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

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Alkoxysilane reagents find widespread application in the fields of immobilized catalysts1–3 and reversed-phase chromatography,4–9 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,10 and especially modified silica.11–13 CP/MAS NMR spectroscopy,14 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.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.8 According to 13C NMR spectroscopy there are always more alkyl 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 alkoxyl groups. This discrepancy was attributed to reaction of free alcohol, formed by condensation reaction, with surface silanol groups.9 An IR study, however, suggested reaction of surface siloxane groups with the alkoxysilane reagents.20 Both studies were unfortunately complicated by residual alkoxide 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 modified 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 chlorotrimethyloxysilane5,7,13 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).

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{SiOCH}_2\text{CH}_3 + \text{HO}[\text{SiO}_2] & \rightarrow \\
\text{(CH}_3\text{)}_2\text{Si}[\text{SiO}_2] + \text{CH}_3\text{CH}_2\text{O} & (1)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} + \text{HO}[\text{SiO}_2] & \rightarrow \\
\text{CH}_3\text{CH}_2\text{O}[\text{SiO}_2] + \text{H}_2\text{O} & (2)
\end{align*}
\]

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

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{SiOCH}_2\text{CH}_3 + [\text{SiO}_2] & \rightarrow \\
\text{(CH}_3\text{)}_2\text{Si}[\text{SiO}_2] + \text{CH}_3\text{CH}_2\text{O}[\text{SiO}_2] & (3)
\end{align*}
\]

Reaction 3 explains the quantitative retenation 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 retention 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.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...
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 species and has its origin in their different mobilities.

Further evidence against reaction 2 comes from the fact that the number of ethoxy groups is diminished when less rigorously dried silica SiO$_2$(25) 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 SiO$_2$(600) (6.5% carbon content as determined by elemental analysis) than for SiO$_2$(25) (4.5%). SiO$_2$(600), modified with I, is remarkably stable toward hydrolysis, probably due to its high hydrophobicity. This suggests its application as a reversed-phase stationary phase. The coverage of 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, SiO$_2$(25), modified with I, leads to rapid decomposition of chromocene, as does commercial silylated silica prepared with chlorosilanes.

In conclusion, the use of I and $^{13}$C solid-state NMR spectroscopy showed unequivocally that addition of alkoxysilane 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 ethoxyxilane reagents and for modifying silica with alkoxysilanes for chromatography. Monoethoxysilanes have the additional advantage of providing a clean reaction without crosslinking 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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(31) The $^{13}$C CP/MAS NMR spectrum of the material is not changed after boiling in H$_2$O for 8 h.