

# On the nature of chemical binding of organic silanes to water-free silica surfaces: a high-resolution solid-state NMR spectroscopic study

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# On the Nature of Chemical Binding of Organic Silanes to Water-Free Silica Surfaces: A High-Resolution Solid-State NMR Spectroscopic Study

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Methoxytrimethylsilane (A), dimethoxydimethylsilane (B), and trimethoxymethylsilane (C) were used to silylate porous silica gel, which was very thoroughly dried with thionylchloride. Products were characterized with elemental analysis and by CP/MAS NMR ( $^{29}\text{Si}$  and  $^{13}\text{C}$ ).

Under these conditions monofunctional silane A yields monodentate silane-to-surface links (trimethylsilyloxysilanes) plus some esterification of silanol sites by methanol, resulting from the main reaction. Bifunctional silane B yields mono- and bidentate silane-to-surface links under the described reaction conditions. Trifunctional silane C also yields mono- and bidentate links. Cross-linked tridentate groups are formed only after exposure to air or reaction with water. © 1988 Academic Press, Inc.

## INTRODUCTION

During recent years much effort has been devoted to the study of coupling organic silanes to silica surfaces. Apart from observations that physisorption may occur, the formation of covalent chemical bonds has been demonstrated (1). The covalent bonds between the multifunctional silane and the silica surface may be characterized as mono-, bi-, or tridentate and all three notations are in use in the literature. Figure 1 gives the three structures, which could in principle be formed in the reaction between the trifunctional methyltrimethoxysilane and silica gel. The structures are encoded 3s (three bonds to the surface), 2s.m (two bonds to the surface and one methoxy group), and s.2m.

In proposing these structures it has been assumed that no water was present during the reaction. In this respect, the present study differs from previous investigations (1c). (See

also Experimental Methods.) When a subsequent treatment with water is applied, the structures of Fig. 2 can be envisaged: s.2h (h stands for a hydroxyl group), 2s.h, 2s.n (n stands for a siloxane bond to a neighboring silane group), s.n.h, and s.2n. When not all the methoxy groups are removed by the water treatment the species s.h.m and s.n.m may be formed as well.

It is impossible, with the resolution presently attainable in MAS NMR, to discriminate between a tridentate linkage to the silica surface (3s) and cross-polymerization along the surface (s.2n, 2s.n) (1).

In the present contribution we describe the reaction between simple mono-, bi-, and trifunctional silanes and silica gel. These reactions were carried out under dry conditions, so that only a limited number of products may be formed. The coupling between silane groups (resulting in 2s.n, s.2n, s.n.h, s.n.m) demands the presence of at least trace amounts

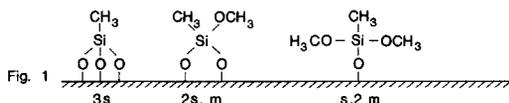


FIG. 1. Possible structures formed in the reaction between the trifunctional methyltrimethoxysilane and silica gel in the absence of water.

of water. Usually, the silica powder is dried by heating at 200°C. This method appears not to be so rigorous that all the water can be removed from the surface completely. Furthermore, a temperature of 200°C may cause dehydroxylation of the silica surface (2). This is an unwanted effect, because the hydroxyl groups are involved in the coupling reaction. In order to leave intact most of the hydroxyl groups, but to remove all the water, an improved drying procedure was used.

Treatment of silica powder with thionyl chloride,  $\text{SOCl}_2$ , results in a rigorous removal of all the water. The reaction products  $\text{SO}_2$  and  $\text{HCl}$  can easily be removed.

The silanes used for the coupling experiments, methoxytrimethylsilane (A),  $(\text{CH}_3)_3\text{SiOCH}_3$ , dimethoxydimethylsilane (B),  $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$ , and trimethoxymethylsilane (C),  $\text{CH}_3\text{Si}(\text{OCH}_3)_3$  were distilled prior to use.

#### EXPERIMENTAL METHODS

Silica gel with an average pore diameter of 50 nm, a mean particle size of 58  $\mu\text{m}$ , and a specific surface area of 600  $\text{m}^2/\text{g}$  was purchased from Alfa Products (Danvers, MA). According to information from the manufacturer, the silica surface contains 4.8 to 5.2 hydroxyl groups/ $\text{nm}^2$ . This porous silica was first dried at 140°C during 24 h and subsequently dried with thionyl chloride ( $\text{SOCl}_2$ ) as follows.

