Fast Characterization of Functionalized Silica Materials by Silicon-29 Surface-Enhanced NMR Spectroscopy Using Dynamic Nuclear Polarization

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Supporting Information

ABSTRACT: We demonstrate fast characterization of the distribution of surface bonding modes and interactions in a series of functionalized materials via surface-enhanced nuclear magnetic resonance spectroscopy using dynamic nuclear polarization (DNP). Surface-enhanced silicon-29 DNP NMR spectra were obtained by using incipient wetness impregnation of the sample with a solution containing a polarizing radical (TOTAPOL). We identify and compare the bonding topology of functional groups in materials obtained via a sol–gel process and in materials prepared by post-grafting reactions. Furthermore, the remarkable gain in time provided by surface-enhanced silicon-29 DNP NMR spectroscopy (typically on the order of a factor 400) allows the facile acquisition of two-dimensional correlation spectra.

Hybrid organic–silica materials are an important class of composite materials of widespread interest in modern chemistry, ranging from fundamental developments to advanced applications. They consist of organic parts which are covalently bound to a silica matrix.1 Their preparation involves either post-grafting of organosilicon reagents, typically organotrialkoxysilanes, onto silica supports or direct co-hydrolysis and co-condensation of organotrialkoxysilanes with tetraalkoxysilane precursors in sol–gel processes with5–8 or without5–8 structure-directing agents. When structure-directing agents are used, it is also possible to control the organization of the materials (e.g., cubic, vermicular, or hexagonal networks) and the density and placement of the organic functionalities (regular distributions on the surface of the pores and/or in the walls of the materials), providing access to highly tunable materials and thereby to numerous properties.

Understanding the activity of functionalized silica materials requires a molecular-level characterization of the functional groups, particularly their conformations and modes of binding/interaction to/with the surface. In particular, it is well recognized that a given surface silicon atom bearing a functional group can have a variable number n of Si–O–Si bonds, leading to so-called T1, T2, or T3 substructures. These bonding schemes lead to very different geometries on the surface, as illustrated in Figure 1A for organic–inorganic hybrid materials containing phenol functionalities.7 Knowledge of the surface incorporation patterns and the conformations of functional groups for such materials is clearly an essential step toward developing smart functional substrates.

There are no readily available analytical methods to characterize different surface incorporation patterns and conformations. Diffraction techniques are not well suited for structural studies of surface species, and infrared spectroscopy does not provide enough information for such complex organic functionalities. Nuclear magnetic resonance studies of silica-based materials are thus particularly attractive. Cross-polarization magic angle spinning (CPMAS)23Si NMR studies have been extensively used where applicable, since they provide narrow spectra with atomic resolution that can easily characterize the bonding environment of silicon atoms near the surface.4,5,10–19 However, NMR suffers from low sensitivity, and in many cases the functionalized silicon T1 sites are too dilute to be readily observed; the spectra provide mainly information about the bulk surface species Q4 and proton-rich Q6 sites (Si–OH). In most cases, little or no evidence of incorporation patterns of the functional groups can be obtained because of the low sensitivity of the method, unless one resorts to very long, often unreasonable, acquisition times. Further, as a direct result of this low sensitivity, multidimensional NMR methods to characterize the conformations of the functional groups are precluded.

In recent work9 we overcame the sensitivity problem of the NMR technique for surfaces by combining magic angle spinning (MAS) with dynamic nuclear polarization (DNP).20,21 We adapted methods developed for studying biomolecular solids22 to functionalized silica materials by dissolving the biradical TOTAPOL22 into a suitable solvent mixture, which was then used to wet the solid by incipient wetness impregnation. At low
temperatures (∼100 K) we showed that it is possible to transfer magnetization upon saturation of the highly polarized electron spin to the 1H nuclei of the sample by continuous irradiation of the electron resonance with intense microwaves generated by a gyrotron.23 We were able to transfer the enhanced 1H magnetization to the 1H nuclei of the sample by continuous irradiation of the dipolar-coupled proton network, including the surface protons, with DNP with the same number of scans in the same time is possible to enhance the sensitivity of the surface-anchored organic species by a factor εff~50 compared to a similar experiment without DNP. In spectacular contrast, the spectrum obtained with DNP with the same number of scans in the same time is enhanced by a factor εeff~21, and both the Qn and Tn sites are now clearly visible, allowing their detailed characterization.

