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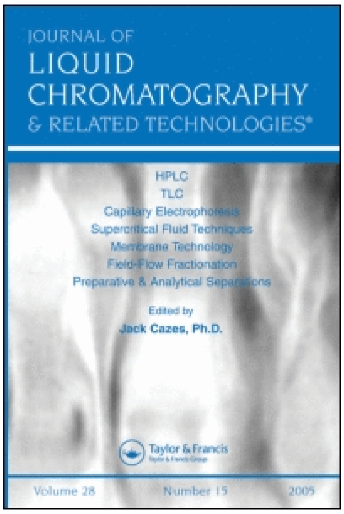

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REACTIONS OF ETHOXYSILANES WITH SILICA: A SOLID-STATE NMR STUDY

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ABSTRACT

Ethoxysilanes are of growing interest in the fields of immobilized catalysts and chromatography. In spite of this, the reactions of ethoxysilanes with silica surfaces are still not fully explored. This contribution demonstrates that besides the reaction temperature and the degree of dryness of the silica surface, the solvent plays a crucial role during the silanization step: Optimal surface coverage can, for example, be obtained either without solvent or with hydrocarbons like *iso*-octane or pentane under mild reaction conditions. Hereby, ^{13}C and ^{29}Si solid-state NMR spectroscopy serves as a powerful analytical method. The modified silica can be successfully applied for the purification of bifunctional phosphines and their carbonylnickel complexes.

INTRODUCTION

Alkoxysilane reagents are important for a variety of chemical applications: In the form of bifunctional phosphine linkers they can be used in order to immobilize catalysts on inorganic supports,[1-7] most often on silica.[8] The other application lies in the field of silanized silica for chromatography.[9-24]

The most powerful method in order to characterize silane modified silica is solid-state NMR spectroscopy.[3-7,11-29] Using Magic Angle Spinning (MAS,[25-29]) and Cross Polarization (CP,[25-29]) the surface species can be detected without any difficulties arising from the bulk material.

The advantages of alkoxysilanes as compared to chlorosilanes, are that no acidic byproducts are formed upon reaction with silica, which could destroy sensitive transition metal complexes when they are immobilized on silica or chromatographed. Furthermore, due to addition reactions of alkoxysilanes to surface siloxane groups, there is no need for "endcapping" in a further step.[31]

However, in contrast to the reactions of chlorosilanes, comparatively few studies deal with the reactions of ethoxysilanes with silica surfaces.[4,5,11,13,15,22,24,31] Triethoxysilanes are most interesting, because they should provide a strong bonding to the support via up to three siloxane bonds.

Up to now, the dependence of the number of siloxane bonds formed on the reaction temperature and the degree of dryness of the silica used has been primarily studied. In the following, we want to shed some light on the influence of the solvent used for the silanization procedure.

EXPERIMENTAL SECTION

a) Solid-State NMR Spectroscopy

All the spectra were recorded on a BRUKER MSL 300 NMR spectrometer, equipped with a 7 mm broadband double bearing MAS probehead and ZrO_2 rotors. The modified silica was loosely filled into the rotors under air. Cross polarization (CP) and Magic Angle Spinning (MAS) with a rotational speed of 4 kHz was applied for all the spectra shown. The contact times were 5 ms (^{13}C), 1 ms (^{31}P) or 6 ms (^{29}Si), if not stated otherwise, and the relaxation delays 4 s (^{13}C, ^{31}P), and 10 s (^{29}Si).

For all measurements, 500 to 1000 transients gave satisfactory signal to noise ratios. All spectra were recorded at room temperature (298 K). The ^{13}C, ^{29}Si, and ^{31}P NMR spectra were referenced with respect to external solid adamantane, $[(CH_3)_3Si]_4Si$, and $NH_4H_2PO_4$, respectively. For the exponential multiplication, line broadening factors of 40 Hz (^{13}C) and 60 Hz (^{29}Si, ^{31}P) were applied.

b) Preparation of the Silica

The silica was dried in a vacuum of about 10^{-2} Pa for 12 h either at 600 °C (SiO_2(600)) or 25 °C (SiO_2(25)) prior to use. All the experiments were carried out with Merck silica 40 (specific surface area: 750 m^2/g; average pore size: 40 Å; particle size 0.063 - 0.2 mm). All solvents used were rigorously dried by standard procedures.

c) Silanization Procedures

All the silanization reactions were carried out following this scheme: 1 g of silica was suspended in about 50 mL of the indicated solvent. Then 1 mL of the ethoxysilane was added and the reaction mixture stirred for 12 h at the temperature given in the text. Finally the supernatant solution was decanted and the silica was washed three times with pentane, before it was dried in vacuo for about 4 h.