15 g of predried silica was stirred for 5 min

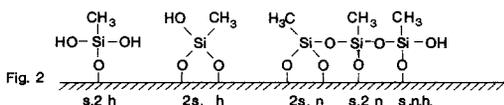


FIG. 2. Possible structures formed after water treatment of a silica gel treated with methyltrimethoxysilane under dry conditions.

at room temperature with 15 ml thionyl chloride in 100 ml dichloromethane. The silica powder was filtered off in an argon atmosphere and washed three times with dry hexane. Solvents were subsequently removed under reduced pressure (0.1 mbar). The dried silica was stored in hypovials in an argon atmosphere. According to elemental analysis the chloride content was  $\leq 0.1\%$ , which is equivalent to maximally one chlorine atom per 35  $\text{nm}^2$ . This chlorine may either be chemically bonded to the surface or be present in the form of physically adsorbed hydrogen chloride.

To check whether or not the drying procedure attacks surface silanol groups we subjected the dried powder to a coulometric Karl-Fisher titration. At 900°C dehydroxylation of the silica surface takes place and the amount of water evolved was measured. It was found that one hydroxyl group per 20  $\text{\AA}^2$  is present. This matches exactly the specifications given by the supplier (*vide supra*). We thus conclude that the drying procedure with thionyl chloride leaves the surface hydroxyl groups intact.

For the coupling reactions 10 g of silica powder was treated at elevated temperature (Table I) with a 2 vol% solution of silane A, B, or C in 100 ml toluene. The suspension was stirred for 2 h under argon. The modified silica was filtered off in an argon atmosphere and washed three times with dry toluene. The powder was dried for 3 h at room temperature *in vacuo* (0.1 mbar).

All solvents used were dried with molecular sieves (4  $\text{\AA}$ ), and the residual water contents were measured with a coulometric Karl-Fisher titration. The water contents were  $\leq 1$  ppm, which is the detection limit of this method. The coupling product obtained with silane C

TABLE I

Coupling agent	Reaction temperature (°C)	Carbon content (%)
$(\text{CH}_3)_3\text{SiOCH}_3$ (A)	50	6.5
$(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$ (B)	70	5.6
$\text{CH}_3\text{Si}(\text{OCH}_3)_3$ (C)	90	5.0

was treated with water at room temperature for 1 h, filtered off, and dried at 0.1 mbar. The carbon content after this treatment is reduced to 2.5%. (See Table I for comparison.)

The NMR experiments were carried out essentially as reported earlier (3). In a number of cases a double air-bearing MAS probehead was used. Contact times were 6 ms for  $^{29}\text{Si}$  CP/MAS NMR and 1–3 ms for  $^{13}\text{C}$  CP/MAS NMR. Pulse interval times were 1 and 2 s, respectively.

## RESULTS AND DISCUSSION

### *Monofunctional Silane*

Figure 3 shows the  $^{29}\text{Si}$ -NMR spectra of the primary coupling products of silanes A, B, and C with silica gel. Figure 3A, which refers to silane A, shows only one signal in the silane region at 12.3 ppm and, following the literature (1), this signal has been assigned to the monodentate coupling product. During the reaction free methanol is also formed. In spite of washing and subsequent drying under reduced pressure, we find by IR and  $^{13}\text{C}$ -NMR

(50 ppm) a small amount of methoxy groups, even after treatment of the reaction product of the monofunctional silane and silica gel with water. This methanol is either chemically or physically (as methanol) bonded to the silica surface.  $^{13}\text{C}$ -NMR chemical shifts do not easily allow one to distinguish between these two possibilities despite the results of Bayer *et al.* (5). Cross-polarization characteristics can be used to distinguish between bonded (rigid) and adsorbed moieties although due care should be taken not to overinterpret the results (6). A sample was prepared by coupling methanol to the silica surface directly. The  $^{13}\text{C}$  CP/MAS NMR showed only one signal at 50.2 ppm with an optimal contact time of 3 ms. The  $^{13}\text{C}$ -NMR spectra of the coupling products of monofunctional silane with silica gel showed a similar signal, with the same cross-polarization behavior, comprising ca. 10% of the total  $^{13}\text{C}$ -NMR signal area. In view of the above evidence we propose that methoxy groups are chemically bound to the silica surface.

The occurrence of the above-mentioned esterification at relatively mild conditions in a dry atmosphere may have consequences, e.g., for the preparation of properly defined reversed-phase materials for HPLC (4, 5).

