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New Approaches to Surface-Alkoxylated Silica with Increased Hydrolytic Stability

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Surface-alkoxylated silica can be prepared by reacting precipitated silica with high-boiling and polymeric alcohols. The structure of the products was investigated through ^{13}C and ^{29}Si MAS NMR experiments. The influence of the alkoxy group structure and density on the hydrolytic stability of the alkoxylated silicas was determined through contact with boiling water. Use of polymeric or branched alcohols increased the hydrolytic stability of surface-alkoxylated silicas compared to straight-chain alcohols. The rate of surface substitution is increased by both acid and base catalysis.

Introduction

Surface modification of inorganic oxides forms the basis of a vast range of applications, from adsorbents and catalysts to sensors.[1] Essentially, the success of such applications depends on a close control of the surface properties of the materials produced by covalent bonding of organic molecules to hydroxyl groups on the surface of the inorganic oxide. In many cases, silanes are used as the oxide-binding moiety of the organic molecule that gives the surface the special and tailored properties necessary for a particular application.

Silica has been the most widely used substrate for such modifications due to its low price, ready availability in a wide range of specific surface areas, and chemical and mechanical stability. A plethora of silane-based compounds is available, and their reactions with silica are well understood.[2] The well-known esterification reaction of silanol groups on the silica surface, $\equiv$SiOH, with various alcohols to produce surface-alkoxylated silica, $\equiv$Si$-$OR, is an attractive and possibly less expensive route to materials with a functionality similar to that of their silane-based counterparts.

The surface-esterification reaction has been the subject of many investigations. Initial studies focused on the direct esterification of silanols with alcohols, which was normally carried out in neat alcohol under autoclave conditions.[3−6] Alternative, milder synthetic routes were found through intermediate activation of the silica surface, through either chlorination[7,8] or treatment with aminosilanes.[9] Compounds more reactive than alcohols, such as ortho esters, acetals, and ketals, have also been used for the synthesis of this class of compounds.[10,11] All these synthetic methods have an additional advantage over silanes in that the reagents cannot enter side reactions as the alkoxy- and chlorosilanes commonly employed do. Traces of water can lead to premature hydrolysis and subsequent oligomerization of silanes with more than one hydrolyzable ligand. This leads to oligomeric clusters which may become deposited on the surface and disturb the intended monolayer.[12] Therefore, and because of the easier synthetic access to alcohols than silanes, the alkoxylation reaction has been used to prepare functional materials.[13,14] Recently, mesoporous silica was used as a substrate.[15]

In applications where the long-term stability of the functional surface is essential, the surface-alkoxylated silica suffers from the inherent hydrolyzability of the $\equiv$Si$-$OR bond. Although many authors mention the hydrolytic instability of surface-alkoxylated silica, there appear to be only a few systematic studies of this matter.[16,17]

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To the best of our knowledge, there has been no systematic investigation into the role of the alkoxy group structure and surface density on the rate of hydrolysis. Furthermore, the simple synthetic methods in the literature where alcohols are used in large excess do not lend themselves to polymeric alcohols. In this paper a synthetic method that overcomes these problems and permits the use of high-boiling and polymeric alcohols is described. The results of investigations of some of the factors that influence the hydrolysis of the materials obtained through this method are also presented.

Experimental Section

Materials. The precipitated silica used was Degussa FK 320 with a measured BET surface area of 145 m^2/g (N_2).

Reagent grade alcohols (1-octanol (Lancaster), 2-ethyl-1-hexanol (Acros), 1-octadecanol (BDH), and methanol (Panreac Quimica)) were used as provided or dried by stirring over CaH_2 at 100 °C and then distilled under reduced pressure.

The solvents (xylene isomer mixture (Scharlau, p.a.) and dimethyl sulfoxide (DMSO) (Scharlau, p.a.)) were used as provided or dried over and distilled from CaH_2.

Octyl bromide was synthesized from 1-octanol according to the literature.[18]

Poly(vinyl alcohol) (PVA) (BDH) was used as provided, $M_n = 15000$, $M_w/M_n = 1.37$.

