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Toward Single-Site Functional Materials—Preparation of Amine-Functionalized Surfaces Exhibiting Site-Isolated Behavior

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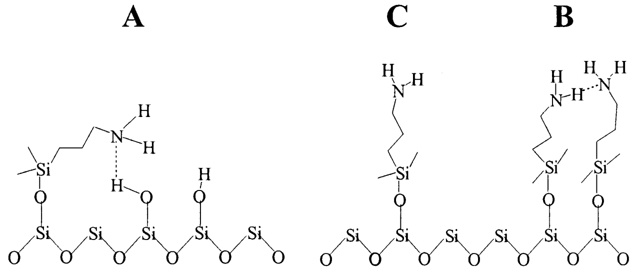
A well-defined amine-functionalized silica surface displaying evidence of isolated amine sites is prepared using a molecular patterning technique. A tritylimine patterning agent is used to spatially position the amine sites a minimum distance from each other, resulting in an organic loading of 0.345 mmol of NH_2/g of solid. The amine-functionalized silica and its precursors were characterized by multiple techniques including thermogravimetric analysis, nitrogen physisorption, FT-Raman spectroscopy, and ^{13}C and ^{29}Si cross-polarization magic-angle spinning (CPMAS) NMR spectroscopy. The reactivity of the amine surfaces are further characterized using probe reactions. All of the amine sites in the patterned material are observed to react uniformly, unlike amine-functionalized silicas prepared using traditional techniques. Furthermore, the patterned aminosilica showed evidence of site isolation, whereas a densely loaded amine-functionalized silica synthesized by traditional methods did not.

Introduction

Amine-functionalized silica has been synthesized for a number of years for use in catalysis,[1] adsorption,[2] and separations.[3] Despite this widespread use, the preparation of *well-defined* aminosilica surfaces is not straightforward due to the myriad ways that the primary amine can interact with its environment. In particular, the weakly basic amine site can interact with the weakly acidic silica surface (Scheme 1A); the amine sites can also hydrogen bond with adjacent amine groups (Scheme 1B) or they can be relatively noninteracting if the amines are isolated (Scheme 1C). Presently, there are two common methods used to prepare amine-functionalized silicas. The first is to contact a silica material with an alkoxyaminosilane solution, thereby grafting the silane onto the silica surface.[4] The second approach involves the co-condensation of an alkoxyaminosilane with tetraethyl orthosilicate (TEOS), a direct synthesis method.[5] These methods generally result in a continuous or semicontinuous loading of amine groups immobilized on the silica surface with a distribution of types of sites present (vide supra). This can be advantageous when the goal is to maximize the number of amines on the surface. However, it can be a major disadvantage in many applications as well. In catalysis, molecular scale structure−property relationships cannot be developed when multisited solids are used. For instance, one may wish to know if a specific reaction catalyzed by amines requires a single amine site or if multiple amines in close proximity are needed. In this case, a solid with a random distribution of amine groups will not be useful, as there will be isolated amines present as well as amines hydrogen-bonded to other amines or the silica surface. In another example, if the amine is used as an anchor for further functionalization of the surface, the immediate environment around each amine site can be critically important. As mentioned above, the amine ligands may be close enough to hydrogen bond, creating multiple types of amines, with potentially different chemical reactivities, present on the surface. Second, when attempting to functionalize the surface-immobilized ligands, the steric hindrance that results from the closeness of the amines to each other can prevent high conversion.[6] An example of this phenomenon is depicted in Scheme 2 and is described in the literature, where incomplete conversion is ob-

Scheme 1



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(1) For example: (a) Müller, C. A.; Schneider; M.; Mallat; T.; Baiker, A. *Appl. Catal., A* **2000**, *201*, 253. (b) Fey, T.; Fischer, H.; Bachmann, S.; Albert, K.; Bolm, C. *J. Org. Chem.* **2001**, *66*, 8154. (c) Wight, A. P.; Davis, M. E. *Chem. Rev.*, in press.

(2) For example: (a) Kramer, J.; Garcia, A. R.; Driessen, W. L.; Reedikj, J. *Chem. Commun.* **2001**, 2420. (b) Evans, J.; Zaki, A. B.; El-Sheikh, M. Y.; El-Safty, S. A. *J. Phys. Chem. B* **2000**, *104*, 10271. (c) Walcarius, A.; Etienne, M.; Bessiere, J. *Chem. Mater.* **2002**, *14*, 2757.

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(4) Kallury, K. M. R.; Macdonald, P. M.; Thompson, M. *Langmuir* **1994**, *10*, 492.