RESULTS

1. ^{13}C CP/MAS Spectra

All the studies presented here were carried out with trimethylethoxysilane (**1**), vinyltriethoxysilane (**2**), and 3-chloropropyltriethoxysilane (**3**). The silica was dried in vacuo at 600 °C (SiO_2(600)) or at 25 °C (SiO_2(25)), in order to condense surface silanol groups or to remove adsorbed water.[8] When pure $(CH_2{=}CH)Si(OEt)_3$ (**2**) is reacted with both types of silica, the ^{13}C CP/MAS spectra of the materials shown in Fig. 1 result.

The ^{13}C NMR signals at 16.6 ppm and 58.4 ppm stem from the methyl and methylene groups of residual silane- or surface-bound ethoxy groups.[31] The resonances at 129.7 and 135.1 ppm, with their rotational sidebands and, therefore, larger CSA (Chemical Shift Anisotropy,[25-29]) can be attributed to the CH_2 and CH carbon atoms, respectively.[32] This assignment is in accord with the halfwidths of the vinyl carbon signals. The CH group gives a broader ^{13}C resonance, because it is less mobile than the CH_2 group, which can rotate about the Si-CH axis.

While, in the case of rigorously dried silica (Fig. 1 B), a large amount of ethoxy groups is retained on the surface, silicas containing more Si-OH groups lead to a lower ratio of EtO groups to vinyl groups (Fig. 1 A). The analogous observation is made, when $Cl(CH_2)_3Si(OEt)_3$ (**3**) is reacted with silica. Again,

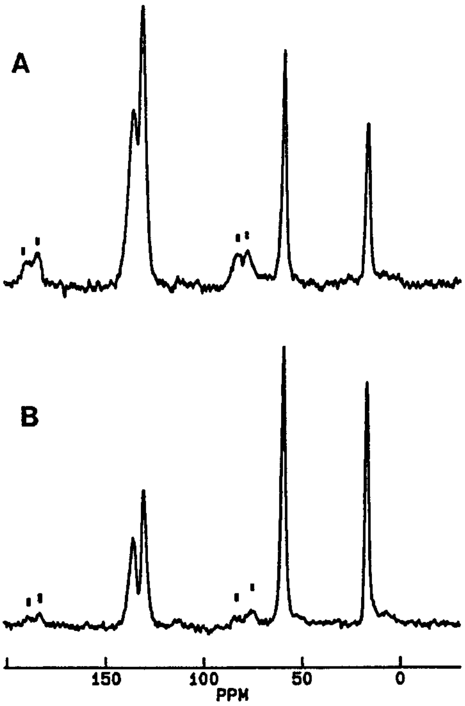

Figure 1. 75.5 MHz ^{13}C CP/MAS spectra of vinyltriethoxysilane (**2**) after reaction with SiO_2(25) (A) and SiO_2(600) (B). Details see text and Experimental Section.

the resonances of ethoxy groups (17.0 and 58.3 ppm) are visible besides those of the $ClCH_2$ (45.8 ppm), CH_2Si (8.8 ppm), and $CH_2CH_2CH_2$ (25.8 ppm) signals.