### *Bifunctional Silane*

Figure 3B shows a more complicated spectrum than Fig. 3A. Apart from the bulk silicon signals in the region from  $-100$  to  $-110$  ppm, two groups of signals are found. The first comprises three signals from  $-4$  to  $-9$  ppm, and the second consists of a rather broad signal between  $-16$  and  $-17.5$  ppm (possibly two or three overlapping signals). At first sight these groups of signals may be assigned to mono- and bidentate structures, respectively. (See also below for the products obtained with trifunctional silane.)

It is known that chemical shift differences of  $+7$  to  $+9$  ppm exist for silicon, incorporated in cyclotrisiloxanes with respect to cyclotetrasiloxanes (7). The small differences be-

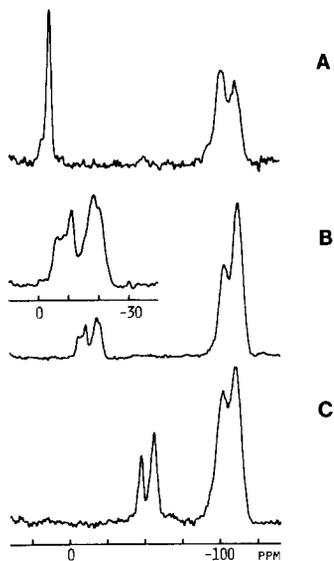


FIG. 3.  $^{29}\text{Si}$ -NMR spectra of the primary coupling products of silanes A, B, and C (top to bottom) with silica gel under dry conditions.

tween cyclotetrasiloxanes and larger ring systems are assumed to be obscured by chemical shift dispersion due to different surface sites. We surmise that in the present case the  $^{29}\text{Si}$ -NMR signal near  $-9$  ppm is to be assigned to a bidentate species of the type 2s analogous to Figs. 1 and 2 in a cyclotrisiloxane structure and that the broad signal near  $-17$  ppm belongs to similar species in D4 and larger ring structures. The signals near  $-4$  and  $-6.5$  ppm may then be assigned to monodentate structures of the types s.h and s.m, respectively.

Since the reactions have been carried out in a dry atmosphere (see Experimental Methods), structures of the type s.h must have been formed subsequently (the NMR measurements were carried out in ambient atmosphere).

One complicating factor is that although in the  $^{29}\text{Si}$ -NMR spectra of the silylation products the four signals mentioned above could always be distinguished, their relative intensities differ by some 10 to 15%. In the course of this investigation, five different batches of material, obtained by reacting silica gel with dimethoxydimethylsilane, have been investigated.

### Trifunctional Silane

Figure 3C shows two strong signals at  $-48.0$  and  $-56.3$  ppm. These signals are assigned to mono- (s.2m) and bidentate (2s.m) linkages, respectively. Signals near  $-65$  ppm are generally ascribed to either a tridentate linkage (3s) or a cross-linked group (2s.n, s.2n) along the silica surface or perpendicular to it. In Fig. 3C only a very weak signal at  $-64.4$  ppm is discernable. Under our experimental conditions (dry atmosphere, *vide supra*) cross-linking during synthesis is not expected since this requires water. We conclude, therefore, that tridentate bond formation between trimethoxymethylsilane and silica gel is difficult, at least with the silica gel used in this study.

Heating the primary coupling product of trimethoxymethylsilane with silica gel has no noticeable effect on the  $^{29}\text{Si}$ -NMR spectrum. Upon treatment with water the primary prod-

uct yields the  $^{29}\text{Si}$ -NMR spectrum depicted in Fig. 4 (bottom). After subsequent heating the top spectrum is obtained. The intensity of the signal at  $-64.4$  ppm has clearly increased. An increase of this signal also occurs when the original material is exposed to air, in agreement with Maciel's results (1).

Upon water treatment, the  $^{29}\text{Si}$ -NMR signal at  $-48.0$  ppm disappears, while a signal at  $-44.9$  ppm arises. Also the signal at  $-56.3$  ppm is replaced by one at  $-54.3$  ppm. Finally, the ratio between the signals at  $-54.3$  and  $-44.9$  ppm (Fig. 4) is clearly larger than that between the signals at  $-56.3$  and  $-48.0$  ppm (Fig. 3C). These changes can be interpreted as follows.

The assignments of the different  $^{29}\text{Si}$ -NMR signals are relatively straightforward. The signal at  $-48.0$  ppm stems from s.2m groups. Upon reaction with water these groups yield primarily s.2h groups, resonating at  $-44.9$  ppm (ca. 1.6 ppm shielding per  $\text{OCH}_3$  group compared with an OH group), s.2n groups ( $-65$  ppm), and s.n.h groups ( $-54.3$  ppm).

