

# NOTES

## Note on the Silylation of Inorganic Oxide Supports

### INTRODUCTION

Organosilanes are widely used to alter the surface characteristics of inorganic oxides (2, 3, 6, 11, 12, 21). For example, organosilane-bonded silica gels are available for use as bonded-phase chromatographic support resins (3, 19, 20). In composite systems, organosilanes serve as coupling agents to promote adhesion between filler and polymer matrix (1, 13, 18). Polymers may be chemically bonded to solid substrates by way of graft polymerization in which reactive surface sites are generated by silylation of the surface with an appropriate silane coupling agent (4, 11). In particular, silane-modified substrates may be ideal for the study of fundamental phenomena such as the dependence of surface chemistry on colloidal interaction (11, 12) and polymer adsorption (6, 16). The latter studies utilized organosilanes with the general formula  $R_nSiX_{4-n}$ , where X is a hydrolyzable group (i.e., halogen, amine, alkoxy, acyloxy) and R represents a nonhydrolyzable organic radical. The desired surface characteristics of the silylated substrate are determined by the choice of the functionality of the R groups. The method of silylation, however, is generally contingent upon the choice of X, the hydrolyzable group. Although several experimental procedures have been utilized in the silylation of alkoxy-silanes, a quantitative comparison of the silane surface coverage for the different silylation techniques is lacking.

The purpose of this note is to report on three different silylation techniques for vinyltriethoxysilane which have been used in our recent studies on polymer adsorption (16) and graft polymerization (4) onto silica substrates. The overall silylation reaction mechanisms are discussed and the bonded silane yields are compared. Finally, results on the stability of the silylated substrates in water are discussed.

### EXPERIMENTAL

Silylation of porous and nonporous silica particles (see Table I), with a vinyltriethoxysilane obtained from Petrarch Systems (Bristol, PA), was carried out by way of the aqueous and anhydrous techniques described below. The sources of the silica particles are as follows: Nonporous I (Novacite L207-A, Malvern Minerals Co., Hot Springs, AR), Nonporous II (Pellicular Silica, Whatman Inc., Clifton, NJ), Porous I (LPS-1, Whatman Inc.), Porous II (Nucleosil 1000-10, Rainin Co., Woburn, MA). Hydrochloric acid, ethanol, acetic acid, potassium hydroxide, and xylene were of analytical grade. The BET surface areas and pore size distributions of the supports were determined by nitrogen adsorption using the Quantachrome Autosorb-1 (Syosset, NY). Thermogravimetric analysis (Perkin-Elmer TGS-2, Norwalk, CT) was used to determine the amount of bonded silane. Complete combustion of the bonded silane was achieved in an air atmosphere and a maximum temperature of 700°C.

### Pretreatment

Prior to silylation the silica particles were washed thoroughly with dilute (1.0 M) hydrochloric acid to remove contaminants as well as trace amounts of iron (7). The substrate was then thoroughly washed with deionized water. In addition to cleaning of the substrate, prolonged immersion of the silica particles in aqueous solution leads to hydrolysis of surface siloxane groups to form silanol groups (9). Surface silanol groups provide the necessary reactive sites for silane bonding.

### Aqueous Silylation

The one-step aqueous silylation procedure that was used in this study closely follows the method recommended by the manufacturer (17). In a typical one-step aqueous silylation reaction a 2% solution of vinyltriethoxysilane in 95:5 ethanol:water, adjusted to pH 5.0 with glacial acetic acid, was allowed to react for 30 min. Under these conditions the alkoxy-silanes are hydrolyzed to produce hydroxysilanes which undergo condensation polymerization to generate polysilanes. Subsequently, a predetermined amount of clean, dry silica was added to the solution and the slurry was stirred for 15 min. Upon the addition of a substrate with surface hydroxyl groups, hydrogen bonds form between the polysilanes and the support silanol groups. The silica particles with the chemisorbed silane were then filtered and washed thoroughly with ethanol. The silane layer was cured by heating the silica particles under vacuum at a temperature of 50°C. Curing of the substrate results in covalent bonding of the silane to the surface by way of a condensation reaction (2).