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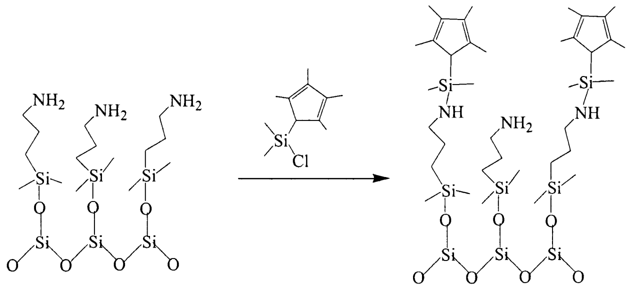
10.1021/cm020952z CCC: $25.00

Scheme 2



served when functionalizing aminopropylsilica with silylcyclopentadienyl groups.[6] Another difficulty in working with amine ligands immobilized on a silica surface is the possible interaction of the amine with surface silanols.[7] As shown in Scheme 1A, since the alkyl chain is flexible, the basic amine group could fold toward the surface and hydrogen-bond with the mildly acidic surface silanols, making it less likely to participate in further surface-functionalization reactions

Clearly, for some applications, a well-defined amine surface with site-isolated amine groups on the surface is desired. Previously, Wulff et al. demonstrated that it is possible to position two amines a specific distance from each other by connecting them via a hydrolyzable linkage and utilizing a grafting technique.[8] Sasaki and co-workers utilized a similar technique to position three amines on a silica surface.[9] Subsequently, Katz and co-workers immobilized up to three amines a specific distance from each other via direct synthesis of imprinted silica.[10] In all of these cases it was possible to position amines a specific distance from each other, but only at low loadings. Wulff et al. reported loadings of 0.09−0.2 mmol of amine/g of solid; Katz and co-workers reported 0.07−0.23 mmol of amine/g of solid. At higher loadings, there is nothing that prevents the amines from becoming closer than the distance prescribed by the imprinting or patterning technique that was utilized (see Scheme 3a). Here, we report a molecular patterning technique that allows for the preparation of well-defined, isolated amines on a silica surface in relatively high loading (see Scheme 3b). This method eliminates the common problems described above that limit amine reactivity such as amine−silanol interactions, amine−amine interactions, and steric constraints.

Experimental Section

General Considerations. The following chemicals were commercially available and used as received: 3,3,3-Triphenylpropionic acid (Acros), 1.0 M $LiAlH_4$ in tetrahydrofuran (THF) (Aldrich), pyridinium dichromate (Acros), 2,6 di-*tert*-butylpyridine (Acros), dichlorodimethylsilane (Acros), TEOS (Aldrich), 3-aminopropyltrimethoxysilane (Aldrich), hexamethyldisilazane (Aldrich), terephthaloyl chloride (Acros), anhydrous toluene (Acros), and *n*-butyllithium in hexanes (Aldrich). Anhydrous ether, anhydrous THF, anhydrous dichloromethane, and anhydrous hexanes were obtained from a packed bed solvent purification system utilizing columns of copper oxide catalyst and alumina (ether, hexanes) or dual alumina columns (tetrahydrofuran, dichloromethane).[11] Tetramethylcyclopentadiene (Aldrich) was distilled over sodium metal prior to use. Anhydrous methanol (Acros) was further dried over 4-Å molecular sieves prior to use. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques under dry, deoxygenated argon or in a drybox under a deoxygenated nitrogen atmosphere.

Synthesis of Tritylimine Patterning Agent ([3-(Trimethoxysilanyl)propyl]-(3,3,3-triphenylpropylidene)amine) (1). 3,3,3-Triphenylpropanal was synthesized from 3,3,3-triphenyl propionic acid under argon using standard Schlenk techniques.[12] Triphenylpropionic acid (4.373 g, 14.46 mmol) was added to a flask with THF. The flask was then cooled in an ice−water bath and 8.97 g of pre-cooled 1.0 M $LiAlH_4$ in THF was added dropwise. After the evolution of hydrogen completed, the mixture was stirred at room temperature for 30 min. The solution was then added to a suspension of pyridinium dichromate (6.00 g, 15.95 mmol) in methylene chloride and allowed to stir for 6 h. The reaction mixture was subsequently diluted with diethyl ether and filtered through a silica column, which was washed with several portions of diethyl ether. The filtrate was collected, and through rotary evaporation, the aldehyde was isolated in 60% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 3.6 (d, 2H), 7.1−7.3 (multi, 15 H), 9.5 (t, 1H).

The aldehyde (1.0 g, 3.5 mmol) was then refluxed with 3-aminopropyltrimethoxysilane (0.501, 2.8 mmol) in dry methanol for 24 h. The methanol was removed in vacuo. The imine product was then recrystallized from methanol (38% yield). NMR data: ^1H NMR (300 MHz, CD_3OD): δ 0.4 (2 H), 1.51 (2 H), 3.14 (2 H), 3.49 (9 H), 3.61 (2 H), 7.22 (15 H), 7.42 (1 H).[13]

Synthesis of SBA-15. SBA-15 was synthesized by literature methods.[14] The as-prepared material was calcined using the following temperature program: (1) increasing the temperature (1.2 °C/min) to 200 °C, (2) heating at 200 °C for 1 h, (3) increasing at 1.2 °C/min to 550 °C, and (4) holding at 550 °C for 6 h. Prior to functionalization, the SBA-15 was dried under vacuum at 150 °C for 3 h and stored in a drybox.