All alkoxylated silica samples were stored over P_4O_{10} under nitrogen, rather than in vacuum, to minimize the deposition of phosphoric acids on the silica.

NMR Spectroscopy. All spectra were recorded on a Varian Inova 200 spectrometer at room temperature. The operation frequencies were 50.2935 MHz for ^{13}C and 39.7274 MHz for ^{29}Si. Samples were placed in a 7 mm ZrO_2 rotor and spun at 4.9 ± 0.1 kHz. The ^{13}C MAS NMR single-pulse excitation spectra were obtained using a ^{13}C 90° pulse length of 5 μs and high-power proton decoupling during the acquisition time of 30 ms. The recycle time was set to 0.5 s (4 s for samples with methanol), and typically 8000 scans were accumulated. Spectra were referenced externally to the methyl resonance of hexamethylbenzene, set to 17.4 ppm. A 1 Hz line-broadening was employed.

For ^{29}Si CPMAS experiments a ^1H 90° pulse of 6 μs was employed. The Hartmann−Hahn match was set up with poly(dimethylsilane), which was also used as an external reference for ^{29}Si, set to −34.5 ppm. The spectra were obtained using a contact time of 2.5 ms and a recycle time of 4 s under high-power proton decoupling during the acquisition time of 30 ms. Typically, 2048 scans were accumulated, and a 30 Hz exponential line-broadening was applied.

Synthesis of Octylated Poly(vinyl alcohol) (OctPVA). A 2.3 g (0.1 mol) sample of sodium was dissolved in 50 mL of absolute ethanol and filtered into 50 mL of DMSO. Excess ethanol was evaporated from this solution under reduced pressure. A 4.4 g (0.1 mol) sample of PVA was dissolved in 50 mL of hot DMSO. The PVA solution was added dropwise to the base with stirring under nitrogen. After the base addition was completed, the reaction mixture was stirred for 1 h. A 17.3 mL (0.1 mol) sample of octyl bromide was added dropwise, and the solution was then stirred overnight at room temperature. The reaction mixture was poured into hot aqueous sodium chloride, which afforded a very tacky precipitate. It was collected and dissolved in boiling ethanol and reprecipitated with aqueous sodium chloride. This was collected, washed with water, and dried. Yield: 3.55 g, 33% (based on the actual stoichiometry). The OH:octyl ratio was determined to be 4:3 from the ^1H NMR of a solution of the product in $CDCl_3$.

Synthesis of Alkoxylated Samples. *(1) General Reflux Method*. To a suspension of 3 g of silica in 50 mL of xylene was added 3 mL of the respective alcohol. A continuous solid−liquid extractor containing about 0.5 g of CaH_2 and a condenser with a $CaCl_2$ drying tube was mounted onto the reaction flask, and the mixture was refluxed, carefully regulating the heating rate to obtain a continuous and stable flow of xylene through the extractor. After the mixture was refluxed for 18 h, the sample was filtered and washed with ethyl acetate several times. Samples prepared using an alcohol solid at room temperature were placed in a Soxhlet extractor and extracted with xylene refluxing over CaH_2 for at least 3 days. Samples made using methanol were filtered and washed with dry ethyl acetate under dry nitrogen. Finally, samples were dried at 0.1 Torr, first at room temperature for several hours and then at 130 °C for >5 h.

(1a) Catalyzed Reactions. The catalyst (heptylamine (0.5 mL), toluenesulfonic acid (100 mg), or methanesulfonic acid (50 mg)) was added to the mixture and refluxed as in the general reflux method above.

(1b) Substitution of Methoxylated Silica. In the method above, methoxylated silica was used instead of unreacted silica. The product was washed and filtered under nitrogen as above.

When the polymeric alcohol was used, 336 mg of OctPVA was dissolved in 20 mL of chloroform and 3 g of silica added. The chloroform was evaporated, and the resulting silica with physisorbed polymeric alcohol was suspended in 50 mL of xylene and refluxed and isolated as above.