A related two-step aqueous phase silylation technique that was used in this comparative study is based on the strong pH dependence of the rates of the hydrolysis and condensation reactions (15, 18). In order to promote the hydrolysis reaction and the ensuing formation of hydrogen bonds, a 2% aqueous solution of vinyltriethoxysilane, adjusted to pH 2.5 with glacial acetic acid, was mixed for 30 min. A predetermined amount of clean, dry silica was added to the solution and was allowed to react with the silane for 2 h. The reaction solution was then titrated with potassium hydroxide to pH 10.5 in order to promote the condensation of the silane hydroxyl groups with the substrate silanol groups. The slurry was mixed for 2 h at these conditions. The silica particles were then filtered, washed thoroughly with deionized water, and dried under vacuum at 50°C.

### Anhydrous Silylation

Silylation under anhydrous conditions (i.e., in an organic solvent) avoids the formation of polysilanes which can form in the aqueous silylation process. It is important to note that proper drying of the substrate at elevated temperatures under vacuum is necessary to remove adsorbed

TABLE I  
Substrate Characteristics

Silica type	Average particle diameter ( $\mu\text{m}$ )	BET surface area ( $\text{m}^2/\text{g}$ )	Average pore diameter ( $\text{\AA}$ )
Nonporous I	40	12 <sup>a</sup>	—
Nonporous II	5	2	—
Porous I	15	250	150
Porous II	10	50	1000

<sup>a</sup> Nonporous silica core with porous silica outer layer.

water from the substrate surface, thus ensuring the desired anhydrous reaction condition. However, extreme caution must be taken to ensure that the drying step does not lead to the condensation of surface silanol groups to form siloxane bonds. Although there is no distinct cutoff where removal of adsorbed water ends and silanol condensation begins, drying temperatures between 100 and 200°C are commonly employed (9). In this study the silica particles were dried at 150°C under vacuum overnight to remove adsorbed water.

The anhydrous silylation reaction was performed with a predetermined amount of clean, dry silica in a reflux condenser, for 5 h, using a 10% solution of vinyltriethoxysilane in xylene. The condenser was kept at a temperature above the boiling point of the displaced alcohol (in this case ethanol) but below the boiling point of the silane solution. The particles were then washed several times with xylene and allowed to cure overnight at 50°C under vacuum.

The stability of the surface-bonded silane was ascertained by Soxhlet extraction of the modified supports in water

for a specified period of time, and the subsequent thermogravimetric analysis of the silylated silica particles.

## RESULTS AND DISCUSSION

The kinetics of the anhydrous surface silylation reaction with vinyltriethoxysilane onto both porous and nonporous substrates are shown in Fig. 1. The amount of bonded silane increases rapidly at the start of the reaction and eventually reaches a plateau. These results are qualitatively similar to those obtained by Engelhardt and Mathes (8) for the anhydrous silylation of *N*-(3-triethoxysilylpropyl)acetamide onto silica in benzene. The plateau value of the silane surface coverage for the anhydrous silylation reaction onto the nonporous silica substrate, on a surface area basis, is more than twice the value obtained for the porous silica substrate. The difference in the silane surface coverage for the two supports may be an indication of the dissimilarity in the number of surface hydroxyl groups which are available for silylation. The available surface hydroxyl groups for a silylation reaction are determined by both the surface hydroxyl concentration and the accessible surface area for silylation. Surface hydroxyl concentrations vary markedly for different types of silica and are strongly influenced by the method of production as well as the silica crystal structure (9). The Nonporous II silica and the Porous I silica are produced by entirely different methods; the first is a naturally occurring quartz silica and the second is produced by a gel precipitation process. Thus, it is plausible that the variation in the chemical structure of the two substrates could lead to significant differences in the surface hydroxyl concentrations. In addition, the size of the pores relative to that of the silane molecule determines the fraction of the substrate

