

Reactions of Ethoxysilanes with Silica: A Solid-State NMR Study

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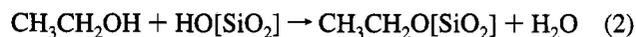
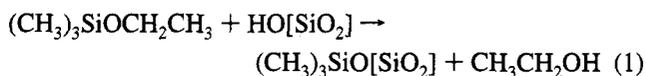
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Alkoxysilane reagents find widespread application in the fields of immobilized catalysts^{1–3} and reversed-phase chromatography,^{1,4–8} because they provide strong bonding via up to three siloxane groups and high surface coverage without acidic reaction products. In spite of this, the nature of the coupling reaction of alkoxysilane reagents with the silica surface is still a matter of debate. In this paper it is demonstrated unequivocally by solid-state NMR spectroscopy that ethoxysilane reagents react directly with siloxane bonds of dehydrated silica.

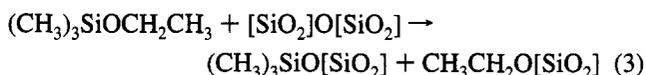
²⁹Si and ¹³C solid-state NMR spectroscopy nowadays provides the most detailed information about the nature and reactivity of inhomogeneous catalysts,⁹ their support materials,^{9,10} and especially modified silica.^{4–7,11–18} ²⁹Si CP/MAS NMR spectroscopy,¹⁰ e.g., showed that trialkoxysilane reagents do not exclusively form three siloxane bonds upon condensation reaction with silica surface silanol groups: there always exists a distribution of silane species bound by one, two, and three siloxane bonds.^{5–7,14,19} Furthermore, the presence of polysiloxane, incompletely coating the surface, cannot be excluded.^{6,14} Consequently, residual alkoxide signals can be found in the ¹³C CP/MAS NMR spectra of the modified silica materials. However, the intensities of the ²⁹Si NMR signals do not match the intensities of the corresponding ¹³C NMR signals.⁶ According to ¹³C NMR spectroscopy there are always more alkoxy groups present than would be anticipated from the silane region of the ²⁹Si CP/MAS NMR spectra, which shows all surface-bound silane species carrying residual alkoxy groups. This discrepancy was attributed to reaction of free alcohol, formed by condensation reaction, with surface silanol groups.⁶ An IR study, however, suggested reaction of surface siloxane groups

with the alkoxysilane reagents.²⁰ Both studies were unfortunately complicated by residual alkoxy groups bound to the silane reagents and cross-linking. Therefore, in order to find out the true mechanism, the reaction of the silica surface with alkoxysilanes was studied using the monoethoxy reagent trimethyl-ethoxysilane (**1**).

When silica SiO₂(600)²¹ is modified²² with **1**, the silane region of the ²⁹Si CP/MAS NMR spectrum²³ shows a signal at 13.7 ppm, matching the data for silica modified with chlorotrimethylsilane^{5,7,13} or hexamethyldisilazane.^{11,15} The ¹³C CP/MAS NMR spectrum²³ obtained after reaction of SiO₂(600) with **1** at 25 °C is shown in Figure 1A. The signal at –0.4 ppm corresponds to the trimethylsilyl carbon atoms, and the signals at 59 and 16 ppm correspond to the methylene and methyl carbon atoms of a surface-bound ethoxy group. The relative signal intensities of about 1 to 3 of ethoxy and trimethylsilyl signals did not change when reaction temperatures up to 160 °C or simple high-power decoupling and long pulse delays (60 s) were applied, which can be anticipated from the high mobility of both methyl and ethoxy groups.^{4,12,17} Therefore, the ethoxy groups are retained quantitatively. Since no residual ethoxy groups can be left at the surface-bound silane, there are, in principle, two possible explanations for this observation: The first possibility is that the ethanol from the condensation reaction of **1** with surface silanol groups (reaction 1) reacts quantitatively with further surface silanol groups (reaction 2).



The other possibility is an addition reaction of **1** with surface siloxane groups:



Reaction 3 explains the quantitative retainment of the ethoxy groups without further assumptions and has its analogs, for example, in the reactions of Cp*₂Th(CH₃)₂,²⁴ BF₃,²⁵ NH₃, and H₂O²⁶ with surface siloxane groups. The sequence (1)/(2), however, requires reaction 2 to be faster than reaction 1 in order to allow quantitative retainment of the ethoxy groups. But under these reaction conditions, ethanol does not react with silica. This can be anticipated from the sluggish reaction of other alcohols with silica.^{7,27,28} Even after silica SiO₂(600) or SiO₂(25)²¹ is boiled in ethanol for 24 h, there is only a small number of chemically bound ethoxy groups. The latter correspond to the

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(21) The silica was obtained from Merck (silica 40) and dried in vacuo (10^{–2} Pa) at 25 °C (SiO₂(25)) or 600 °C (SiO₂(600)) for 24 h in order to remove adsorbed water or condense surface silanol groups, respectively, and stored under dry nitrogen.

(22) In a typical experiment 1 g of silica was suspended in about 20 mL of dry toluene. After addition of 0.1 g of **1**, the slurry was stirred for 12 h at 25 °C. Then the liquid was decanted, the residue washed three times with toluene, and the silica dried in vacuo. Experiments without solvent gave the same results.