2. The Influence of Reaction Time

When SiO_2(600) is treated with an excess of pure **2** for 12 h at 60 °C, after washing and drying, a material results, whose ^{29}Si CP/MAS spectrum is displayed in Fig. 2 A. Adding again an excess of **2** and stirring the slurry for three more days at 60 °C, leads to the ^{29}Si CP/MAS spectrum shown in Fig. 2 B. While the signal intensities of the HO-SiO_3 and SiO_4 ^{29}Si resonances at -102 and -110 ppm are somewhat sensitive to changes of the contact time, as described in ref.,[13] the signal intensities within the silane region were not

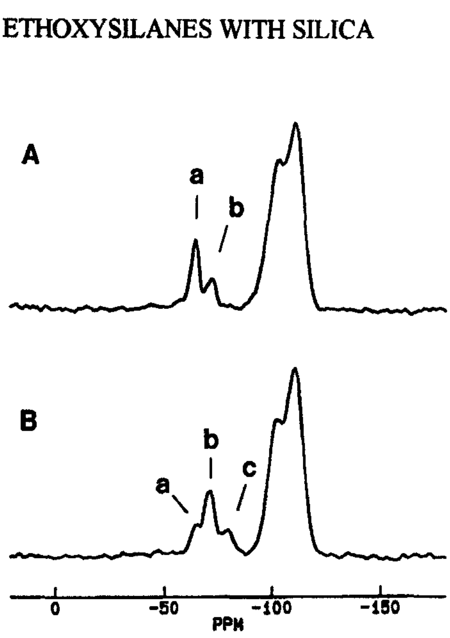

Figure 2. 59.6 MHz ^{29}Si CP/MAS spectra of $SiO_2(600)$ after reaction with vinyltriethoxysilane (2) for 12 h (A) and for 3 days (B). a, b, and c denote silane species with 1, 2, and 3 siloxane bonds. Details see text and Experimental Section.

altered within the range of contact times from 5 to 12 ms. Both spectra of Fig. 2 are recorded with a contact time of 6 ms and the same batch of silica is employed. Therefore, a rough estimate of quantities should be feasible. While the silanol signal is shrinking somewhat with prolonged heating of the material, the overall signal intensity in the silane region remains roughly unchanged. The assignment of the resonances a, b, and c (Fig. 2) at -65.7, -71.6, and -79.8 ppm is made in analogy for example to refs.:[12,13,22,25] The more siloxane bridges to the support are formed, the lower is the resonance frequency. The resonance at -65.7 ppm corresponds to $(CH_2{=}CH)Si(OEt)_2\text{-}O\text{-}\{SiO_2\}$ exclusively, while cross-linking might take place in the case of the other two resonances with more than one siloxane group.

When silica $SiO_2(25)$ is applied for the same reactions, the intensities of the silane signals b and c are greater, while the sum of the silane signal intensities is somewhat lower than in the case of $SiO_2(600)$. The analogous trends are observed in all the above reactions, when the chloropropylsilane **3** is used instead of **2**. The silane signals corresponding to a, b, and c have the chemical shifts -51.5, -58.7, and -65.7 ppm. When all the materials described in this paragraph are treated with an excess of $Me_3Si(OEt)$ at 80 °C in toluene for 12 h, the ^{29}Si CP/MAS spectra do not even show traces of surface bound **1**.

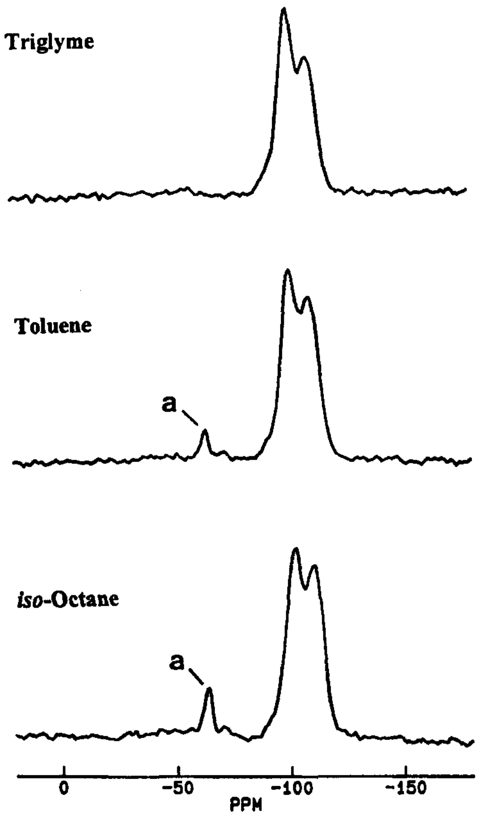

Figure 3. 59.6 MHz ^{29}Si CP/MAS spectra of SiO_2(600) after reaction with vinyltriethoxysilane (2) in the solvents indicated. Details see text and Experimental Section.