Synthesis of SBA-15 Functionalized with Patterning Agent (2). Patterning agent **1** (0.5 g/1.12 mmol) was added to 2 g of SBA-15 with anhydrous toluene and stirred at room temperature under argon for 24 h. The resulting solid was filtered and washed with toluene in a drybox, dried under vacuum at room temperature overnight, and then stored in a drybox. TGA showed 0.39 mmol/g SiO_2 of patterning agent was immobilized on the SBA-15.

Silanol Capping Reaction (3). The synthesis of **3** was carried out by contacting a large excess of hexamethyldisilazane with **2** in anhydrous toluene at room temperature under argon for 24 h. The resulting solid was filtered and washed with toluene and hexanes in a drybox, dried under vacuum at room temperature overnight, and then stored in a drybox.

Hydrolysis (4). **3** (0.5 g) was added to 50 g of a 2:2:1 solution of H_2O/MeOH/HCl (38 wt %). The mixture was stirred in air at room temperature for 5 h. The solid was collected via filtration, washed with water, methanol, and THF, and then dried under vacuum at room temperature overnight.

Second Silanol Capping (5). **4** was reacted with HMDS using the same procedure as in preparing **3**.

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(13) The imine has limited solubility in common NMR solvents. As a result of this, NMR spectra showed very broad peaks, preventing the determination of multiplicity.

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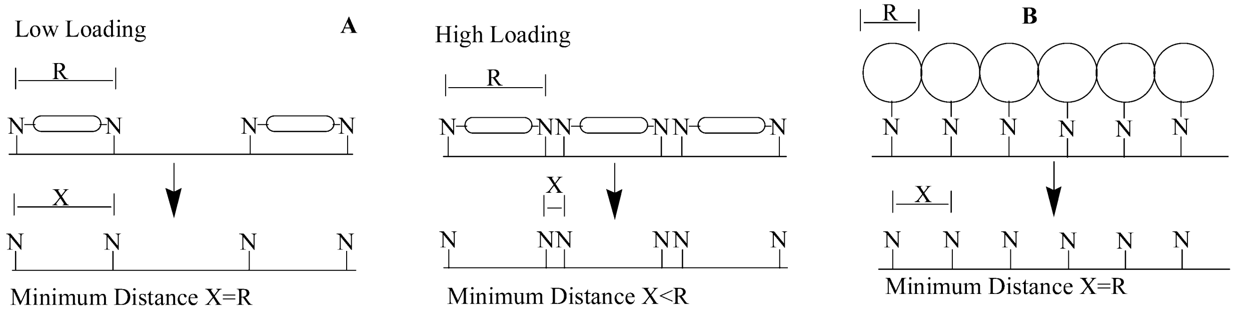
Scheme 3



Synthesis of Densely Loaded APTMS-Functionalized SBA-15 (6)−Control Sample. Excess 3-aminopropyltrimethoxysilane (0.5 g, 2.79 mmol; APTMS) was added to 1 g of SBA-15 in anhydrous toluene. The mixture was allowed to stir for 24 h at room temperature under argon. The resulting solid was filtered, washed with toluene, dried under vacuum at room temperature overnight, and then stored in a drybox. TGA showed 1.15 mmol/g SiO_2 of APTMS was immobilized on the SBA-15.

Synthesis of Chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane. Tetramethylcyclopentadiene (6.02 g, 0.049 mol) was added to a Schlenk flask with anhydrous diethyl ether (150 mL). The mixture was cooled to 0 °C. *n*-Butyllithium (32 mL of 1.6 M solution in hexanes) was slowly added to the Schlenk flask. After addition of the *n*-BuLi, additional ether (200 mL) was added to the flask. The mixture was allowed to stir overnight. The deprotonated cyclopentadiene ($LiCpMe_4$) was collected via filtration and washed with ether and hexanes in a drybox.

Next, excess dichlorodimethylsilane (7.075 g, 0.0548 mol) was added to a flask with anhydrous THF (70 g). The mixture was cooled, and then $LiCpMe_4$ (1.484 g, 0.0116 mol) was slowly added over 75 min in the drybox. The contents were subsequently stirred overnight. The excess, unreacted dichlorodimethylsilane and THF were removed via vacuum. Hexanes were then added to dissolve the product and precipitate lithium chloride, which was removed via filtration in the drybox. The hexanes were then removed in vacuo, allowing for the collection of a pale yellow oil product in 83% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 0.10 (s, 6 H), 1.67 (s, 6 H), 1.88 (s, 6 H), 2.85(s, 1 H).

