exchanges during processing, for example R may be -H (silanol), -CH₃ (methoxy) or -CH₂CH₃ (ethoxy). A clear illustration of the processing dependence of the functionality of the Q³ species is that among the silylated aerogel samples (1-4), the amount of ethoxy groups (≡Si-O-CH₂CH₃) is highest for a waterglass based aerogel (4), i.e. for a material whose precursors do not

contain ethoxy groups, but for which the hydrogel was exchanged into ethanol during processing (Fig. 1, Tables 1-2). This observation highlights the efficiency of the alcoholysis reaction $\equiv\text{Si-OH} + \text{CH}_3\text{CH}_2\text{OH} \leftrightarrow \equiv\text{Si-O-CH}_2\text{CH}_3 + \text{H}_2\text{O}$, i.e. the inverse of the classical hydrolysis reaction. In other words, ethoxy groups from the solvent can replace silanol groups on the silica surfaces. The efficiency with which surface groups can exchange with the solvent strongly depends on the chemistry of the exchange liquids and exchange conditions (temperature, time): the waterglass samples have both the lowest (3) and highest (4) ethoxy content of the four investigated aerogels. Note that the notoriously high efficiency of the hydrolysis of alkoxides such as TEOS or TMOS during sol formation is assisted by the continuous removal of one of the main reaction products ($\equiv\text{Si-OH}$) and the simultaneous regeneration of one of the main reagents (H_2O) by condensation reactions ($2 \equiv\text{Si-OH} \leftrightarrow \equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O}$) that run in parallel to the hydrolysis reaction.

During silylation, at least some but usually the majority of the terminal groups are replaced by trimethylsilyl groups through the formation of $\equiv\text{Si-O-Si}(\text{CH}_3)_3$ bonds and by converting Q^3 into Q^4 . Thus, the final Q^3/Q^4 ratio of a hydrophobic silica aerogel depends on two factors: i) the initial Q^3 content which is related to the particle size and surface area and ii) the efficiency of the silylation. An example of this is the somewhat higher proportion of Q^3 in the waterglass based aerogels (3-4) compared to the alkoxide based materials (1-2), which is primarily due to the smaller particle size (Fig. 1, see above).

The production of low density, superinsulating silica aerogels by ambient pressure drying typically requires high degrees of silylation: all four investigated samples have ca. 3 mmol/g of TMS groups (Table 2), corresponding to ca. 4 TMS molecules per nm^2 of surface area (BET). For comparison, partially silylated samples with 1.5 to 2 TMS groups per nm^2 shrank significantly during drying, with final densities between 0.275 and 0.399 g/cm^3 ³³. Our results on samples prepared by different synthesis routes (Table 2) demonstrate that sufficiently high degrees of silylation can be achieved by all investigated hydrophobization agents (HMDZ, HMDSO, TMCS). Thus, the final selection of the

hydrophobization agent will depend on raw materials cost and processing simplicity. The latter is determined by factors such as solvent miscibility and compatibility, corrosion of reaction vessels (e.g. reaction with TMCS produces HCl) and reaction kinetics.

4. CONCLUSIONS

A wide variety of synthesis routes have been developed for the production of silylated silica aerogels following the feasibility demonstration for ambient pressure drying. The ^1H - ^{29}Si heteronuclear correlation spectra presented here demonstrate the successful grafting of the TMS groups onto the silica surfaces for all investigated routes. In addition, our quantitative NMR data demonstrate the uniformity in surface chemistry of silylated silica aerogels, regardless of the type of precursor, gelation solvent or hydrophobization agent. This uniformity extends to the morphology, as shown by SEM and TEM, and the macroscopic physical properties. In contrast, silica open-porous foams prepared from MTMS and DMDMS precursors have very different chemistries, morphologies and properties. For the industrial production of silylated, hydrophobic silica aerogel materials, the precursors and processes can be selected primarily on the basis of process simplicity, energy consumption and raw materials cost as all synthesis routes can deliver excellent materials on the laboratory scale.

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Conflict of interest declaration

The authors declare no competing financial interest.

Supporting Information Available

Detailed information on sample synthesis and characterization is available in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

TOC graphical abstract

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