

An Alternative Preparation of Organofunctionalized Silica Gels and Their Characterization by Two-Dimensional High-Resolution Solid-State Heteronuclear NMR Correlation Spectroscopy

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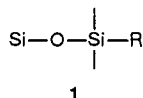
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Abstract: High-resolution solid-state ^{29}Si CP/MAS NMR spectroscopy has been used to characterize methyl functionalized silica gels prepared by the copolymerization of tetraethoxysilane and methyltriethoxysilane. One-dimensional ^{29}Si CP/MAS NMR indicates that the two components are present in the correct proportions in the gel, but it is not sensitive to the degree of mixing. A two-dimensional $^1\text{H}/^{29}\text{Si}$ correlation experiment clearly demonstrates that the two components are not phase-separated, but are mixed in the final gel.

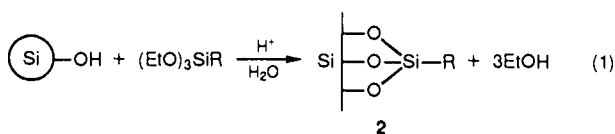
Introduction

Immobilized reagents, where a reactant molecule is covalently bonded to an inert support matrix, are materials of considerable interest in a variety of areas, including catalysis, ion-exchange resins, polymer composite formulations, peptide synthesis, and in the concentration and removal of toxic materials.¹ The support matrices are commonly inorganic oxides or cross-linked polymer systems such as styrene/divinylbenzene.

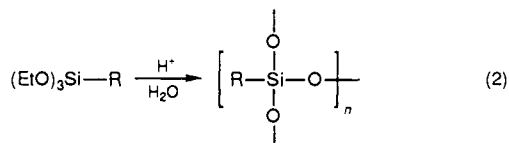
Silica gel has frequently been used as a convenient, inert, high-surface-area, and nonswelling support that can be easily removed by filtration from the reaction medium if necessary. In these systems, the bonding of the reactant functionality, R, to the surface is via a bridging silicon attached to the silica surface by an Si-O-Si linkage as in 1:²



These functionalized silica gels are usually made by activating the silica surface to produce hydroxyl groups and then reacting it with a trichloro (or trialkoxy)silane. The reaction is often represented as in eq 1.



However, the trifunctional silane can also be considered as a trifunctional monomer molecule that would polymerize to give a highly cross-linked polysiloxane polymer as in eq 2. Reaction



1 may be favored by making the system as anhydrous as possible, but this is difficult to do because of the hydrophilic nature of the silica surface, and in practice there may well be an unknown amount of self-condensation of the organosilane occurring, giving oligomeric polysiloxane species bonded to the surface, making the reproducibility of these reactions somewhat variable. Further, the number and concentrations of the surface hydroxyl functionalities $\text{Si}(\text{OH})_2$ and $\text{Si}(\text{OH})_3$ make it unlikely that many species of structure 2 can be formed, leaving latent functionalities

on the bridging silicons that can be activated on subsequent exposure to water.

Thus, structure 2 will not represent the true structure of the immobilized reagent formed from a trialkoxysilane. In the present work, we outline the use of an alternative preparation of functionalized materials of this general type and the characterization of these systems by two-dimensional solid-state NMR techniques.

Experimental Section

Spectra. ^{29}Si MAS NMR spectra were obtained at 79.6 MHz using a Bruker MSL 400 spectrometer. The experimental parameters for both the one- and two-dimensional spectra are detailed in the appropriate figure captions.

Materials. Typical experimental conditions for the preparation of the different gels are as follows.

(1) **Silica Gel.** The high-purity silica gel samples were synthesized by the acid hydrolysis of tetraethoxysilane (TEOS), using the method described by Peri and Hensley.³ A 60-mL volume of concentrated HCl was added dropwise, with constant stirring, to 100 mL of a solution of TEOS (40 vol %) in ethanol. The solution gelled in about 1 h. After standing overnight, the gel was broken into small pieces and placed in 200 mL of 50% ethanol in distilled water by volume. After standing for 12 h, the gel was washed with distilled water several times until the eluant pH was 7, then dried at room temperature for a week. It was ground to a fine powder and characterized by ^{29}Si solid-state MAS NMR.

(2) **Polymethylsiloxane.** Polymethylsiloxane was prepared by the same procedure as that used for silica gel above, except that the starting material was methyltriethoxysilane (MTES) instead of TEOS.