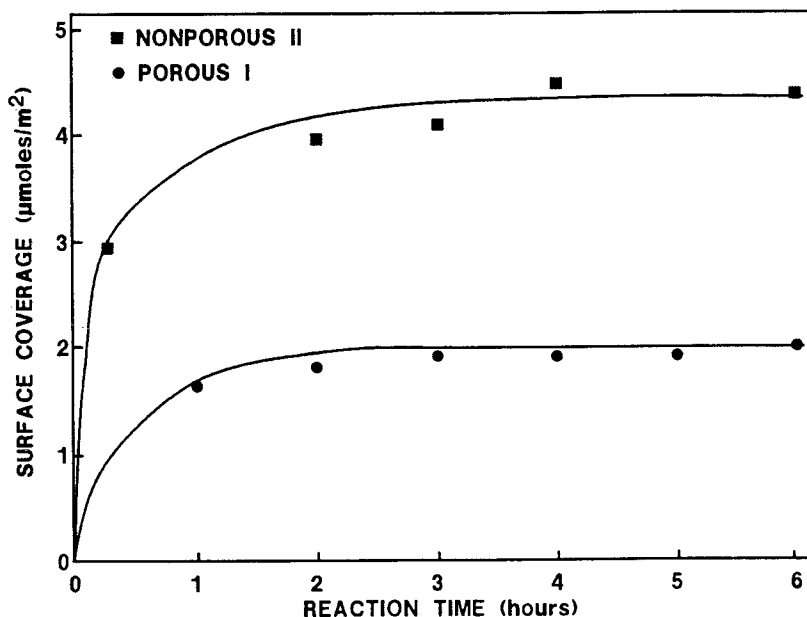


FIG. 1. Anhydrous silylation of vinyltriethoxysilane onto silica.

TABLE II  
Surface Concentration of Vinyltriethoxysilane<sup>a</sup>

Substrate	Silylation method	Surface concentration ( $\mu\text{mole}/\text{m}^2$ )
Nonporous I	Aqueous (one-step)	0.08
	Anhydrous	3.15
Nonporous II	Aqueous (one-step)	1.10
	Aqueous (two-step)	3.50
	Anhydrous	4.30
	Anhydrous	33.00 <sup>b</sup>
Porous I	Aqueous (one-step)	0.50
	Aqueous (two-step)	1.50
	Anhydrous	2.00
Porous II	Anhydrous	2.90

<sup>a</sup> Surface concentrations are reported for the plateau region (see Fig. 1).

<sup>b</sup> Anhydrous silylation with adsorbed surface water (16).

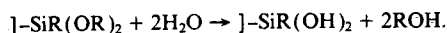
pores, and thus the surface area, which is accessible to the silane molecule. It is also worth noting that such size exclusion effects due to the porous structure of various silica particles have been demonstrated previously for the silylation of n-octadecylsilane (3). For the porous silica substrates used in this study, the silane surface coverage obtained via the anhydrous silylation reaction, given in Table II, was larger for the substrate with the larger average pore diameter (see Table I).

The anhydrous silylation reaction with vinyltriethoxysilane was found to yield a greater coverage of bonded silane than either one of the two aqueous phase silylation techniques (see Table II). For example, the one-step aqueous phase silylation reaction performed in the ethanol: water solvent led to a bonded silane coverage of at most 25% of that obtained by the anhydrous silylation technique onto the same substrate. The two-step aqueous phase silylation technique produced silane surface coverages only as high as 80% of those obtained by the anhydrous silylation method onto the same substrate. One possible explanation for the differences in the amount of bonded silane for the aqueous and anhydrous silylation techniques is the formation of polysilanes during the aqueous silylation reaction. It has been demonstrated by both Raman spectroscopy (10) and NMR spectroscopy (15) that polysilanes are formed in aqueous solutions. Steric hindrance of these large polysilane molecules may limit the surface coverage and leads to nonuniform silylation and low yields. This postulate is consistent with the observations of Cheng and McCown (5), who clearly demonstrated a decrease in the surface coverage due to the increased size of a reactive polysilane molecule for the case of various n-alkylsilanes. The lower silane yield due to the steric hindrance of large polysilane molecules should become even more pronounced when the substrate is porous. For porous substrates, the diffusion of the polysilanes into the pores may become the rate limiting step. In addition, some micropores

may be totally inaccessible to polysilanes. Therefore, in order to obtain a high degree of silane coverage it is essential to limit the formation of polysilanes.