Figure 1C shows a comparison of DNP NMR spectra of material I prepared by two different methods, either by the sol–gel process or by post-grafting the phenol group onto a SBA-15-type support (see Supporting Information for details). The spectra clearly show very different patterns for the functionalized Tn species, where the silicon atoms are directly bound to at least one organic moiety. The figure indicates the characteristic resonance frequencies at −77 ppm for T3 species (SiO)3SiR and at −66 ppm for the T2 forms ((SiO)2SiR(OX), X = H or Et) and upfield bands (−60 ppm) related to T1 ((SiO)SiR(OX)2), as well as a trace amount of physisorbed organosilicon compound, (XO)SiR (T0, −57 ppm). From the spectra of Figure 1C, it is immediately apparent that grafting (RO)3SiR groups onto SBA-15 produces a wider distribution of Tn species, centered on T2, as compared to the hybrid method which produces mainly T3 surface sites, with a few T2 sites. The hybrid material is clearly a better substrate for controlled chemistry.

We note that the intensities in the spectra allow qualitative estimates of the relative populations of the different Qn and Tn sites. As with any CPMAS experiment, the 1H−29Si CP transfer used to enhance the surface depends to some extent on the local proton density. For example, in material I, the Qn sites can be polarized from the protons of the SiOH groups that are only two bonds away, while for the Tn sites, the 1H spins are three bonds away, in the ortho positions on the aromatic ring. This situation can be contrasted with the case of SBA-15 functionalized with SiH groups (II, Figure 2A), where the 1H spin is directly linked to the Tn site. Indeed we see in Figure 2B that, at very short CP mixing times (τCP = 0.5 ms), the Tn sites are selectively enhanced, with almost no signal from Qn sites. The signals of the Qn sites build up progressively as τCP is increased and polarization is transferred from more distant spins. This suggests that the enhanced polarization diffuses from the radical across the entire dipolar-coupled proton network, including the surface protons, consistent with observations of DNP in biosolids.24,25 Direct 1H−29Si transfer by CP from solvent protons farther away from the

Here we show that surface-enhanced NMR spectroscopy using DNP can be extended to silicon-29 nuclei on surfaces, allowing rapid acquisition of multidimensional spectra. We determine the incorporation patterns and conformations of functional groups in a range of hybrid materials. Figure 1B shows the dramatic effect on the sensitivity of the 29Si CPMAS spectrum of compound I (all the materials used here were prepared as described in the Supporting Information). The figure shows spectra recorded with and without microwave irradiation of materials impregnated with 9.2 mM TOTAPOL in a 90:10 D2O:H2O solution added to a dry powder of mesostructured hybrid material. In the ordinary low-temperature spectrum, acquired in 35 min with 2048 scans, only a few Qn sites are (barely) observable. Note that CP from 1H to 29Si preferentially “lights up” the surface Qn sites of the material, since there are no 1H atoms in the bulk. The Qn sites are actually of little interest in this study. We focus attention on the distribution of the surface Tn sites, which indicates the incorporation of organic functionalities, with resonances between −50 and −80 ppm. From the synthetic method, we expect a ratio of around 1 silicon atom linked to a functional group per 30 silicon atoms (either surface or bulk) (see Supporting Information). Since there are far fewer Tn than Qn sites, the former are invisible in the spectrum of Figure 1B without DNP. In spectacular contrast, the spectrum obtained with DNP with the same number of scans in the same time is enhanced by a factor εeff~21, and both the Qn and Tn sites are now clearly visible, allowing their detailed characterization.

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surface (if present) is clearly much less efficient. In the spectra of Figure 2B, the surface SiH groups were observed with an enhancement of $\varepsilon_{\text{Si}} = 19$ and with only 16 scans in 24 s! Under such enhanced conditions, we can acquire 2D $^1$H--$^{29}$Si correlation spectra of the surface species in only 8 min. The 2D spectrum of Figure 2C shows that both $T_2$ and $T_3$ silicon sites correlate with the SiH protons.

To further explore the conformation of the functional groups and to test the generality of the approach, we acquired surface-enhanced $^{29}$Si spectra from a range of materials. Notably, DNP yielded high-sensitivity spectra with $\varepsilon_{\text{Si}} = 29$ for pure nonporous flame silica (surface area of 200 $\text{m}^2/\text{g}$) impregnated with the $\text{H}_2\text{O}/\text{D}_2\text{O}/\text{TOTAPOL}$ solution (see Supporting Information). Evidently, the porous nature of the silica material is not crucial for a surface DNP enhancement.

In Figure 3 we show spectra obtained with surface-enhanced DNP applied to different functionalized hybrid materials (III–VI). In all cases the DNP enhancement factors are good ($\varepsilon_{\text{Si}} \approx 20$, one case $\varepsilon_{\text{Si}} \approx 10$), and in all these materials $T_3$ along with $T_2$ species are clearly observed. For materials V and VI, the $T_4$ species occur with a characteristic chemical shift of $-66$ ppm (instead of $-77$ ppm as in the phenol derivatives) since the silicon atoms are bound to an aliphatic $-\text{CH}_2-\text{CH}_2-$ moiety instead of an aromatic unit. The shorter distance between the aliphatic CH$_2$ protons and T$_3$ silicon atom in compounds V and VI compared to III and IV explains the more efficient CP transfer, and thus the more intense T$_3$ signals. As with the hybrid form of I, incorporation of the functional groups through surface T$_3$ sites is highly favored in all these materials.