(3) **Methyl-Substituted Silica Gel. Method 1.** A methyl-substituted silica gel was synthesized by anchoring a methyl-bearing silicon onto the surface of silica gel using the following procedure. The silica gel (~5 g, Fisher S-157; predried in vacuo at ~150 °C overnight) was refluxed with an excess of MTES in dry toluene for 12 h. After filtration, the solid was soxhlet-extracted with dry toluene for 12 h and then washed with acetone and water several times. The solid was refluxed in H_2O for 12 h and dried in vacuo at ~150 °C for 12 h.

Method 2. Methyl-substituted silica gels were also synthesized by copolymerization of TEOS and MTES. The procedure was the same as that used for the preparation of the silica gel described above, except that mixtures of various mole ratios of TEOS and MTES were used as starting reagents instead of TEOS alone. Final products contained up to 50% of methyl-substituted silicons.

Results and Discussion

Material Design. For many applications of functionalized silica gels it will be advantageous if the reactant functions are isolated from each other and randomly distributed over the gel, i.e., that the structures approximate as closely as possible the ideal formulation represented by 1. In this way they will be most available

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(3) Peri, J. B.; Hensley, A. L., Jr. *J. Phys. Chem.* 1968, 72, 2926.

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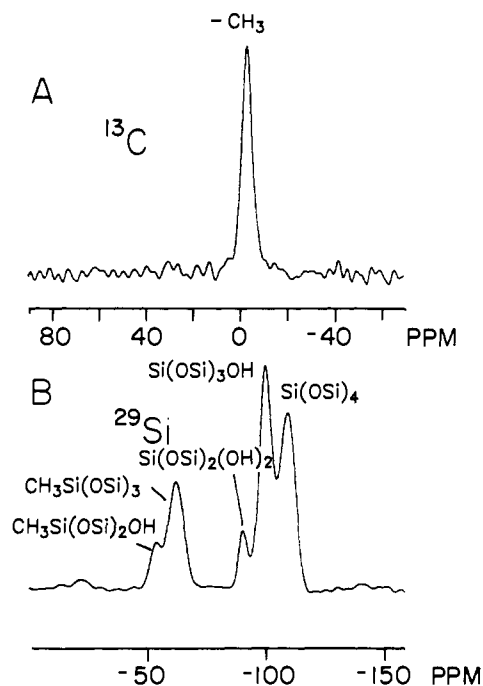
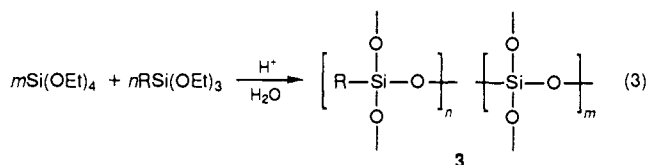


Figure 1. ^{13}C and ^{29}Si CP/MAS NMR spectra of methylsilica gel prepared by method 2. The spectra were obtained at 110.6 and 79.5 MHz, respectively (proton frequency 400 MHz). For the ^{13}C spectrum, 800 scans were accumulated using a 1.0-ms contact time and 2.0-s repetition time. For the ^{29}Si spectrum, 320 scans were accumulated using a 22.0-ms contact time and 5.0-s repetition time. The sample was spun at 3.2 kHz.

for subsequent reaction. By approaching the problem as a cross-linking copolymerization reaction, such materials may be produced in a direct one-step synthesis by incorporating the functionalized silane concurrently with the formation of the silica gel itself, as in eq 3.



Following the conditions outlined in the Experimental Section, a number of such materials have been synthesized with a variety of typical ligands $\text{R} = -\text{CH}_3$, $-(\text{CH}_2)_3\text{NH}_2$, $-\text{CH}_2\text{CH}_2-\text{C}_4\text{H}_4\text{N}$, and functionalized phosphines. Incorporations (of functionalized silicons) as high as 50% were obtained.

Characterization. In the characterization of the materials, two questions must be answered. First, it must be established that the organic functionality is chemically intact and that it is present in the correct proportion to the total material. Second, the distribution of the functionality throughout the matrix should be described; that is, it must be established that it is not composed of unconnected silica gel and polyorganosiloxane or "domain structures" formed from silica gel and the polyorganosiloxane. The first of these is relatively straightforward and can be achieved using one-dimensional high-resolution solid-state ^{29}Si NMR spectroscopy. The second problem is much more difficult but, as we will demonstrate, may be solved at least semiquantitatively by two-dimensional heteronuclear solid-state NMR connectivity experiments.

