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

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Received July 8, 2002 ; E-mail: ktm2@psu.edu

The surface hydroxyl concentration of amorphous oxide fibers is a controlling factor for their interface chemistry with the environment, coatings, or the matrix phase in composites. The accessible hydroxyl units play a central role in adsorption, wetting, and polymer adhesion and are a sensitive function of materials processing. However, quantification of the hydroxyl content and reactivity at fiberglass surfaces is challenging due to their amorphous character, low surface areas, and complex morphologies. While an assortment of physical and chemical methods are used for the determination of the hydroxyl concentration for bulk materials and high-surface area particulates,[1–6] few methods exist to routinely measure the concentration of accessible hydroxyl groups on surfaces of multicomponent glass fibers.[7,8] We present here a solid-state nuclear magnetic resonance (NMR) approach that combines the known chemical reactivity of surface hydroxyl units with high-resolution spectroscopy for advanced characterization.

In most cases, NMR spectroscopy is not sufficiently surface sensitive for quantitative probing of the interfaces of low to moderate surface area samples. However, the sensitivity of NMR for quantifying surface reactive species can be increased using binding chemistry of probes containing highly sensitive NMR nuclei (such as ^{19}F or ^{31}P). Reactions of chlorosilanes or related hydrolyzed species with hydroxyl groups at surfaces are well known in the science and engineering of chromatographic materials[9] and therefore present straightforward avenues for surface modification. In this report, we focus on studies of materials functionalized with (3,3,3-trifluoropropyl)dimethylchlorosilane (denoted TFS), containing $-CF_3$ end groups. ^{19}F is an ideal nucleus for NMR, as it has a nuclear spin of $^1/_2$, a high gyromagnetic ratio, and a natural isotopic abundance of 100%.

Initial binding and quantification studies were performed on two model porous silica systems with high surface areas. The first silica is a chromatographic-grade silica gel (J. T. Baker, 20−200 mesh, treated as received). The second sample is a microporous silica gel made by the sol/gel process using alkoxysilane. The ^{19}F MAS NMR spectra of the two porous silica materials after treatment with TFS are presented in Figure 1a,b. The spectra reveal peaks at −69 and −73 ppm with respect to neat CFCl$_3$, indicative of ^{19}F in $-CF_3$ groups. Supported by cross-polarization ^{1}H/^{13}C and ^{1}H/^{29}Si MAS studies of the treated chromatographic gel (see the Supporting Information), these spectra represent covalently bonded TFS species and provide signals from three ^{19}F nuclei for every accessible surface hydroxyl site.

An external quantification standard (68.4 mg of sodium trifluoroacetate in the same sample volume) provides a calibrated ^{19}F MAS NMR signal amplitude per fluorine atom. Direct quantitative measures of the number of fluorine atoms per gram of TFS-treated
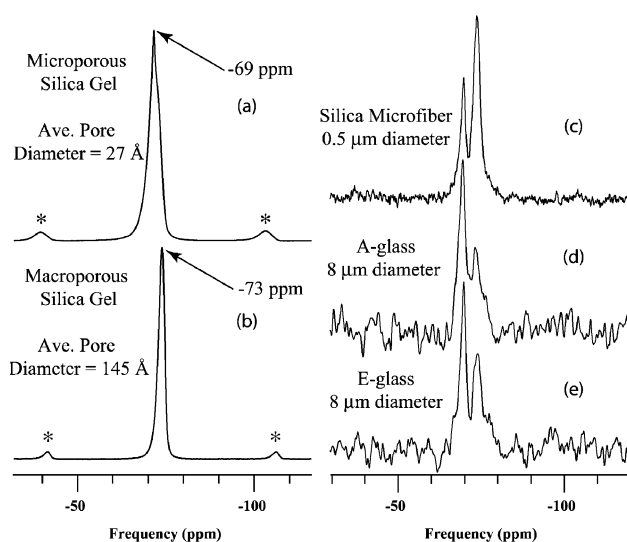
Figure 1. The ^{19}F MAS NMR spectra of silica gels and fiberglass materials contain resonances from TFS molecules covalently bonded at surface hydroxyl sites.

Table 1. Sample Characteristics and Accessible Hydroxyl Quantification Results for Porous Silicas and Glass Fibers

sample	surface area (m^2/g)	coverage (OH/nm^2)
chromatographic gel	273.94	1.33
microporous gel	487.26	0.78
silica microfiber	1.64	1.23
A glass fiber	0.24	0.78
E glass fiber	0.19	1.31

porous silicas are obtained by proper scaling of integrated ^{19}F MAS NMR signal intensities by the number of experimental scans and well-characterized instrumental receiver gain settings. With the assumption that all accessible hydroxyl groups are consumed in reactions with an excess of TFS in the treatment,[9] and the hydroxyl coverage does not exceed the sterically hindered limit (2.5−3.0 OH/nm^2),[10] the coverage of TFS accessible hydroxyl groups is then determined (Table 1).

