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Lewis Acid Mediated Functionalization of Porous Silicon with Substituted Alkenes and Alkynes

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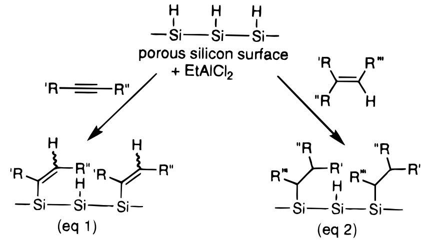
Silicon surface chemistry is of fundamental importance because of the ubiquitous role of silicon in modern technology and yet is only just beginning to be investigated.[1] Virtually all microprocessor chips in electronic products are based upon crystalline silicon wafers.[2] Control of silicon surface chemistry is crucial to allow access to technologically interesting thin films for fabrication of new electronic devices.[3] Canham and co-workers showed in 1990 that silicon wafers could be etched to produce a microns-thick porous layer (termed porous silicon) which exhibits photoluminescence upon exposure to UV light.[4] Potential applications for porous silicon include use as chemical sensors,[5] optoelectronic devices[6] such as electroluminescent displays,[7] photodetectors,[8] and as a matrix for photopumped tunable lasers.[9] As a result, modification and characterization of photoluminescent porous silicon surfaces has become an area of intense interest.[10] In this work we report a mild and general approach for covalent modification of the surface of porous silicon through $EtAlCl_2$ mediated hydrosilylation of readily available alkynes and alkenes which yields surface bound vinyl and alkyl groups, respectively, as outlined in eqs 1 and 2.[11]



This method is tolerant of a wide variety of functional groups as has been demonstrated through the formation of nitrile, hydroxy, and ester terminated surfaces (Figure 1). Porous silicon functionalized with hydrophobic groups using this technique demonstrates remarkable stability to such adverse conditions as boiling aerated water and boiling aqueous KOH (pH 10).

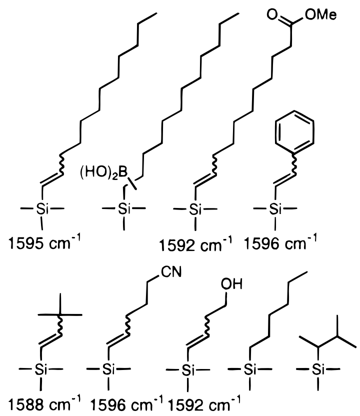


Figure 1. Functional groups covalently bound to the surface of porous silicon through $EtAlCl_2$ mediated hydrosilylation of alkynes and alkenes. The numeric values correspond to the ν (C=C) of the surface-bound vinyl group as measured by transmission FTIR.

Hydrosilylation of olefins and alkynes proceeds under a wide variety of reaction conditions. Commonly used late transition metal catalysts[12] were avoided because of the potential for activation of the weaker Si−Si bonds[13] on the surface (bond strengths: Si−Si = 340 kJ/mol, Si−H = 393 kJ/mol).[14] Lewis acid catalyzed or mediated reactions seemed ideal for functionalization of porous silicon because of the mild reaction conditions involved.[15] $AlCl_3$ is known to be an effective catalyst for hydrosilylation of both alkynes[16] and alkenes.[17] Since $EtAlCl_2$ is soluble in nonpolar solvents whereas $AlCl_3$ is not, it was chosen as the Lewis acid to avoid multiphasic reactions on the surface of porous silicon.[18] Addition of 10 μL of a commercial 1.0 M hexanes solution of $EtAlCl_2$ (10 μmol) to a 0.28 cm^2 area of porous silicon (galvanostatically etched, n type, P-doped, (100) orientation, 0.83 ohm•cm resistivity Si wafer, 75 mA/cm^2 current density with illumination by a 300 W tungsten filament bulb, 1:1 solution of EtOH/49% aqueous HF) followed by 3 μL of 1-dodecyne (14 μmol) under nitrogen resulted in clean incorporation of dodecenyl groups on the surface in 1 h at room temperature as shown by transmission FTIR (Figure 2a). The resulting disubstituted carbon−carbon double bond appears at 1595 cm^{-1}. Neither the stereochemistry nor ratio of possible regioisomers of surface-bound olefins were determined, but molecular hydrosilylation of alkynes catalyzed by $EtAlCl_2$ yields exclusively cis alkenes with perfect regioselectivity when the alkyne is terminal (100% anti-Markovnikov addition), as are all the alkynes examined here.[16] The C=C stretching frequency of the surface bound dodecenyl group correlates well with that reported for the related molecular compound, (Z)-1-triethylsilyl-1-dodecene (1605 cm^{-1}), also produced through hydrosilylation of 1-dodecyne with triethylsilane catalyzed by $EtAlCl_2$.[16] Other pertinent features observed by FTIR include the ν (C−H) stretches of the decyl chain between 2960 and 2850 cm^{-1} and δ (C−H) methylene and methyl bending modes at 1466 and 1387 cm^{-1}. Hydrophobic