In contrast with the aqueous silylation techniques, silane polymerization is eliminated in the anhydrous silylation reaction. Therefore, it is generally assumed that the silane has formed a monomeric "brush-like" coverage (8). It is important to note that multilayer coverage can be obtained when, due to incomplete drying of the substrate, adsorbed water remains on the substrate surface (16). The adsorbed water may react with the alkoxy groups of the surface-bonded silane to form silanol groups. Silane molecules in solution may then react with the silanol groups of the surface-bonded silane to form a multilayer coverage (14). Parnas *et al.* (16) have shown that a silane surface concentration as large as  $33.00 \mu\text{mole}/\text{m}^2$  may be obtained under these reaction conditions (see Table II).

Since alkoxy silane-modified silica resins can be used in aqueous liquid chromatography applications, it is of interest to comment on the stability of the vinyltriethoxysilane used in this work. The stability of the silane-modified silica supports in aqueous solution was determined by Soxhlet extraction. The weight loss as a function of extraction time for the Nonporous II support silylated by the anhydrous technique is shown in Fig. 2. The total mass of the bonded phase decreases rapidly in the first 4 h of water exposure. The decrease in mass, however, is attributable to the hydrolysis of alkoxy groups. The hydrolysis of the unbound alkoxy groups will occur upon exposure of the silylated surface to an aqueous medium as follows:



By taking into account the hydrolysis of the residual alkoxy groups, it is evident that the silane-bonded layer is stable in aqueous solutions at neutral pH. Stability studies for a wide range of pH (1.0–9.5) have corroborated these results. Finally, since basic solution generally tends to favor the condensation reaction (18), one may readily replace the residual alkoxy groups with hydroxyl groups in a basic solution without harming the bound silane. For example, the substitution of the ethoxyl groups, for bonded triethoxysilanes, by hydroxyl groups is particularly convenient for assuring good dispersion of the silylated silica particles in aqueous systems (4, 16).

## CONCLUSION

The silylation of both porous and nonporous silica supports with vinyltriethoxysilane was studied using aqueous and anhydrous techniques. For the same support material, the anhydrous silylation technique resulted in silane surface concentrations that were much larger than those obtained by the aqueous silylation methods. It is suggested, consistent with previous studies, that the polysilanes formed in the aqueous reaction solution sterically hindered the silylation reaction and led to the reduced surface coverage. It is suggested that the differences in the silane surface concentrations obtained by the anhydrous silylation technique onto the various silica supports were due to the differences in the available surface hydroxyl concentration as well as

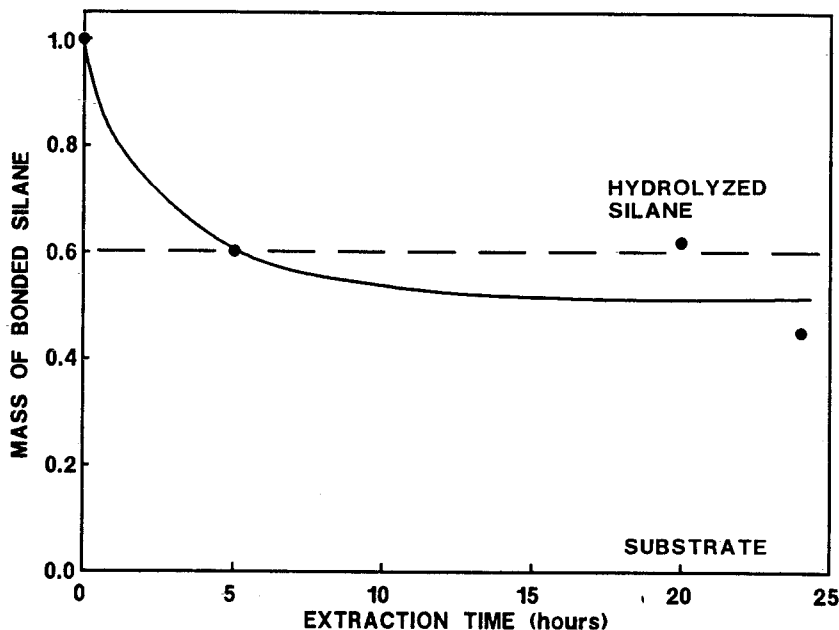


FIG. 2. Water exposure of anhydrous silylated support.

the accessible surface area. More work is needed in this area to elucidate the separate effects of each of these two factors. Finally, the support-bonded silane layer was found to remain intact upon exposure to aqueous solutions of a wide range of pH.

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