The facile acquisition of 2D $^1$H--$^{29}$Si correlation spectra allows us a more detailed conformational analysis of the functional groups. In particular, Figure 4 shows spectra of materials V and VI. The short mixing time ($\tau_{\text{CP}} = 0.5$ ms) favors transfer from $^1$H in close proximity to silicon atoms. As expected, it is apparent that the $T_3$ nuclei correlate with the aliphatic protons of the organic $-\text{CH}_2-\text{CH}_2-$ moiety. In contrast, the $Q_3$ and $Q_4$ silica sites correlate with the SiOH protons at 4–5 ppm (and possibly with protons of the frozen solvent) and, remarkably, with the aromatic imidazolium unit (at $\sim 9$ ppm). This indicates a close proximity between the imidazolium units and the silica framework. This observation is in line with expectations for compound V (Figure 4A), since it is anchored to the silica surface at two points and is thus embedded in the solid.

Noteworthily, when the same experiment is performed on compound VI, which contains a flexible tether (propyl chain) with only one anchor at the surface, the spectrum of Figure 4B shows that we observe a strong correlation peak between the silica surface Q$_3$ sites and both the imidazolium and the mesitylene protons (not resolved in the proton dimension) of the organic unit. In this case the aromatic groups might be expected to point outward into the cavity. However, the two-dimensional correlation spectrum clearly shows a close proximity between the aromatic rings and the Q$_3$ sites of the surface, suggesting that the imidazolium units (or at least a significant fraction of them) are likely to be folded back toward the silica surface, rather than being in the cavity. Thus, this scaffold should be used with care as a support for active sites.

Imidazolium moieties have an affinity for polar media like water,$^{36}$ so it is surprising that these grafted species do not “stand up” but are flattened out on the surface. Apparently, with a flexible tether, electrostatic interactions can dominate over

![Figure 2](image1.png)

**Figure 2.** (A) DNP-enhanced silicon-29 CPMAS spectra of II as a function of the CP mixing time $\tau_{\text{CP}}$. Spectra were recorded with 16 scans. (B) Contour plot of a two-dimensional $^1$H--$^{29}$Si spectrum of II recorded with DNP. 64 $t_1$ increments with eight scans each were recorded with $\tau_{\text{CP}} = 1.0$ ms. Total experimental time was 8.5 min.

![Figure 3](image2.png)

**Figure 3.** DNP-enhanced silicon-29 CPMAS spectra of a series of functionalized mesoporous hybrid materials. The organic fragments incorporated into the silica matrix are indicated. Spectra were recorded with 2048 scans in a total experimental time of 35 min each, with $\tau_{\text{CP}} = 6.0$ ms. The dilution factors among functionalized and nonfunctionalized silicon atoms used in the synthesis of these hybrid materials were 1/30 for III and IV and 1/19 for V and VI (see Supporting Information).
folded back onto the surface. This will have consequences regarding
necessarily point into the pore cavities but can be at least in part be
species. These results clearly demonstrate the power of multidimen-
the orientation, mobility, and activity of materials based on these
incorporation of functional groups through T3 sites, while post-
other than NMR can determine such conformational features.
would require a quantitative study and the investigation of a
tain conformational information, more detailed interpretation
Figure 4. Contour plots of a surface-enhanced two-dimensional
envisaged since other state-of-the-art NMR techniques, such as
grafting leads to more disordered surface attachment.
Furthermore, two-dimensional $^1$H–$^{29}$Si correlation spectra allow us to determine the incorporation patterns of functional groups on silica surfaces in a few minutes and confirm that a controlled sol–gel process favors incorporation of functional groups through T3 sites, while post-
grafting leads to more disordered surface attachment.

In conclusion, DNP-enhanced $^{29}$Si spectra allow us to determine
the incorporation patterns of functional groups with atomic resolution.

solvation effects. Note that while these spectra thus clearly con-	ain conformational information, more detailed interpretation
would require a quantitative study and the investigation of a
wider range of organic functionalities. Note also that no method
other than NMR can determine such conformational features.

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ASSOCIATED CONTENT

Supporting Information. Sample preparation and experi-
mental methods. This material is available free of charge via
the Internet at http://pubs.acs.org.

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Figure 4. Contour plots of a surface-enhanced two-dimensional
$^1$H–$^{29}$Si correlation spectrum of V (A) and VI (B). For each spectrum
a total of 48 $f_t$ increments with 112 scans each were recorded in a total
experimental time of 1.5 h each, with $\tau_{CP} = 0.5$ ms.