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S0002-7863(97)04012-2 CCC: $15.00

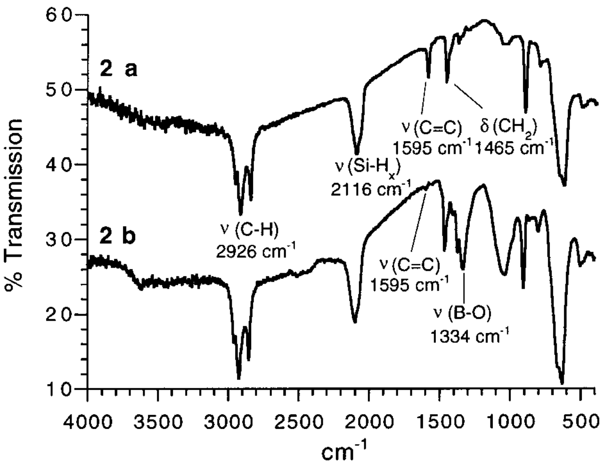
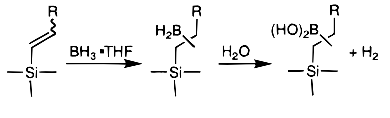


Figure 2. FTIR (transmission mode) of monolayers prepared through (a) hydrosilylation of 1-dodecyne mediated by $EtAlCl_2$ on porous silicon resulting in covalent attachment of a dodecenyl group and (b) hydroboration of the olefin of the dodecenyl group with 0.8 M BH_3•THF.

alkynes incorporated onto the surface in a similar manner include phenylacetylene and the bulky *tert*-butylacetylene. In all cases, the ν (Si−H) centered around 2100 cm^{-1} diminishes in intensity, indicating that Si−H groups are consumed in the hydrosilylation reaction (see Supporting Information section). Preferential disappearance of one type of silicon hydride group over another was not noted, as has been observed in other reactions on porous silicon.[19] The reaction did not proceed in the absence of $EtAlCl_2$.

To clearly demonstrate that the stretch observed at 1595 cm^{-1} is indeed an olefinic stretch, the dodecenyl terminated surface was hydroborated with excess 0.8 M BH_3•THF in THF under nitrogen followed by quenching of the surface in air and rinsing with excess THF.[20]



(eq 3)

As observed by transmission FTIR in Figure 2b, almost quantitative disappearance of the stretch at 1595 cm^{-1} was observed with concomitant appearance of a new stretch at 1334 cm^{-1} which corresponds to the B−O stretching frequency.[21] Cross-linked B−O groups may also be present because of their high local concentration. The stereochemistry of the borane addition has not been determined although it is expected that the boron atom will add preferentially to the least hindered carbon, that being the carbon β to the surface silyl group.[20]