Reaction of Chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane with Silica Materials. Chlorodimethyl-(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane (excess) was added to a mixture of amine-functionalized silica with hexanes in a drybox. 2,6-Di-*tert*-butylpyridine (excess) was added as a proton sponge. The mixture was allowed to react while stirring for 24 h. The solid was filtered and washed with hexanes and THF in the drybox. The solid was then contacted with another aliquot of chlorodimethyl-(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane and the procedure was repeated.

Synthesis of 7 and 8 from 5 and 6, respectively. In a typical reaction of the amine-functionalized solids **5** and **6** with terephthaloyl chloride, 0.10 g of **5** (0.037 mmol NH_2) was added to a flask with terephthaloyl chloride (2.36 mg, 0.013 mmol) in dichloromethane. The mixture was allowed to stir at room temperature for 24−36 h in a drybox. The resulting solid was removed from the drybox and then filtered and washed with water, methanol, dichloromethane, and hexanes. The solid was then dried under vacuum at room temperature overnight.

Characterization. Cross-polarization magic angle spinning (CP-MAS) NMR spectra were collected on a Bruker DSX 300-MHz instrument. Samples were spun in 7-mm zirconia rotors at 5 kHz. Typical ^{13}C CP-MAS parameters were 10000 scans, a 90° pulse length of 4 μs, and a delay of 4 s between scans. Typical ^{29}Si CP-MAS parameters were 2000 scans, a 90° pulse length of 5 μs, and a delay of 10 s between scans. FT-Raman spectra were obtained on a Bruker FRA-106. At least 256 scans were collected for each spectrum, with a resolution of 2−4 cm^{-1}. Thermogravimetic analysis (TGA) was performed on a Netzsch STA409. Samples were heated under air from 30 to 1000 °C at a rate of 5 °C/min. The organic loading was measured by determining the weight loss from 200 to 650 °C. Nitrogen physisorption measurements were conducted on a Micromeritics ASAP 2010 at 77 K. Samples were pretreated by heating under vacuum at 150 °C for 8 h.