(2) Steel Bomb Method. A 2 g sample of dried silica (130 °C, 0.1 Torr, >18 h) was placed in a 25 mL stainless steel bomb and mixed with 8 g of dried alcohol. The container was flushed with nitrogen, the lid was fixed and then the container was maintained at 160 °C for 72 h. The product was isolated as above.

Surface Density Determination. The carbon content of the alkoxylated silica was determined by elemental analysis (Otago University). The surface density, ρ, of alkoxy groups was then calculated using the number of carbons, n_C, of the alcohol and the BET surface area, A, of the unmodified silica:

$$\rho = (\%\ \mathrm{C})/(n_C \times 12.01 \times A)$$

Hydrolysis. The alkoxylated silica was dropped into boiling distilled water and refluxed for variable times. The reaction mixture was then filtered rapidly and washed with some additional distilled water, and the solids were dried at 0.1 Torr, first for 2 h at room temperature and then at 130 °C. The remaining alkoxy group density was then determined as above.

Results and Discussion

Synthesis and NMR Spectroscopy. The esterification reaction between silanols on the silica surface and alcohols is an equilibrium reaction. The first step is physisorption of the alcohol to the silica surface by means of hydrogen bonding, followed by a condensation reaction:

$$\equiv\mathrm{Si{-}OH} + \mathrm{ROH(l)} \rightleftharpoons \equiv\mathrm{Si{-}OH{\cdots}H{-}OR} \rightleftharpoons \equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \quad (1)$$

To push the reaction toward completion, the water produced was removed azeotropically by the refluxing xylene. The condensed azeotrope was then allowed to percolate through CaH_2 to remove this water before re-entering the reaction vessel, permitting a continuous system with a lower water concentration (down to 0.0005%[19]) than that which is attainable through the standard use of a Dean−Stark trap (0.038%[20]).

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Table 1. Alkoxylated Silicas Prepared and Summary of the Results

sample name	alcohol	preparation method	RO surface density (μmol/m^2)	time to sink in boiling water
A	1-octanol	reflux	2.6	20 min
B	1-octanol	autoclave	4.7	3 h
C	1-octadecanol	autoclave	3.1	
D	1-octadecanol	reflux	1.0	
E	methanol + 1-octanol	reflux	(MeOH) 11, (1-octanol) 2.0	1 min
F	OctPVA	reflux	3.0	4 h
G	2-ethyl-1-hexanol	autoclave	3.5	4 h

The progress of the surface-alkoxylating reaction between 1-octanol and precipitated silica was followed by thermogravimetric analysis (TGA) and carbon microanalysis. TGA showed that it was necessary to wash the samples repeatedly and heat them to 130 °C in vacuo to remove traces of solvent and physisorbed alcohol. The TGA trace of such a sample heated in air shows a weight loss commencing at about 230 °C and continuing to about 800 °C. This weight loss, however, gave consistently higher values of the surface density than the carbon microanalyses. A systematic investigation with various alcohols showed a 1.9% weight loss in addition to that corresponding to the burnoff of the alcohol, irrespective of the alcohol employed. This is attributed to water held within the silica structure, or created through the formation of siloxane bridges upon heating to higher temperatures.[1] Therefore, carbon analyses were employed for the determination of the RO surface density.

Refluxing the reagents in xylene in the absence of CaH_2 leads to lower RO surface densities, depending on the water content of the silica and reagents. This shows that the use of CaH_2 moves the equilibrium toward a silica surface with a higher degree of esterification. Predrying the silica had no influence on the resulting surface density when CaH_2 was used. However, predrying was very important for obtaining high surface densities in the autoclave reaction, which does not provide any way of removing the water formed. The results for the surface densities of the investigated alcohols are summarized in Table 1. The higher surface densities attained in the autoclave reaction can be attributed to the higher reaction temperature (160 °C vs 135 °C for refluxing xylene) as the esterification reaction is endothermic.[4]

It was found that the esterification reaction can be catalyzed by both amines and acids. Use of an amine led to the same amount of chemisorbed alcohol as without catalyst, but in a much shorter time (the coverage of 1-octoxy groups employing a heptylamine catalyst and 2 h of reflux is the same as that without catalyst after 18 h of reflux). The use of amines as catalysts was not pursued any further, as it was found that traces of catalyst remaining in the product had a negative effect on the hydrolytic stability of the material (vide infra).