3. The Influence of the Solvent

In order to study the influence of the solvent, silica SiO_2(600) can be reacted with **2** and **3** under identical reaction conditions (80 °C, 12 h) but using different solvents, namely CCl_4, *iso*-octane, toluene, and triglyme. In analogous runs at 25 °C, ether, acetone, and pentane is applied.

Three representative ^{29}Si CP/MAS spectra of the materials are displayed in Fig. 3. Since the silane signal intensities are not very sensitive to the CP parameters used, a rough quantitative judgment might be allowed. In the case of the solvents ether, acetone, and triglyme, no silane signals could be detected in the ^{29}Si CP/MAS spectra (Fig. 3, top trace). CCl_4 gave a spectrum analogous to the one when toluene was applied (Fig. 3, middle spectrum), while pentane resulted in comparable silane signal intensity, but with a ratio of about 1 : 1 of species a and b. *iso*-Octane leads to maximal silane signal intensity and the nearly exclusive presence of species a bound by one siloxane bridge to the support. The surface coverage, however, does not reach the one found when silica is treated with **2** without any solvent (Fig. 2). The results of the reactions of **3** with SiO_2(600) parallel closely the ones found for **2**. When the materials described in this and the previous paragraph are treated with triglyme at 80 °C or with acetone at 25 °C for 12 h, the overall surface coverage with silanes does not change.

4. Chromatographic Purification of Phosphines and their Nickel Complexes

Bifunctional phosphines, like $Ph_2P(C_6H_4)SiMe_2SiOEt$ (**4**) and $Ph_2P(C_6H_4)Si(OEt)_3$ (**5**) and their carbonylnickel complexes,[33] are difficult to purify. Most often they do not crystallize and due to their weight, they cannot be sublimed. Ordinary chromatography does not help here, because **4** and **5** are immobilized on silica. Silane modified silica, however, is suitable for the purification of these species. While commercial Me_2SiCl_2- modified silica leads to major loss of phosphines, optimal results have been obtained with the silica modified with **1** and described in Ref. 31.

For example, when **4** is applied to a column packed with Me_3Si-O-$\{SiO_2\}$/pentane, all pentane-soluble impurities can be removed by elution with this solvent. Due to strong adsorption of **4** on the stationary phase, it does not migrate with pentane. The adsorption can be seen in the ^{31}P CP/MAS spectrum after drying the column material.

The narrow linewidth and the NMR behavior are indicative of merely adsorbed phosphine.[3,34] The phosphines and nickel complexes can be eluted as a narrow band by applying a solvent mixture of pentane and THF in the ratio 8 : 2. The purity of the nickel complexes can, for example, be checked by ^{61}Ni NMR spectroscopy.[35] Strongly colored orange-brown impurities stay on the column, while the phosphines and their complexes are eluted as colorless oils. There is usually only minimal loss of the substrates and the absence of phosphine species on the stationary phase can again be checked by ^{31}P CP/MAS spectroscopy.

DISCUSSION

1. Addition or Condensation Reactions?

Figure 1 shows that in the case of rigorously dried silica $SiO_2(600)$, more ethoxy groups are retained than with $SiO_2(25)$. This rough quantitative interpretation should be allowed regarding the high mobility of all the groups present[20,21,24] and, keeping in mind, that both spectra have been recorded under identical conditions and they display the same species. Therefore, these results with the triethoxysilanes **2** and **3** follow the trend already observed for the monoethoxysilane **1**.[31] However, the results for **2** and **3** are not that clearcut. For example, the ratio of vinyl to ethoxy groups as found in spectrum 1 B is about 1 : 2 which means that on average one ethoxy group of originally three is lost during the immobilization. Therefore, the addition reaction of the triethoxysilane group to surface siloxane groups[31,33] is not the only reaction taking place here. There must be either a condensation reaction with residual surface silanol groups or some cross-linking between adjacent surface bound silanes.