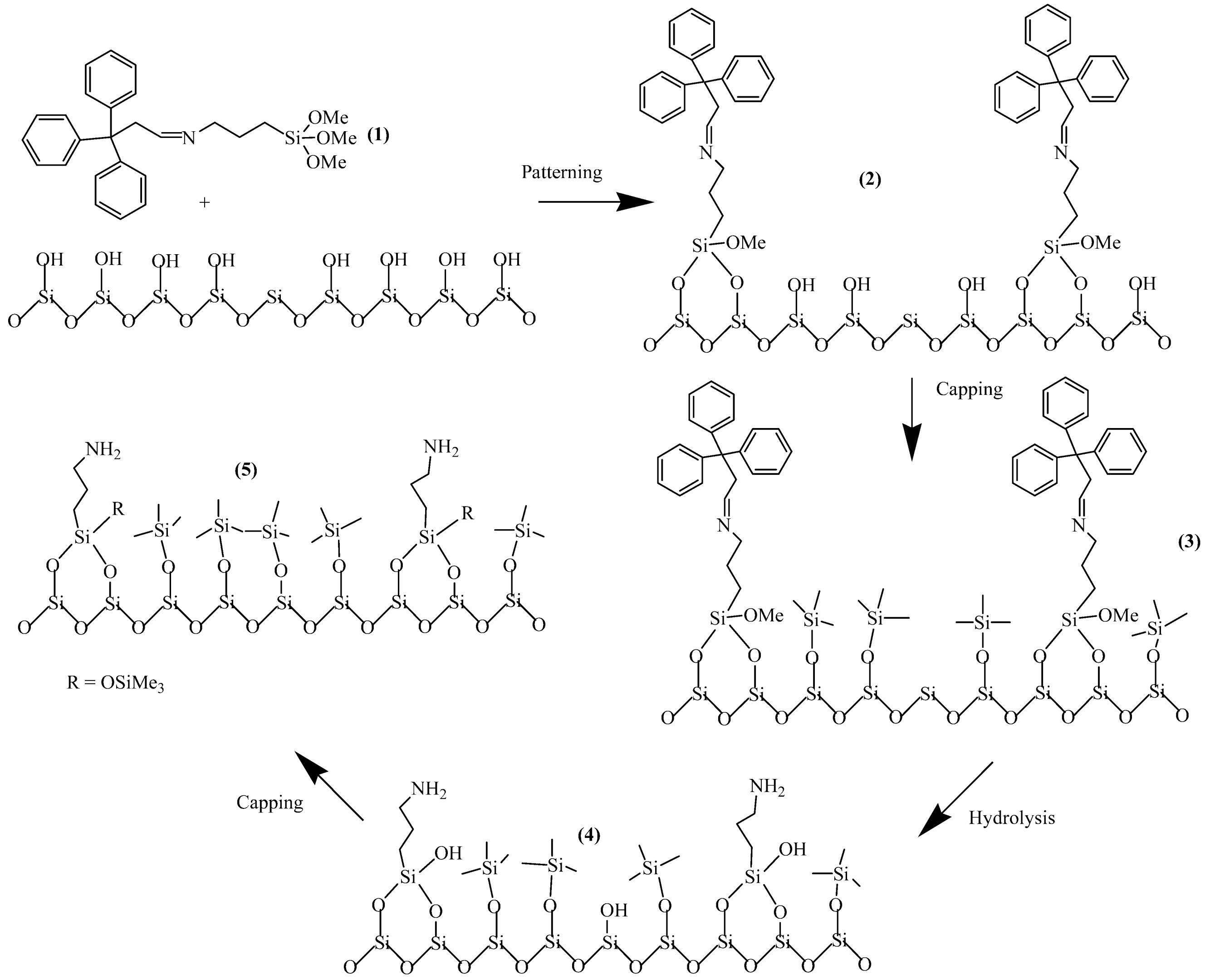
Results and Discussion

To synthesize the well-defined, isolated amine functionalities on silica, a bulky tritylimine ([3-(trimethoxysilanyl)propyl]-(3,3,3-triphenylpropylidene)amine) was employed as a patterning agent, as shown in Scheme 4. A trityl group was chosen as the pattern due to its large size and overall symmetry. The patterning agent was synthesized via condensation of 3,3,3-triphenylpropanal and 3-aminopropyltrimethoxysilane. The trityl group not only limits the overall organic loading on the surface but also can ensure site isolation by spacing the amines a minimum distance apart. The imine patterning agent was contacted with mesoporous silica SBA-15 with an average pore diameter of 50 Å. The imine-functionalized solid was then reacted with hexamethyldisilazane (HMDS) to cap excess surface silanols. This prevents the silanols from participating in later stages of the synthesis and prevents silanol−amine interactions after hydrolysis. After capping, the tritylimine was then hydrolyzed, removing the bulky trityl group. All steps up to the hydrolysis were carried out under rigorously dry conditions to facilitate only functionalization of the silica surface and prevent the formation of silane layers via the direct linkage of silanes to each other. After hydrolysis, the amine-functionalized solid was reacted with another aliquot of HMDS to cap any surface silanols formed as a result of the acid treatment.

The organic loading was quantified by thermogravimetric analysis (TGA). The loading of the patterning agent was determined to be 0.39 mmol/g of solid. After the initial hydrolysis, TGA showed 0.345 mmol of amine/g of solid; 89% of the imine patterning agent is hydrolyzed to the amine. This hydrolysis treatment routinely hydrolyzes 89−93% of the imine. A second hydrolysis treatment can be used to remove additional imine, resulting in 93−95% total hydrolysis.

^{29}Si CP-MAS NMR experiments were used to characterize the silica framework of the materials. Figure 1 shows the spectra of the materials at various stages of the synthesis. The spectrum of calcined, unfunctionalized SBA-15 (Figure 1A) shows three overlapping peaks at −92, −100, and −107 ppm. These peaks correspond

Scheme 4



to the Q^2, Q^3, and Q^4 silicon resonances, respectively.[15] The signals for these resonances can also be seen in the functionalized samples (Figure 1B−D). The alkyl linkages to the surface can be characterized by the Si−C bond resonances at −46, −56, and −67 ppm, which correspond to the reaction of 1, 2, and 3 methoxy groups with the silanols on the surface.[16] As the predominant resonance is at −56 ppm, the initial reaction of the patterning agent with the surface appears to be through mostly two linkages (Figure 1B). Hence, on a single patterning agent molecule, two methoxy groups react with the surface, evolving methanol, and the third methoxy group remains intact on average. Figure 1C shows the spectra of the material after the capping reaction. The ^{29}Si resonance characteristic of the capping agent can be seen at 13.6 ppm. After hydrolysis (Figure 1D), the ^{29}Si spectra show evidence of mostly double and triple surface−silane linkages, with no visible single linkages. The signal at 13.6 ppm remains strong. Also noteworthy is that, during the functionalization of the silica with silanes, the intensity of the Q^2 and Q^3 peaks decreases, and the Q^4 peak increases in accordance with some silanols being consumed during their grafting reactions.

Figure 2A shows the ^{13}C CP-MAS NMR spectrum for the tritylimine patterning agent supported on SBA-15. The characteristic signals of the immobilized patterning agent are noted in Table 1A. Figure 2B shows the spectrum after reaction of the supported imine with HMDS. The methyl carbons on the capping agent are seen at −0.4 ppm. This signal is very large, indicating many free silanols are still present after the patterning agent is reacted with the silica, and therefore only a small fraction of the available silanol groups reacted with the patterning agent, in contrast to when aminopropyltrimethoxysilane is used as the reactant. The ^{13}C spectrum of the hydrolyzed sample is depicted in Figure 2C. Table 1B shows the peak assignments.[17] The major change upon hydrolysis is the appearance of the carbon adjacent to the amine group, which can be seen at 42 ppm. For complete hydrolysis, the peaks associated with the patterning agent (164, 145, and 126 ppm) should no longer be present. Despite the strong peak that corresponds to the formation of an amine, a small peak can still be seen at 126 ppm (corresponding to the