(23) All measurements were made with a Bruker MSL 300 NMR spectrometer using 7 mm ZrO₂ rotors: spinning speed, 4 kHz; external references, tetrakis(trimethylsilyl)silane (²⁹Si) and adamantane (¹³C); proton 90° pulse, 6 μs.

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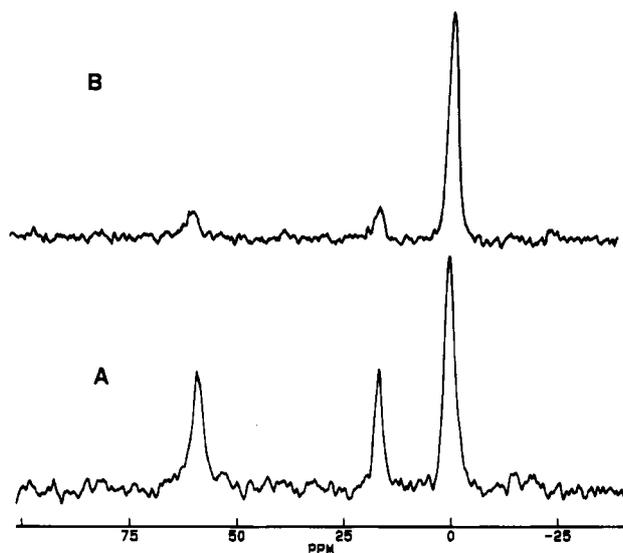


Figure 1. ^{13}C CP/MAS NMR spectra (75.5 MHz) of highly dehydrated silica $\text{SiO}_2(600)^{21}$ (A) and hydrophilic silica $\text{SiO}_2(25)^{21}$ (B) modified with $(\text{CH}_3)_3\text{SiOCH}_2\text{CH}_3$: contact time, 5 ms; pulse delay, 4 s; 1000 scans.

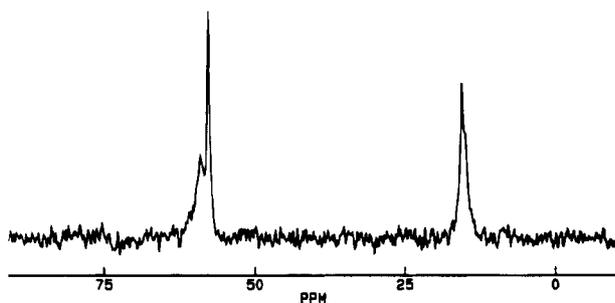


Figure 2. ^{13}C CP/MAS NMR spectrum (75.5 MHz) of silica $\text{SiO}_2(600)^{21}$ treated with ethanol (see text): contact time, 5 ms; pulse delay, 4 s; 4000 scans.

broad signals at 58.7 and 15.0 ppm in Figure 2. The partly overlapping narrow signals at 57.5 and 15.5 ppm with a line width of about 50 Hz can be attributed to physically adsorbed ethanol.^{27,29}

Using CP, the optimal signal intensity for the adsorbed ethanol was obtained for contact times of 5 (Figure 2) to 6 ms. The signals decreased to half their original size with a contact time of 3 ms. When a 1 ms contact time was applied, the signals of the adsorbed species were reduced to little shoulders at the broad signals of the chemically bound ethoxy groups. However,

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the intensity of the narrow signals increased about 5-fold, when simple high-power decoupling was applied instead of CP. This behavior is typically observed with adsorbed in contrast to chemically bound species³⁰ and has its origin in their different mobilities.³⁰

Further evidence against reaction 2 comes from the fact that the number of ethoxy groups is diminished when less rigorously dried silica $\text{SiO}_2(25)^{21}$ containing fewer siloxane groups is used, which can be seen in Figure 1B. However, their mere presence suggests that reaction 3 is even preferred to reaction 1. This is also supported by the observation that the surface coverage is greater under the applied reaction conditions for $\text{SiO}_2(600)$ (6.5% carbon content as determined by elemental analysis) than for $\text{SiO}_2(25)$ (4.5%). $\text{SiO}_2(600)$, modified with **1**, is remarkably stable toward hydrolysis,³¹ probably due to its high hydrophobicity. This suggests its application as a reversed-phase stationary phase. The coverage of $\text{SiO}_2(600)$ with trimethylsilyl and adjacent ethoxy groups is even sufficiently dense to allow reversed-phase chromatography of highly sensitive organometallic compounds. For example, the material can be stirred with a solution of chromocene for more than 48 h without signs of decomposition of the latter. In contrast, $\text{SiO}_2(25)$, modified with **1**, leads to rapid decomposition of chromocene, as does commercial silylated silica prepared with chlorosilanes.

In conclusion, the use of **1** and ^{13}C solid-state NMR spectroscopy showed unequivocally that addition of alkoxy silane reagents to surface siloxane groups of silica does take place and might even be the preferred reaction pathway. Consequently, in contrast to common practice, highly dehydrated silica with a maximum number of siloxane groups should be applied both for the immobilization of catalysts with bifunctional ethoxysilane reagents³ and for modifying silica with alkoxy silanes for chromatography.^{4–8} Monoethoxysilanes have the additional advantage of providing a clean reaction without cross-linking and therefore well-defined surface bound species. Since each trimethylsilyl group inevitably has an adjacent ethoxy group, there is no more need for “end capping” in an additional step.

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