On the other hand, in the case of $SiO_2(25)$, there are more OEt- groups present than there should be, according to the corresponding ^{29}Si CP/MAS spectrum. This again, corroborates the assumption of addition reactions taking place.[31,36]

These results, however, mean that there is always a variable amount of ethoxy groups present and, that determinations of surface coverages by elemental analysis are not very reliable without the knowledge of the ethoxy group ratio, as determined by ^{13}C CP/MAS spectroscopy.

2. The Reaction Time and Temperature

When silane modified silica is heated for a prolonged period of time with additional ethoxysilane present, the surface coverage with silane does not increase substantially, which can be seen in Fig. 2. This means that the ethoxysilanes already cover the silica surface with maximal density, even if they are bound by only one siloxane bond to silica. The already surface-bound vinylsilane groups, due to sterical reasons, prevent the attack of further silane reagent. This assumption is further corroborated by the finding, that no traces of Me_3Si groups can be found on the surface, when the material of spectrum 2 A is treated with **1**. This means that a) no endcapping is necessary or possible when alkoxysilane reagents are used to modify silica and b) that monoethoxysilanes should lead to the same dense surface coverage as triethoxysilanes. However, prolonged heating in the case of the latter leads to the formation of additional siloxane bonds, which might make the bonding to the support stronger and enhance the lifetime of chromatographic materials or immobilized catalysts.

The formation of more than one siloxane bond to the support is facilitated when the amount of surface silanol groups is increased. This means that in contrast to the formation of the first siloxane bond, where the addition reaction to surface siloxane groups seems to be preferred,[31,33] the formation of one or two more siloxane bridges needs - probably due to steric reasons - adjacent silanol groups. This assumption is corroborated, for example, by the signal intensity of the surface silanol signals, which diminishes on going from spectrum 2A to 2B.

3. Which solvent should be chosen?

The above results and Fig. 3 show, that given one type of silica, the solvent applied plays a crucial role regarding the surface coverage with silanes and the number of siloxane bonds formed. While polar solvents lead to minimal coverages, if at all, the unpolar solvents pentane and *iso*-octane give large signals in the silane regions of the ^{29}Si CP/MAS spectra (Fig. 3). However, maximal signal intensities are obtained without any solvent (Fig. 2). We interpret these findings as being the results of strong adsorption of the solvents on the silica surface.[37] The stronger the adsorption on the surface, the denser is the shielding towards attacking ethoxysilane reagents. However, once siloxane bridges are formed, they are not broken by polar solvents, since the surface coverage stays the same after treatment with polar solvents (results, 3.).

This assumption of strong adsorption of polar solvents on the silica surface is corroborated by the linewidth reduction of suspension NMR signals, when phosphine moieties are detached from the support by polar solvents.[38]

The above results also demonstrate, that regarding the surface coverages, aromatic solvents like toluene, which are commonly used for the silanization procedures, are not optimal. The surface coverages are greater when hydrocarbons like *iso*-octane or pentane are used. These two solvents are indicative of an influence of solvent viscosity on the number of siloxane bridges formed. The less viscous pentane probably allows greater mobility of the surface-bound silane and, therefore, sterically facilitates the formation of further siloxane bonds.

4. Chromatography of Bifunctional Phosphines

Chapter 4 of the Results section shows, that silica modified with alkoxysilane reagents can be applied for the successful chromatographic purification of bifunctional phosphines and their complexes. Although the procedure described is not a real reverse phase chromatography, it is still very useful, simple and effective.

As in the case of **1**, the ethoxysilane groups of **4** and **5** do not remove the silanes already bound to the support via siloxane bonds. Since no acidic byproducts are formed during the silanization step with ethoxysilane reagents, no phosphonium salts are formed on the stationary phase.

CONCLUSIONS

In this contribution, it is demonstrated by solid-state NMR spectroscopy, that during the silanization of silica with ethoxysilanes a) the solvent applied determines the surface coverage and number of siloxane bonds formed, and b) that the number of siloxane bonds formed is further dependent on the reaction time and temperature, and of the degree of dryness of the silica. Silica modified with trimethylethoxysilane can be applied for the purification of bifunctional phosphines and their nickel complexes.

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