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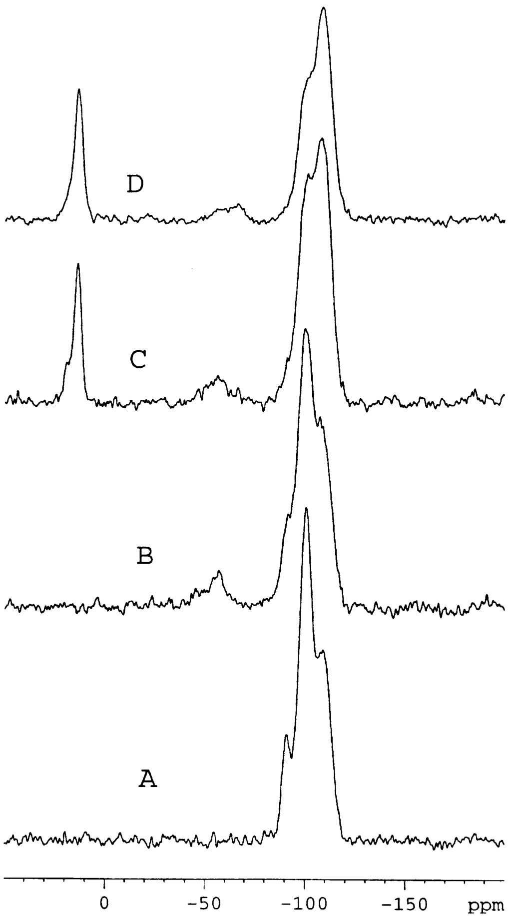

Figure 1. ^{29}Si CP-MAS NMR spectra of (A) calcined SBA-15, (B) SBA-15 functionalized with tritylimine patterning agent (**2**), (C) material after silanol capping reaction (**3**), and (D) after hydrolysis (**4**).

Table 1. ^{13}C NMR Resonances of SBA-15 Functionalized with Tritylimine Patterning Agent (A) and Material after Hydrolysis (B)[a]

A

assignment	resonance (ppm)
$-\mathbf{C}H{=}N-$	165
$-CH_2-\mathbf{C}-(Ph)_3$	145
aromatic carbons	128
$-N{=}CH-\mathbf{C}H_2-$	54
$-Si-O\mathbf{C}H_3$	49
$-CH_2-\mathbf{C}H_2-N{=}$	31
$-Si-CH_2-\mathbf{C}H_2-CH_2$	22
$-Si-\mathbf{C}H_2-$	8

B

assignment	resonance (ppm)
$-Si-O\mathbf{C}H_3$	49
$-CH_2-\mathbf{C}H_2-NH_2$	42
$-Si-CH_2-\mathbf{C}H_2-CH_2$	22
$-Si-\mathbf{C}H_2-$	9

[a] Resonance at 65 ppm is a spinning sideband of the aromatic carbons.

aromatic carbon resonances). This agrees with the TGA results that there is a small fraction of the trityl groups present, likely due to the presence of some nonhydrolyzed patterning agent. Figure 2D illustrates the ^{13}C spectra of densely loaded aminopropylsilica (**6**) control material prepared using traditional grafting techniques ($\geq$1 mmol/g of SiO_2). The resonances characteristic of the amine (7.6, 26.6, 42; 50 ppm is due to methoxy groups) agree with those seen in the hydrolyzed sample and in previous works.[17] It is important to note that because these are CP-MAS spectra, they are not quantitative and the relative abundance of the various carbons is only loosely correlated with the peak area.

Table 2. Nitrogen Physisorption Results at 77 K

sample	BET surface area (m^2/g of SiO_2)	average pore diameter[a] (Å)
SBA-15	736	50
2	649	40
3	436	35
4	697	49

[a] Average pore size determined from desorption isotherm.

Figure 3 shows the FT-Raman spectra for the supported imine (A), hydrolyzed solid (B), and a densely functionalized aminosilica control material (C). The peak at 3062 cm^{-1} corresponds to the ν_{C-H} bands in the aromatic rings, whereas the region from 3000 to 2800 cm^{-1} is characteristic of aliphatic ν_{C-H} bands. The imine can be characterized by the C=N stretching band, which appears at 1595 cm^{-1}. Upon hydrolysis, the peaks associated with the aromatic patterning agent and the imine linkage show a large decrease in intensity. The previously sharp band at 1595 cm^{-1} is reduced to nearly the level of background noise. The peak assigned to the aromatic C−H bands is reduced but is still present. The presence of these peaks confirms the results of the TGA and ^{13}C NMR experiments—some trityl groups remain. Although very little of the trityl groups are still present, the characteristic band ($\nu_{C-H\ \mathrm{aromatic}}$) is a strong Raman signal, which accounts for its high visibility.[18] Amines are typically characterized by the ν_{N-H} band present between 3500 and 3200 cm^{-1}. This peak is not visible in Figure 3B as it is routinely difficult to see the amine band in Raman spectra. This is likely the result of the relatively low amine loading on the solid. The spectrum for the amine-functionalized control material (densely loaded sample) is shown in Figure 3C. The broad peak at 3300 cm^{-1} in this spectrum corresponds to the ν_{N-H} band. Only with the higher loading (~1 mmol of NH_2/g of SiO_2) of the densely functionalized material can the amine peak be seen in the Raman spectra. Despite the absence of a ν_{N-H} band in the FT-Raman spectrum of the patterned aminosilica, it is known that amine is present based on the ^{13}C NMR results.