One-Dimensional CP/MAS NMR Experiments. It has previously been shown that CP/MAS NMR spectroscopy can be used to characterize functionalized gels⁴⁻⁶. In particular, in the case of ^{29}Si spectra, Maciel and co-workers⁴ have shown that the signals

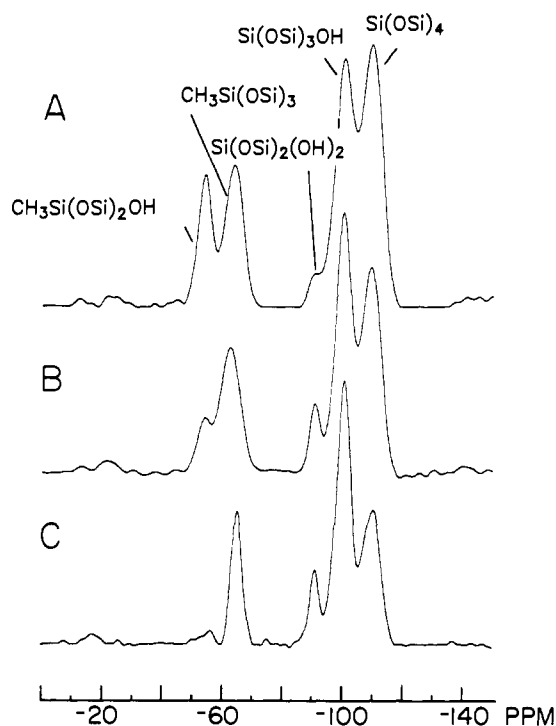
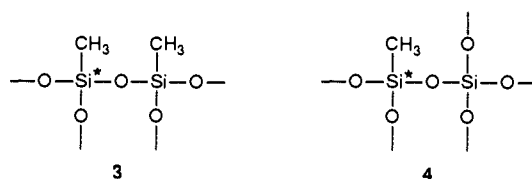


Figure 2. ^{29}Si CP/MAS NMR spectra of different types of modified silica gels and mixtures. The conditions used to obtain the spectra were the same as in Figure 1: (A) methyl-substituted silica gel prepared by method 1; (B) methyl-substituted silica gel prepared by method 2; (C) mechanical mixture of silica gel and polymethylsiloxane.

due to various substituents on silicon can be assigned and the average structure of the functionalized gel characterized. Quantitatively reliable data may also be obtained if care is taken with the experiments.^{4,5} Figure 1 shows the ^{13}C and ^{29}Si CP/MAS NMR spectra of a gel incorporating ca. 25% methyltriethoxysilane. The assignments given in the ^{29}Si spectrum follow those previously reported in the literature.⁴

A much more difficult task is to describe the nature of the incorporation of the functionalized silicons into the gel. This is illustrated in Figure 2, which shows the ^{29}Si CP/MAS NMR spectra of a methylsilane-functionalized gel prepared by reaction of the silane with silica gel, a methylsilane-functionalized gel prepared by direct incorporation of the functionalized silane during gel synthesis, and a simple mixture of unfunctionalized silica gel and polymethylsiloxane. As can be seen from the figure, all three spectra are identical in terms of the chemical shift values of the resonances, although the relative peak intensities vary. To some degree this is due to limited resolution, as the signals are relatively broad because of the amorphous nature of the materials, but it is also to be expected that the differences in local silicon environments will be small. The critical distinction is between the local structures 3 and 4. In these, the effect on the local envi-



ronment of the silicon marked (*) is only whether or not the adjacent silicon is substituted by a methyl group (3) or an oxygen functionality (4). Of particular interest in the present work, it is impossible to distinguish the two types of functionalized gels A and B from Figure 2 alone, and other approaches must be taken to solve this problem. One possible approach is to take advantage of the very strong dependence of the cross-polarization process on the internuclear distance ($1/r^3$). Thus, cross-polarization from the methyl groups to the silicon nuclei would only be efficient if

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(5) Fyfe, C.; Gobbi, G. C.; Kennedy, G. J. *J. Phys. Chem.* **1985**, *89*, 281.

(6) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208.