By using an excess of $EtAlCl_2$, alkynes with coordinating functional groups could also be incorporated onto the surface. It was previously noted that if more than 1 molar equiv of Lewis acid was added, alkyne substrates containing silyloxy and benzyloxy groups could be hydrosilylated with triethylsilane. One equiv of the Lewis acid complexes the coordinating group and the remainder mediates the hydrosilylation reaction. In a typical case, 0.2 μL of alkyne (in all cases here, this amounts to less than 3 μmol) were added to the 0.28 cm^2 porous silicon surface previously treated with 10 μL of 1.0 M $EtAlCl_2$ in hexanes (10 μmol) and allowed to react 2 h. Thus, hydrosilylation of 3-butyn-1-ol, 5-cyano-1-pentyne, and methyl 10-undecynoate could be carried out smoothly, resulting in hydroxy, nitrile, and methyl ester terminated surfaces, respectively. If more than 1 equiv of 5-cyano-1-pentyne or methyl 10-undecynoate is added with respect to $EtAlCl_2$, no hydrosilylation occurs because of quantitative coordination of the Lewis acid to either the nitrile or methyl ester. Since $EtAlCl_2$ coordinates to any Lewis basic sites in the unsaturated substrate, it acts as a temporary protecting group, preventing any side reactions. It was noted for 5-cyano-1-pentyne that if trace oxygen was present, extensive oxidation of the porous silicon surface occurred in the absence of $EtAlCl_2$, apparently induced by the nitrile group. In the presence of excess $EtAlCl_2$, however, hydrosilylation proceeded with no accompanying oxidation. Excess $EtAlCl_2$ could be removed easily at the end of the reaction by rinsing with dry THF, EtOH, and CH_2Cl_2.

Alkene hydrosilylation can also be carried out on the surface of porous silicon to yield an alkyl terminated surface. 1-Hexene and the hindered trisubstituted olefin 2-methyl-2-butene both react with a porous silicon surface pretreated with 10 μL of 1.0 M hexanes solution of $EtAlCl_2$ to yield the corresponding alkyl substituted surface. Because olefins are less active than alkynes, a greater volume of substrate must be used (100 μL) and the reaction allowed to proceed 16 h. The regioselectivity of Si−H addition to the alkene was not determined, but for molecular hydrosilylation of trisubstituted olefins, quantitative anti-Markovnikov addition is observed.[17b] Control experiments indicated that hydrosilylation did not proceed in the absence of $EtAlCl_2$.

The hydrophobic alkyl and alkenyl terminated porous silicon surfaces are very stable under highly demanding conditions. For example, the alkyl substituted surfaces formed from hydrosilylation of 1-hexene and 2-methyl-2-butene are both stable to rinsing with a 1:1 solution of EtOH/49% HF (aq) and to boiling 2 h in aerated water (no change in IR spectra). Unmodified porous silicon undergoes substantial oxidation and degradation after 1 h in water at 100 °C.[22] More remarkable, the surface formed from reaction of *tert*-butylacetylene can withstand boiling in aerated basic solutions (pH 10) of aqueous KOH and solutions of 25% EtOH/75% aqueous KOH (pH 10)[23] for 1 h with only minor changes in its FTIR spectrum (see Supporting Information). Unsubstituted porous silicon dissolves rapidly under these conditions. While surface coverage appears by IR to be incomplete for both alkynes and alkenes as evidenced by the remaining silicon-hydride groups left on the porous silicon, the stability of these hydrophobic surfaces suggests that exposed areas of the porous silicon are effectively capped. The remaining unreacted silicon-hydride groups must be sterically inaccessible, even to water and hydroxide ion.

In conclusion, this simple, one-step reaction methodology allows access to porous silicon surfaces terminated with a variety of functional groups. Highly stable porous silicon surfaces have also been formed through incorporation of bulky aliphatic substituents. We are further investigating the scope of this reaction and utilizing the newly incorporated chemical functionalities to carry out further chemistry on the surface.

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Supporting Information Available: FTIR spectra for all functionalized surfaces not shown here and for stability tests of the *tert*-butylethylene terminated surface (12 pages). See any current masthead page for ordering and Web access instructions.

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