N_2 physisorption was also used to characterize the silica material throughout the synthesis; the results are listed in Table 2. As expected, the surface area and pore size decreased after the patterning agent was immobilized and then decreased again after the silica was reacted with the capping agent. Upon hydrolysis, both of the parameters increased almost back to the values for pure SBA-15. This suggests there is not a dense loading of amine groups on the surface, nor is there substantial pore blockage.

As evidenced by TGA, ^{13}C CP-MAS NMR, and FT-Raman spectroscopy, the hydrolysis step does not completely remove the trityl groups from the porous structure. The hydrolysis was repeated several times,

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(18) Baranska, H.; Labudzinska, A.; Terpinski, J. *Laser Raman Spectrometry*; John Wiley and Sons: New York, 1987.

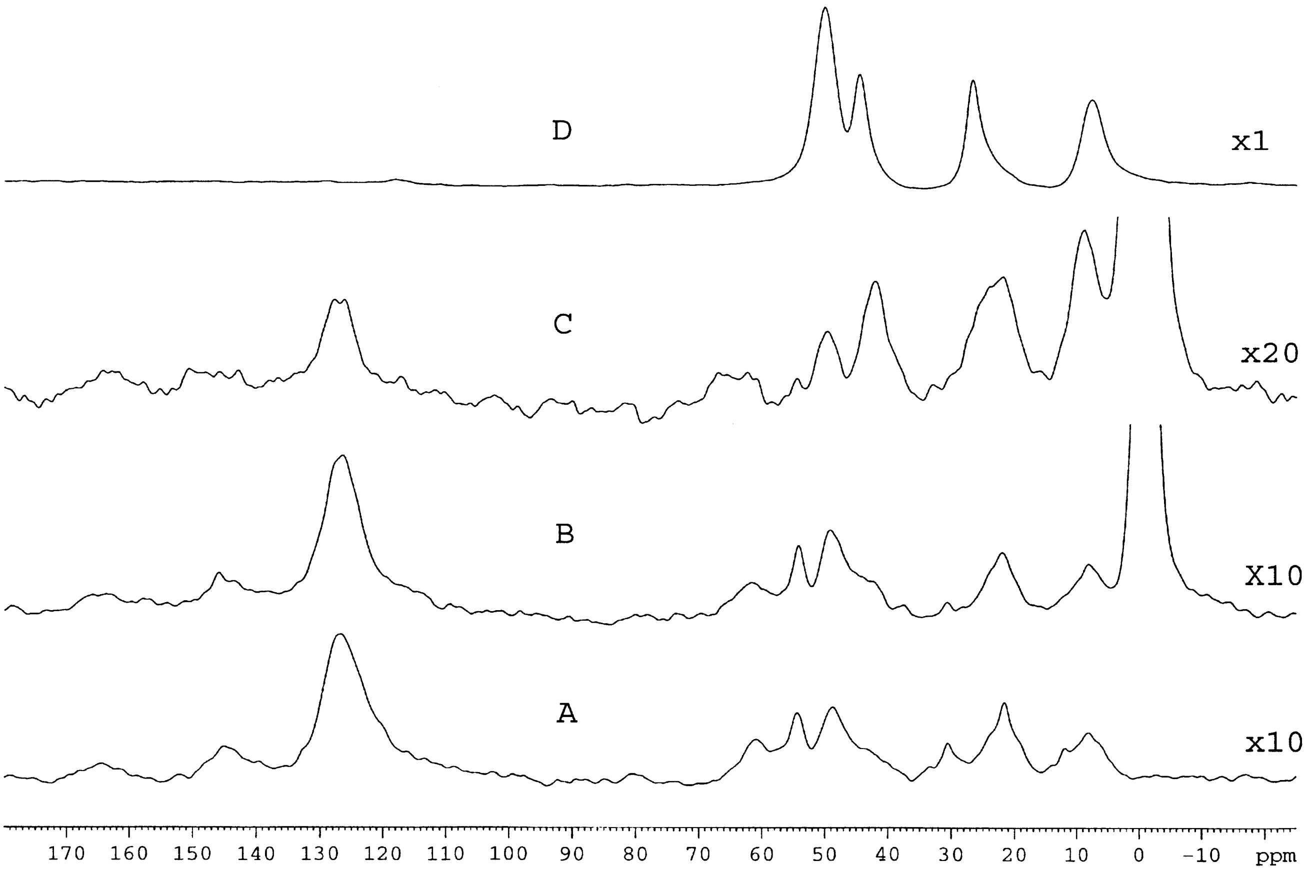


Figure 2. ^{13}C CP-MAS NMR spectra of (A) SBA-15 functionalized with supported patterning agent (**2**), (B) material after silanol capping reaction (**3**), (C) material after hydrolysis (**4**), and (D) densely loaded APTMS-functionalized SBA-15 control material (**6**).