Toluenesulfonic and methanesulfonic acids both accelerated the reaction between precipitated silica and alcohol and led to higher alkoxy group coverage than without acid. Weaker organic acids gave intermediate results. Thus, the type of acid, its concentration, and the reaction time had an influence on the final alkoxy group coverage. However, the acid adsorbed quite strongly to the products, and extensive washing was necessary to remove it. Hence, alkoxy group coverages could not be determined accurately through elemental analysis, precluding a comparison of relative rates of reaction. Therefore, in most cases the reaction was carried out in the absence of catalysts.

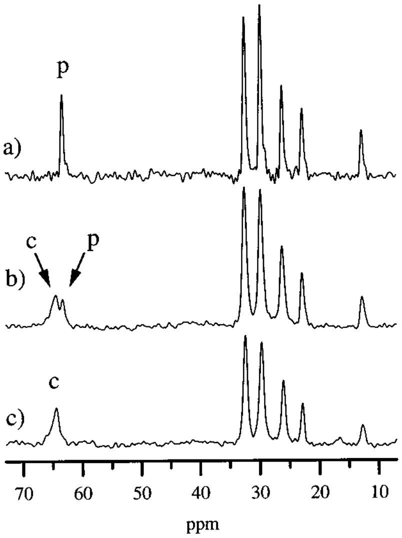

Figure 1. ^{13}C MAS NMR spectra of 1-octanol and precipitated silica. C1 resonances of physisorbed and chemisorbed alcohol marked with “p” and “c”, respectively. (a) Physisorbed alcohol. (b) Raw surface-alkoxylation product. (c) Surface-alkoxylated silica after removal of physisorbed excess alcohol through heating in vacuo.

The esterification reaction was followed through ^{13}C MAS NMR as depicted in Figure 1. The C1 resonance of 1-octanol at 63−65 ppm is of main interest. The change from physisorbed to chemisorbed alcohol, as indicated in eq 1, increased the ^{13}C chemical shift of the C1 carbon by about 1−1.5 ppm. This difference compares very well to the difference in chemical shifts between free alcohols and their respective tetraalkoxysilanes,[21] showing that the alcohol indeed has been chemically bound to the surface. The physisorbed alcohol could be removed by heating the sample in vacuo.

The ^{13}C MAS NMR spectra of the prepared alkoxylated silica reveal interesting details of their structure. Studies of the ^{13}C CPMAS NMR spectra of several different types of self-assembled C_{18} compounds on a variety of substrates have showed that the peak at 33 ppm corresponds to the all-trans conformation of the alkyl chain, whereas conformationally disordered alkyl chains in trans−gauche equilibrium resonate at 30 ppm.[22] Two samples of surface-esterified precipitated silica were prepared with 1-octadecanol: **C** using the autoclave method and thus with a high surface RO density, 3.1 μmol/m^2, and **D** using the reflux method and therefore with a lower RO density, 1.0 μmol/m^2. The ^{13}C MAS NMR of **C** (Figure 2) clearly shows separated peaks at 33 and 30 ppm corresponding to both types of carbon chain conformations. Thus, a minor fraction of the alkyl groups on the surface are in a well-ordered

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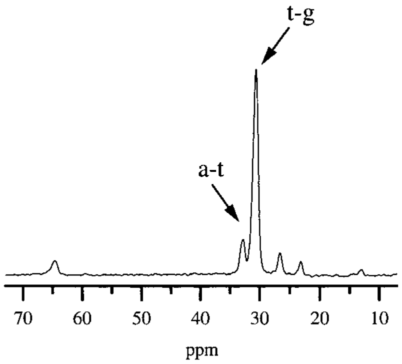