Average pore sizes for the silica samples were obtained via BET and BJH adsorption/desorption calculations, and the chromatographic sample exhibits a much larger average pore diameter. The length of the bound TFS molecule is approximately 7 Å, much smaller than the average pore diameter of the chromatographic sample (145 Å), and therefore the ^{19}F signal from this sample represents bound TFS molecules where the ^{19}F atoms are assumed to not be interacting with nearby $-CF_3$ groups or other species. The resonance here is centered at −73 ppm and has a measured T_1 relaxation time constant of 1.0 s. A shift is observed in the position of the TFS resonance from the microporous gel sample (with

average pore diameter of 27 Å), with a main peak observed at −69 ppm with a T_1 of 0.63 s and a shoulder to the lower frequency side (toward −73 ppm) with a measured T_1 of 0.85 s. Thus, the observed line shapes in Figure 1a arise from ^{19}F nuclei in bound TFS molecules within pores with an average diameter approaching length scales where TFS molecules must interact with one another at these concentrations of hydroxyl sites. We propose that the crowding or "confinement" of the probe molecules in this sample causes a shift in the position of the resonance from the −CF$_3$ group, as each TFS molecule can interact with either nearby TFS molecules or other regions of the silica surface within the pore. The measured decrease in spin−lattice relaxation time is also indicative of a more confined environment with additional mechanisms available for spin−lattice relaxation as the intermolecular interactions are increased.[11]

Lower surface area (0.1−10 m^2/g) materials should be amenable to similar analyses within a reasonable experimental time frame (acquisitions less than 12 h) if the surface concentrations of reactive, accessible hydroxyl groups are comparable. On the basis of the porous silica results above, confinement effects or steric hindrance caused by differences in surface morphology may be indicated by the ^{19}F chemical shifts or spin−lattice relaxation time constants. Three glass fiber samples were studied using the same silylation procedure and ^{19}F MAS NMR protocol: a 0.5 μm diameter silica microfiber sample made by a process that intentionally leads to a microporous structure (99.9% SiO$_2$; Johns Manville, Inc.), an 8 μm diameter A glass fiber (72.8% SiO$_2$, 13.9% Na$_2$O, 8.8% CaO, 4.5% other oxides; PPG Industries, Inc.), and an 8 μm diameter E glass fiber (54% SiO$_2$, 14% Al$_2$O$_3$, 6% B$_2$O$_3$, 23% CaO, 3% other oxides; PPG Industries, Inc.). Surface areas were determined by BET analysis using Kr sorptometry (Table 1).

The quantification of accessible hydroxyl groups on these glasses is obtained from the integrated intensities of the resonances in the ^{19}F MAS NMR spectra (Figure 1c−e). Even with a large number of repetitions of the experiment for data averaging (up to 100 000 scans), the signal-to-noise ratios are reduced from those of the strong signals from the high-surface area porous silica materials. However, the signal strengths are sufficient to reduce the estimated propagated error in the calculation of the surface hydroxyl concentrations (listed in Table 1) to less than 3%.

The concentration of accessible hydroxyl groups on the surface of the silica microfiber is nearly identical to that of the chromatographic silica gel and is consistent with their comparable oxide composition and pore size. The absolute number of reactive hydroxyl species, however, is 2 orders of magnitude lower. In the case of the microporous gel, we attribute the lower (measured) coverage of hydroxyls to the inaccessibility of some sites within the structure. The lower absolute number of hydroxyls/gram on the A and E glass fibers is clearly due to their lower surface areas (i.e., as drawn, they are fully dense glass structures with accessible hydroxyl sites only on the external geometric surface). Of course, interpretation of the per unit area coverage is complicated by the other oxides in the glass fiber compositions, which may introduce other kinds of accessible hydroxyl sites for silane, as well as affect their reactivity. The surface roughness of the glass fibers can also be a factor.

Quite striking is the appearance of two resonances in each spectrum from the fiber samples: one centered at −69 ppm and the second at −73 ppm. The relative intensities of the two peaks change with sample identity, with the signal from the silica microfiber containing the most intensity in the −73 ppm resonance. On the basis of the assignment of resonances from the two porous silica samples, the resonances at −73 ppm are tentatively attributed to signals from the ^{19}F nuclei in TFS molecules in environments free from intermolecular interactions. The resonances at −69 ppm are then assigned to TFS molecules in micropores. Spin−lattice relaxation times measured for ^{19}F in TFS on the surface of the silica microfiber are also consistent with changes in the environment as indicated by the chemical shift information. Measured T_1 values are 0.5 s for the peak at −69 ppm and 0.8 s for the resonance at −73 ppm. The trend implies that the surfaces of the A and E glass fibers are microporous to some depth or are exceedingly rough on the nanoscale.

Using this method, we found that practical quantification appears to be attainable at accessible hydroxyl concentrations on the order of 0.5−1.5 OH/nm^2 from samples with measured surface areas of 0.2 m^2/g or higher. The results obtained fall well within the accepted range of hydroxyl coverage for silica and multicomponent glasses. Further studies will probe accessible hydroxyls on fiberglass surfaces as the bulk composition is varied and when the material undergoes aging in humid or hydrothermal environments. The fact that this method offers not only concentration, but also local environment information, is a key advantage over quantitative static-SIMS[7] or laser desorption spectroscopy[8] measurements. Applications of these measurements to the characterization of the shallow microporosity/nanoroughness associated with hydroxyls at glass fiber surfaces are directly relevant to understanding fiber adsorptivity, strength, and adhesion to polymers.

Supporting Information Available: NMR experimental details, silylation procedure, experimental details of sol/gel synthesis, confirmation of TFS binding, and surface area and pore diameter determination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0275717