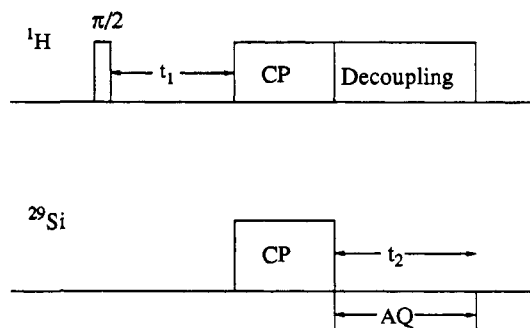


Figure 3. Pulse sequence used for the 2D ^1H - ^{29}Si heteronuclear correlation NMR experiment.

they were in close proximity, and the observation of an $\text{Si}(\text{O}-)_4$ resonance could be taken as evidence for the presence of structure (4). A complicating factor in these experiments is that of all of the hydroxyl groups (which can also act as polarization-transfer sources) must be removed. Attempts have been made to eliminate these protons in the samples currently under investigation by repeated exchanges with D_2O . Although the correct trends were observed (i.e., greatly reduced polarization of backbone silicons on D_2O washing), the difficulty in removing all of the hydroxyl protons, coupled with the considerable affinity of the gels for water, led us to the conclusion that these experiments, although encouraging, could not be considered reliable enough to be used as an absolute proof of the macro-structures of these materials. These difficulties can, however, be overcome by the use of two-dimensional NMR techniques.

Two-Dimensional Heteronuclear NMR Correlation Experiments.

In these experiments, which are the solid-state analogues of heteronuclear NMR correlation experiments in solution,⁷ the heteronuclear correlation, in this case $^1\text{H}/^{29}\text{Si}$, is made through the dipolar interactions. A variety of pulse sequences to implement this type of experiment were first introduced by Ernst and co-workers.⁸ That used in the present work is shown in Figure 3. In the sequence, the frequency encoding of the protons occurs during the period t_1 , polarization transfer to silicon during the cross-polarization period, and acquisition in t_2 . The viability of an experiment of this type between ^1H and ^{29}Si has previously been demonstrated by Vega and co-workers using the hydroxyl protons in zeolite rho.⁹

At first sight, it might seem that this two-dimensional experiment would be limited by the same factors as the one-dimensional CP experiments. However, because the proton spins are relatively isolated, MAS alone gives enough resolution to clearly distinguish the OH and CH_3 signals, thus making it possible to identify the sources of the polarization transfers. The isolation of the proton spins also limits ^1H - ^1H spin diffusion. In addition, because there are two related frequency scales in the experiment, the chemical-shift resolution is better than in the simple one-dimensional experiment. In this section, we demonstrate how the systematic application of these techniques provides information on the distribution of the functionalized silicons throughout the gel matrix. To begin with, two systems of known structure and composition were investigated to establish the reliability of the technique in the present context.

Figure 4 shows the results of the $^1\text{H}/^{29}\text{Si}$ connectivity experiments carried out on unfunctionalized silica gel using the experimental conditions detailed in the figure caption. The one-dimensional spectra shown in the figure are projections of the data onto the F_1 and F_2 axes and can be used to establish the connectivities. However, the intensities of the signals do not reflect those of the corresponding 1D spectra. In Figure 4A, the gel has

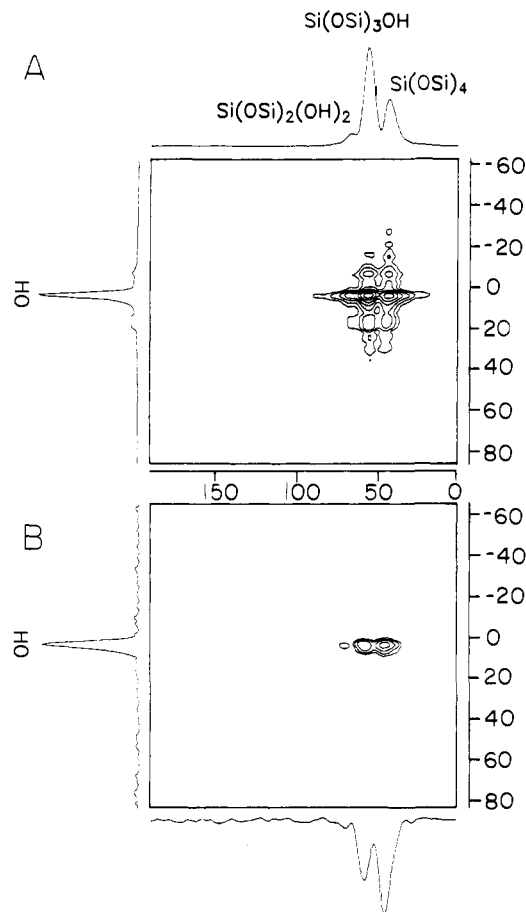


Figure 4. Contour plots of the 2D ^1H - ^{29}Si correlation experiments on silica gel obtained with a 22.0-ms contact time, a 3.0-s repetition time, and a 4.0-kHz sample spinning rate. The vertical axis represents the proton chemical-shift scale and the horizontal axis the ^{29}Si chemical-shift scale. The spectra above and at the side of the figures are the one-dimensional projections. The 2D spectrum was obtained from 64 individual experiments: (A) unwashed silica gel, 80 scans for each individual experiment; (B) D_2O washed sample, 200 scans for each experiment.