Figure 2. ^{13}C MAS NMR spectrum of 1-octadecanol chemisorbed on precipitated silica (**C**). Resonance at 30 ppm corresponding to trans−gauche conformations marked with "t-g" and resonance at 33 ppm corresponding to all-trans conformations marked with "a-t".

all-trans conformation, whereas the major fraction is in a more disordered trans−gauche equilibrium conformation. The spectrum of sample **C** is identical to the spectrum of **D** (not shown). This indicates that both samples have the same ratio of all-trans segments to trans−gauche segments despite their different surface coverages. This is contrary to the intuitive notion of less disorder on denser surfaces. As the difference in chemical shifts between all-trans and trans−gauche conformations has been established for several different compounds and supports ($C_{18}H_{37}NH_2$ on montmorillonite,[23] $C_{18}H_{37}SiCl_3$ on silica,[24] $C_{18}H_{37}PO_3$ on zirconated silica[24]), the effect observed here is not likely to be due to different adsorption sites on the silica surface.

The presence of a considerable fraction of alkyl chains in trans−gauche equilibrium suggests a mobile and dynamic structure of the alkyl group layer. This correlates well with the fact that we were unable to achieve a satisfying cross-polarization from ^1H to ^{13}C in initial NMR experiments. The cross-polarization is only effective in sufficiently slow moving systems, i.e., where the proton relaxation time in the rotating frame, $T_{1\rho}(^1H)$, is sufficiently long. Thus, the spectra shown were acquired through single-pulse excitation experiments.

A methoxylated precipitated silica was prepared by using methanol in the reflux method. By refluxing this material with an excess of 1-octanol under dry conditions, it was possible to exchange methoxy groups with octoxy groups, sample **E**, in a reaction that is also catalyzed by toluenesulfonic acid. Octyl groups are estimated to have replaced 2.0 μmol/m^2 of the initial 11 μmol/m^2 methyl groups. The presence of both methoxy and octoxy groups in the ^{13}C MAS NMR spectrum (see the Supporting Information) of the product is evident. The width and asymmetry of the methoxy peak (at 50.7 ppm) are considerably larger than those for the octoxy group resonance. This suggests that a broad range of bonding environments is available to the methoxy group due to its small size.

Partially octylated poly(vinyl alcohol) (octyl:OH = 4:3, OctPVA) was used to investigate the effect of chemisorption of a polymeric alcohol to the silica surface, providing sample **F**. The polymer strongly adsorbed to the silica. However, it was difficult to determine the ratio between chemisorbed and physisorbed alcohol hydroxy groups. In the ^{13}C NMR spectrum the chemical shifts of the polymer backbone carbon atoms attached to both types of hydroxyl groups appeared as a broad peak at ~65 ppm (Figure 3). The ^{29}Si CPMAS NMR was also ineffective due to two competing effects in the cross-polarization of these materials.[25] Thus, analysis of the hydrolytic stability of **F** was based on circumstantial evidence (vide infra).

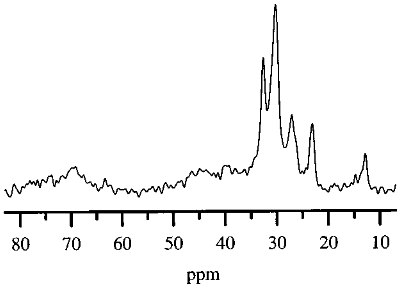

Figure 3. ^{13}C MAS NMR spectrum of OctPVA chemisorbed to precipitated silica (**E**).

Hydrolysis. Fresh alkoxylated silica is hydrophobic, as demonstrated through its phase distribution behavior in benzene/water.[26] The hydrophobicity of the alkoxylated silica can be qualitatively demonstrated as it floats on the surface of water. This is due to the high contact angle of water on the organic surface that prevents water from entering the voids of the silica clusters. Thus, the alkoxylated silica maintains an apparent density lower than 1 and floats. Hydrolysis exposes silanol groups on the surface, which lowers the water contact angle enough for the silica to eventually sink into the water.