The  $-56.3$ -ppm signal is assigned to 2s.m groups and the  $-54.3$ -ppm signal to 2s.h and/or s.n.h groups. Groups of the type s.m.h in the primary coupling product are hardly possible, because water would be needed. The changing relative areas can be explained by the following reactions: 2s.m groups are con-

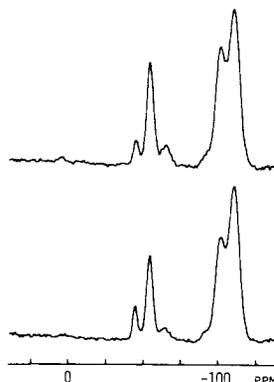


FIG. 4.  $^{29}\text{Si}$ -NMR spectrum of the coupling product of silane C and silica gel after water treatment (bottom) and subsequent heating (top).

verted to 2s.h groups by water. In turn, 2s.h groups may form 2s.n moieties (cross-linking). Furthermore, s.2m groups may yield s.2h groups, which may yield 2s.h, s.n.h, and/or s.2n groups in secondary reactions. Table II summarizes the above analysis.

The complexity of this reaction scheme is one reason that precludes definite, quantitative analyses of the reaction paths. The other reason is that bidentate groups of the type 2s.m may belong to a cyclotrisiloxane or to a larger ring structure. We presume that the signal at  $-56.3$  ppm should be assigned to a 2s.m in a cyclotetrasiloxane ring. Consequently, the counterpart in a cyclotrisiloxane ring could very well resonate near  $-48$  ppm. (See also the discussion concerning the products of the bifunctional silane.) Similarly, 2s.n in large cyclosiloxane rings, giving rise to a signal near  $-65$  ppm, could have "counterparts" near  $-56$  ppm. The observed linewidths in  $^{29}\text{Si}$ -NMR spectra increase in the order monodentate < bidentate < tridentate. In our view this is caused by a chemical shift dispersion (surface site inequivalencies), also visible in, e.g., the silanol signal. The influences of these dispersions become larger with increasing numbers of surface bonds for a given group.

### $^{13}\text{C}$ -NMR

The above analyses by means of  $^{29}\text{Si}$  CP/MAS NMR for the reactions of silanes B and C with silica are corroborated by our results with  $^{13}\text{C}$  CP/MAS NMR. (See also Refs. (8-10).) For the products of B, a  $^{13}\text{C}$ -NMR signal

is found around 49 ppm. Apart from the surface methoxy groups (*vide supra*), this signal may also stem from monodentate groups of the type s.m (see Figs. 1 and 2). The remaining signals are found at  $-2.5$  and  $-4.5$  ppm. We assume that methyl groups, attached to silicon atoms bearing two oxygens, are shielded by about 2 ppm with respect to those bonded to atoms with one oxygen attached directly (as in trimethylsiloxy groups). A further shielding of ca.  $-2.5$  ppm is brought about by replacing a hydroxyl group connected to silicon by a methoxy group, or by an extra bond to either the silica surface or a neighboring silane.

Only a small amount of methoxy groups is expected to be left after water treatment of the coupling product of silica and silane C. This is in agreement with an observed 50% drop in the carbon contents. The  $^{13}\text{C}$  CP/MAS NMR spectrum of the primary coupling product shows approximately a 70% contribution in the methoxy region. This signal is attributable to s.2m and 2s.m groups, but also to Si-O-CH<sub>3</sub> (surface groups). The remainder of the  $^{13}\text{C}$ -NMR signals are located at  $-5.5$  to  $-8$  ppm, in line with the expected extra shielding exerted by the methoxy methyls on the methyls attached directly to silicon.

### CONCLUSIONS

(1) The method of drying silica powder chemically with thionyl chloride is superior to drying the powder physically by means of heating. Furthermore the concentration of surface silanol groups is not affected by this method.

(2) Methanol, which is produced during the coupling reaction of the silane with the silica surface, is partly esterified to the silica surface.

(3) The coupling of the trifunctional methyltrimethoxysilane with silica gel under dry conditions produces no tridentate coupling product.

(4) Water treatment of a previously silylated silica surface causes cross-linking of the silane components (in the case of a multi-

TABLE II

Summary of Reactions

Starting species	Chemical shift relative to TMS (ppm)	Product	Chemical shift relative to TMS (ppm)
2s.m	-56.3	2s.h	-54.3
2s.m	-56.3	2s.n	-65.0
s.2m	-48.0	s.2h	-45.0
s.2m	-48.0	s.n.h	-54.3
s.2m	-48.0	s.2n	-65.0

functional silane). The extent of cross-linking is limited by the surface coverage.

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