not been deuterium-exchanged and an intense signal is observed due to OH protons in the ^1H projection. There is, as expected, a series of intense connectivities to the three silicon environments in the gel. In Figure 4B, the gel has been exchanged twice with D_2O and dried at 100°C , with considerable care being taken to avoid subsequent water adsorption. As can be seen from the figure, there is a very marked decrease in the intensity of the heteronuclear connectivity, but there is still a residual interaction arising from the trace amounts of hydroxyl protons indicated in the projection of F_1 . It is this situation that leads to the possible ambiguities in the one-dimensional experiments described above.

Figure 5 shows experiments carried out on a simple physical mixture of unfunctionalized silica gel and polymethylsiloxane whose one-dimensional ^{29}Si MAS NMR spectrum is shown in Figure 2C. In this case, there should be no connectivity between the methyl protons and any of the silicon nuclei in the gel. Figure 5A shows the experimental results when no deuterium exchange has been carried out. There are clear connectivities to both groups of silicons. In the case of the lower-field, methyl-substituted silicon signal, the connectivity is mainly from the methyl protons, and there is substantial intensity from spinning sidebands consistent with this. In the case of the three high-field signals due to the silica gel, the connectivities must be to hydroxyl protons, as is borne out by the limited sideband pattern. Most importantly, however, the sources of polarization can be unambiguously identified from the chemical shifts. Thus, as indicated in the figure, the two different sets of silicon nuclei are polarized from two distinct proton sources: methyl groups for the polymethylsiloxane and hydroxyl groups for the silica gel. The projection on F_1 identifies their

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(9) Vega, A. J. *J. Am. Chem. Soc.* **1988**, *110*, 1049.

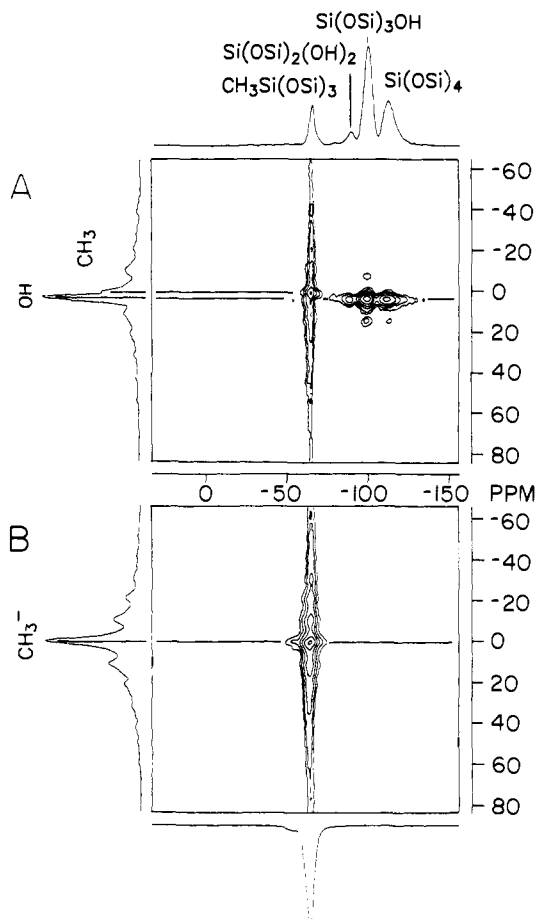


Figure 5. Contour plots of the 2D ^1H - ^{29}Si heteronuclear correlation experiments on a mixture of silica gel and polymethylsiloxane. The spectra were obtained under the same conditions described in Figure 4: (A) untreated sample, 120 scans for each individual experiment; (B) D_2O washed sample, 200 scans for each individual experiment. The spinning rate used (4.3 kHz) was high enough to prevent overlap of spinning sidebands and isotropic peaks between the two sets of resonances.