To study the hydrolysis of the alkoxylated silica samples, they were simply put into refluxing water for variable times, and the carbon content after the hydrolysis and drying was determined. The results are shown in Figure 4 and summarized in Table 1.

The hydrolytic behavior is strongly dependent on the initial RO surface density. Sample **A**, which has an intermediate RO density, hydrolyzed rapidly upon immersion in boiling water. **A** sinks after 20 min, at a surface density of about 1.2 μmol/m^2. Surprisingly, even after 5 h in boiling water some alcohol remained chemisorbed, which was confirmed by NMR. A sample with a higher initial 1-octoxy surface density (4.7 μmol/m^2) prepared under autoclave conditions, **B**, displays a

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[25] The experimental ^{29}Si CPMAS NMR spectra of OctPVA chemisorbed and physisorbed to precipitated silica (see the Supporting Information) can be deconvoluted into three subspectra corresponding to three different types of silicon atoms: Q^2 (=Si(OH)$_2$), Q^3 (≡SiOH), and Q^4 (Si atoms with no hydroxyl groups directly bonded). The presence of the polymeric alcohol on the silica surface has a 2-fold effect: First, the ≡SiO−H distance is elongated through hydrogen bonding to the alcohol oxygen,[29] or the proton is completely removed in the limit of a chemical bond through esterification. This leads to a decrease in the intensities of the Q^2 and Q^3 peaks. Second, it has been shown that magnetization can be transferred from protons in the polymer backbone of poly(vinyl alcohol) to silicon atoms on the silica surface.[30] This and the presence of an additional hydroxyl proton from the alcohol lead to an increase in the intensity of all Q^n peaks. In the system under investigation, it is not possible to separate these two effects. Overall, this results in very small differences between the spectra of physisorbed and chemisorbed OctPVA, analogous to the behavior of 1-octanol.

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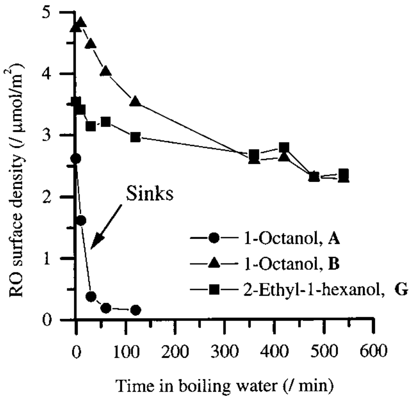

Figure 4. Comparison of the hydrolysis of different alkoxylated silicas in boiling water. The point at which **A** sinks is marked by arrow.

different behavior. It slowly loses some octanol in the course of several hours in boiling water but stays afloat and does not enter a phase of rapid loss of 1-octanol as **A** does.

To study the influence of branching on hydrolysis, a sample was prepared using 2-ethyl-1-hexanol. However, branched alcohols do not attain as high maximal alkoxy group surface densities as linear alcohols for steric reasons. This can be overcome by employing more vigorous reaction conditions. Thus, a sample of precipitated silica reacted with 2-ethyl-1-hexanol under autoclave conditions, **G**, has an initial $C_8H_{17}O$ density similar to that of **A.** The effect of the branching can be followed in Figure 4. **G** loses its bonded alcohol slowest of all alcohols investigated, although it starts with a lower surface density than the straight-chain **A**. **G** stays afloat during the reaction times investigated, in sharp contrast to **A**. Thus, the branching of the alcohol produces a surface-alkoxylated silica with a considerably higher hydrolytic stability than a straight-chain alcohol with the same initial density. Samples prepared with various branched alcohols using the reflux method showed very poor hydrolytic stability and sank in boiling water within 2 min. This indicates that at lower surface coverage the low density is more important than the actual structure in determining the hydrolytic stability. At higher surface densities the structure of the alcohol plays a role in determining the hydrolytic stability of the alkoxylated silica. The hydrolytic stability of **E** is not any different from that of **A**, indicating that the capping of unreacted silanols has no positive effect on the hydrolytic stability.

