

Supporting Information: ^{19}F MAS NMR Quantification of Accessible Hydroxyl Sites on Fiberglass Surfaces

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NMR Experiments:

All ^{19}F MAS NMR experiments were performed on a Chemagnetics/Varian Infinity 11.7-T spectrometer operating at a transmitter frequency of 470.051573 MHz. A Chemagnetics 4-mm HFX probe (model T3-QR, serial no. SW50P48N11) was used with spinning speeds on the order of 15.5 kHz. The $\pi/2$ pulse width for all samples was 3.9 μs in duration. Inversion recovery experiments were utilized for measurements of T_1 and were completed on TFA and fiberglass samples (those with sufficient signal-to-noise) to determine the recycle delays required for full ^{19}F spin relaxation. All chemical shifts were calibrated using TFA as a secondary reference at -79.3 ppm relative to CFCl_3 at 0 ppm. The number of scans acquired, and the receiver gain used, varied by sample depending on the signal-to-noise ratio for that sample. The corresponding integrals obtained were scaled based on the number of scans and receiver gain settings used. A table of receiver gain amplification scaling was provided by the spectrometer manufacturer¹ and verified with direct measurements for ^{19}F standards. High-speed MAS techniques (with rotor spinning frequencies greater than 15 kHz) sufficiently average the CSA and any strong dipolar couplings to allow for superior resolution, especially from terminal $-\text{CF}_3$ groups where rapid rotational motion already provides substantial narrowing on the NMR time scale.

Silylation Procedure²:

All silylations were carried out using (3,3,3-trifluoropropyl)dimethylchlorosilane (TFS). The silylation procedure was identical for all samples studied, and approximately one gram of gel or fiber was used for each treatment. It is important to note that one must avoid prolonged exposure of the sample, solvents, and silylation reagent to the atmosphere, as excess water will deactivate the TFS. The sample was heated in a vacuum oven for 12 hours at 160°C in order to remove adsorbed organics and excess layers of surface water. The sample was then cooled under vacuum to 100°C , and subsequently placed into a Schlenk flask purged with high-purity argon. Anhydrous toluene (50 mL) was injected into the flask using a syringe, followed by introduction of 5 mL of TFS, corresponding to approximately 1.8×10^{22} TFS molecules. The flask was evacuated and subsequently purged with argon. The silylation reaction was allowed to continue for 72 hours at room temperature with constant stirring.

Upon removal from the flask, unreacted TFS was eliminated by vacuum filtration using 50 mL of toluene as a filtration wash. The sample was then cured at 125°C under vacuum to force the condensation reaction between any physisorbed silylation agent and remaining surface silanols. In addition, this curing step ensures that any unreacted silane will be removed, as the boiling point of the silane is 118°C . Upon completion of the curing step, the sample was stored in a dessicator until it was analyzed by NMR.

Sol/Gel Preparation:

The microporous gel was prepared using the sol/gel process³. 20 mL of tetraethoxysilane (TEOS), 40 mL of absolute ethanol, 20 drops of 1 N HCl, and 25 mL of deionized water were mixed. This mixture was heated to 70°C and subsequently cooled to 25°C . The solution was diluted with 85 mL of absolute ethanol, and then allowed to air-dry without any control over temperature or humidity.

Confirmation of TFS Binding:

Cross-polarization $^1\text{H}/^{29}\text{Si}$ and $^1\text{H}/^{13}\text{C}$ CPMAS studies of the TFS after reaction with the chromatographic gel reveal that the heteronuclear H-X ($X = ^{29}\text{Si}$, ^{13}C) dipolar couplings are not averaged due to molecular motion, as would be the case in an unbound state. In the $^1\text{H}/^{29}\text{Si}$ CPMAS spectrum of Figure 1(a), the peak at 12 ppm due to silicon bound to one oxygen and three carbon atoms provides confirmation that the probe molecule used for the ^{19}F NMR analysis is covalently bonded at the oxygen of the surface hydroxyl groups and not physisorbed to the surface⁴. The $^1\text{H}/^{13}\text{C}$ CPMAS spectrum in Figure 1(b) shows broadened lines and minor chemical shift differences in comparison with the liquid state ^{13}C NMR spectrum of the silane, but in all other respects is identical. The broadened lines are the result of decreased mobility of the probe molecule in its bound state, and the minor chemical shift differences are the result of a different chemical environment for the bound probe molecule versus that in the solution state.

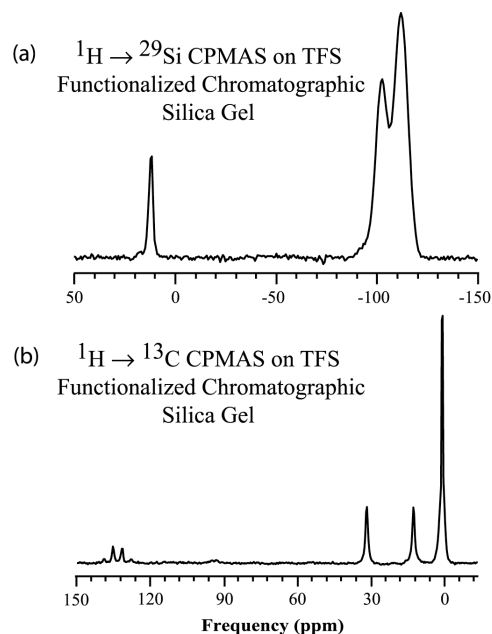


Figure 1. (a) The $^1\text{H} \rightarrow ^{29}\text{Si}$ CPMAS spectrum of chromatographic silica gel after reaction with TFS displays a resonance at 12 ppm. (b) The $^1\text{H} \rightarrow ^{13}\text{C}$ CPMAS spectrum of chromatographic silica gel after reaction with TFS reveals resonances from bound TFS.

Surface Area and Pore Diameter Determination:

Surface area measurements and average pore diameters were obtained via N_2 sorptometry for the silica gels and Kr sorptometry

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for the glass fibers (ASAP 2000, Micromeritics). Adsorption-desorption isotherms were measured and the surface area was calculated using Brunauer-Emmett-Teller (BET) theory. Average pore diameters were estimated using the Barrett-Joyner-Halenda

(BJH) method. The average pore diameter of the fiber samples was not obtained because these calculations may only be made when BET measurements are performed using N₂ sorptometry (high surface area samples).

Table 1. Sample Characteristics and Reactive Surface Quantification Results for Porous Silicas and Glass Fibers

Sample	Mass (g)	Surface Area (m ² /g)	Number of ¹⁹ F atoms	Coverage (OH/nm ²)
Chromatographic Gel	0.0216	273.94	2.15 x 10 ¹⁹	1.33
Microporous Gel	0.0668	487.26	6.91 x 10 ¹⁹	0.78
Silica Microfiber	0.0473	1.64	2.86 x 10 ¹⁷	1.23
A glass fiber	0.0683	0.24	3.78 x 10 ¹⁶	0.78
E glass fiber	0.0684	0.19	5.14 x 10 ¹⁶	1.31

References

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