proton chemical shifts as $\delta = 0.45$ ppm and $\delta = 1.9$ ppm, respectively. Consistent with this interpretation, D_2O exchange of the mixture removes the connectivities to the silica gel, while a very strong connectivity to the polymethylsiloxane silicons with its associated sideband pattern remains (Figure 5B). From the self-consistency of the experiments on these two known materials, it was considered that the technique provided a reliable probe of the macrostructures of other mixed systems, and it was now applied to the methyl-functionalized gels prepared by the copolymerization process as described in the Experimental Section. The gels were first D_2O exchanged and dried to enhance the heteronuclear $^1\text{H}/^{29}\text{Si}$ connectivity from the methyl groups relative to that from hydroxyls. Figure 6 shows the results for two gels containing 50% and 25% methyl-substituted silicons. In the case of the 50% substituted gel, there is a clear heteronuclear connectivity between the methyl groups and the $\text{Si}(\text{O}-)_4$ silicons, as well as a smaller connectivity to residual OH protons. (As previously, the two may be distinguished by their chemical shifts in F_1 .) In addition, there are a number of sidebands in the connectivities consistent as previously with the polarization source being the methyl groups. In the case of the $\text{Si}(\text{O}-)_4$ silicons in the 25% gel, only the connectivity to the methyl groups is observed, perhaps due to more efficient D_2O exchange, as the material may be more compatible to D_2O penetration due to the lower concentration of CH_3 groups. Thus, in both cases, there is clear evidence for the incorporation of the methyl-substituted silicons

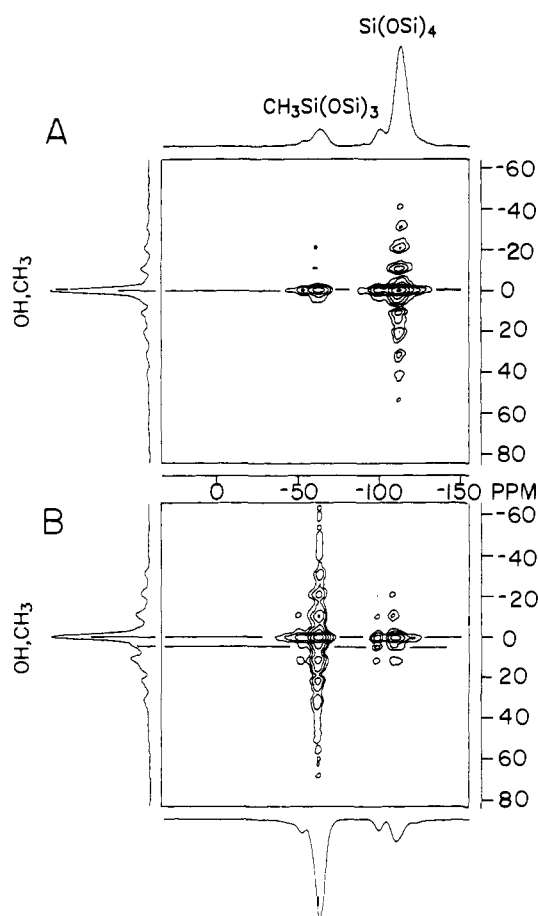


Figure 6. Contour plots of 2D ^1H - ^{29}Si correlation experiments on D_2O -washed methyl-substituted silica gels prepared by the copolymerization process. The spectra were obtained under the same conditions described in Figure 4: (A) 25% MTES used as starting material in the preparation, 280 scans for each individual experiment; (B) 50% MTES used, 200 scans for each individual experiment. The spinning rate used (4.2 kHz) was high enough to prevent overlap of spinning sidebands and isotropic peaks between the two sets of resonances.

throughout the matrix, i.e., the absence of clearly separated domain structures and the presence of substantial numbers of local structural units of type 4. These systems represent a unique type of functionalized silica gel, and their structures may form the starting point for the generation of new materials. It is thus considered that it has been demonstrated that the two components of the composite are "mixed" in the final material. However, the details concerning the "degree of mixing" are not established in a quantitative manner by the present results. The situation is similar to the problem in describing the distribution of monomers in a conventional organic-based copolymer and we are continuing this work by an investigation of the initial stages of the condensation process in solution and the determination of the "reactivity ratios" involved and their dependence on the nature of the substituent groups, R. It should be noted that the general problem encountered in the present work of distinguishing between a domain structure and true blend is a common one in many areas of materials research, and the two-dimensional heteronuclear NMR correlation techniques used in the present work may be of more general applicability.

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