All samples prepared with heptylamine as a catalyst hydrolyzed very quickly (<10 min in boiling water) irrespective of the alcohol structure and surface density. It was found that **B** could be made to sink in less than 5 min by adding submilligram amounts of heptylamine to the boiling water. This demonstrates that heptylamine has a strong catalytic activity in the hydrolysis, paralleling the well-known catalytic effects of amines in the hydrolysis of tetraethoxysilane.[27] The rapid hydrolysis of all samples prepared with an amine as catalyst was attributed to traces of amine that had not been removed by the washing process. Thus, applications of alkoxylated silica where hydrolytic stability is important are confined to amine-free environments.

The study of the hydrolysis of the polymer-based **F** is more complicated than that of monoalcohols, where the hydrolyzed product can be washed off and removed in a vacuum. Because such a removal of residual physisorbed alcohol is not easily achieved for the polymeric OctPVA, the hydrolysis of silica reacted with it cannot be followed by means of the carbon content. Unfortunately, as described above, neither the ^{13}C nor ^{29}Si NMR data allow even a qualitative following of the hydrolysis reaction through a distinction between physi- and chemisorbed polymer. Thus, the only simple means of following the hydrolysis is to observe when the silica sinks from the water surface. For **F** this occurs after 4 h, a 12-fold increase in hydrolytic stability compared to that of **A**, which has the same density of octyl groups on the surface, but lacks the polymer backbone. Thus, the polymer backbone provides a highly increased hydrolytic stability.

The published body of knowledge on the mechanism of the hydrolysis of surface-esterified silica is meager. Ahmed et al. describe studies of the hydrolysis at elevated temperatures (190−250 °C) and conclude that the rate-determining step of the hydrolysis is the reaction of unmodified free silanol groups with neighboring esterified silanols to produce siloxane bridges.[17] However, Utsugi et al. studied the hydrolysis of these materials in boiling water and assumed that the hydrolysis proceeds via nucleophilic attack of water on the silicon.[16] As a comparison, the hydrolytic stability of silane-modified silicas has been well documented in the context of their suitability as stationary phases for chromatography.[28] For these materials, nucleophilic attack by water on the silica silicon has been established as the mechanism of hydrolysis. Assuming similar circumstances for the lower temperatures employed in this study, i.e., favoring the model of Utsugi et al.,[16] the data obtained can be rationalized. As with silanes and $Si(OR)_4$ esters, hydrolysis proceeds slower with branched alkyl groups and a dense layer, due to the steric shielding of the Si−OR bond. The catalytic effect of the amine is identical to that observed in the hydrolysis of $Si(OR)_4$ esters.[27] This hypothesis of nucleophilic attack by water on the surface-esterified alcohol is further corroborated by the hydrolytic stability of the chemisorbed polymeric alcohol. As the polymer is insoluble in water it remains physisorbed to the surface, which provides a steric barrier protecting the remaining chemical bonds to the surface.

Conclusions

We have demonstrated a novel synthetic method for use with polymeric and high-boiling alcohols that gives a convenient route to surface-alkoxylated silica. The hydrolytic stability increases with increased surface alkoxy density and also with increased branching of the alcohol at a given surface density. A strong improve-

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ment in the hydrolytic stability at constant surface density can also be achieved by using a polymeric alcohol containing hydrophobic alkyl groups. The rate of surface alkoxylation can be increased by using an amine catalyst. However, remaining traces of this amine catalyst also severely reduce the hydrolytic stability of the surface-alkoxylated silica.

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Supporting Information Available: ^{13}C MAS NMR spectrum of **E** and ^{29}Si CPMAS NMR spectra of (a) precipitated silica, (b) OctPVA physisorbed to precipitated silica, and (c) **F** with deconvolutions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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