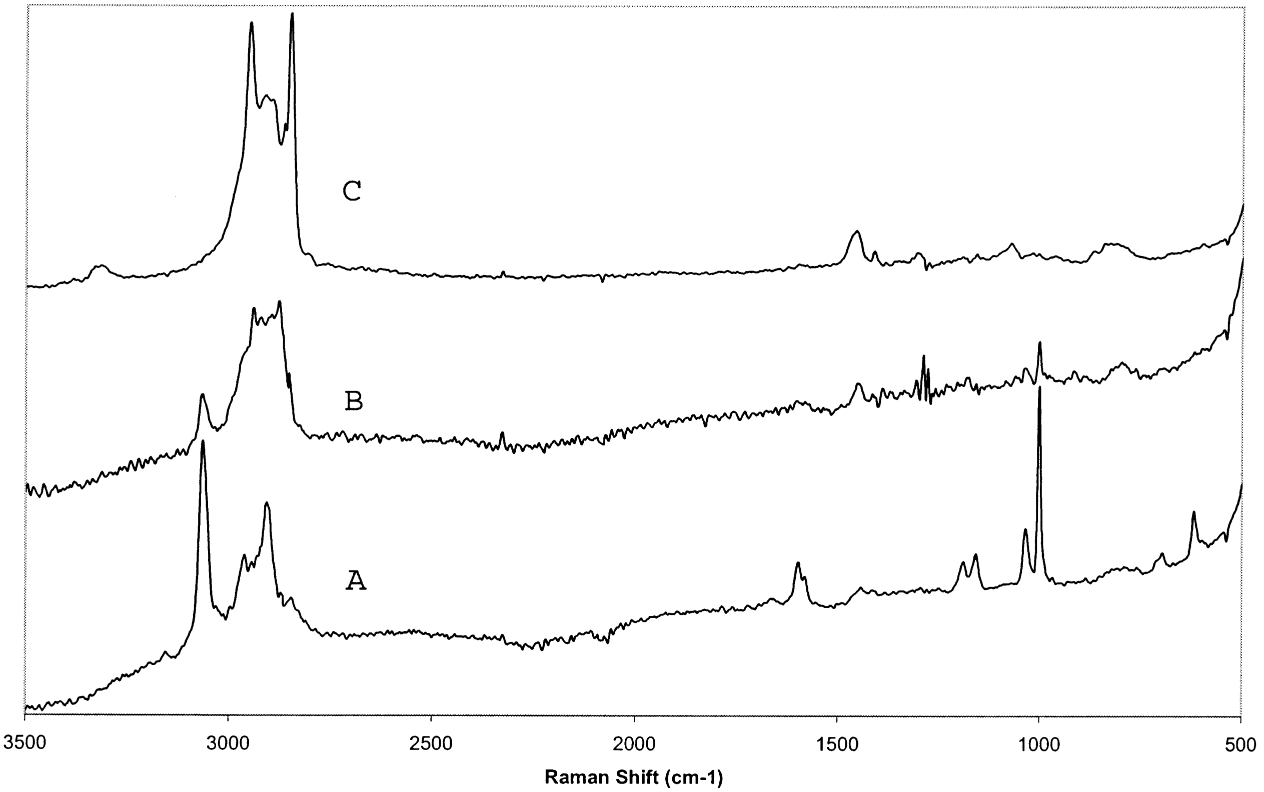
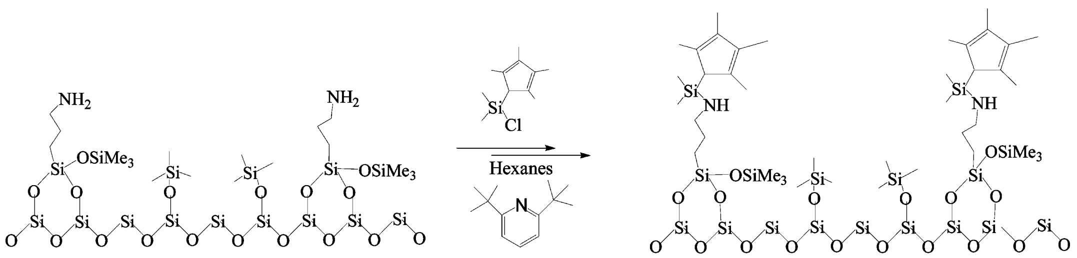


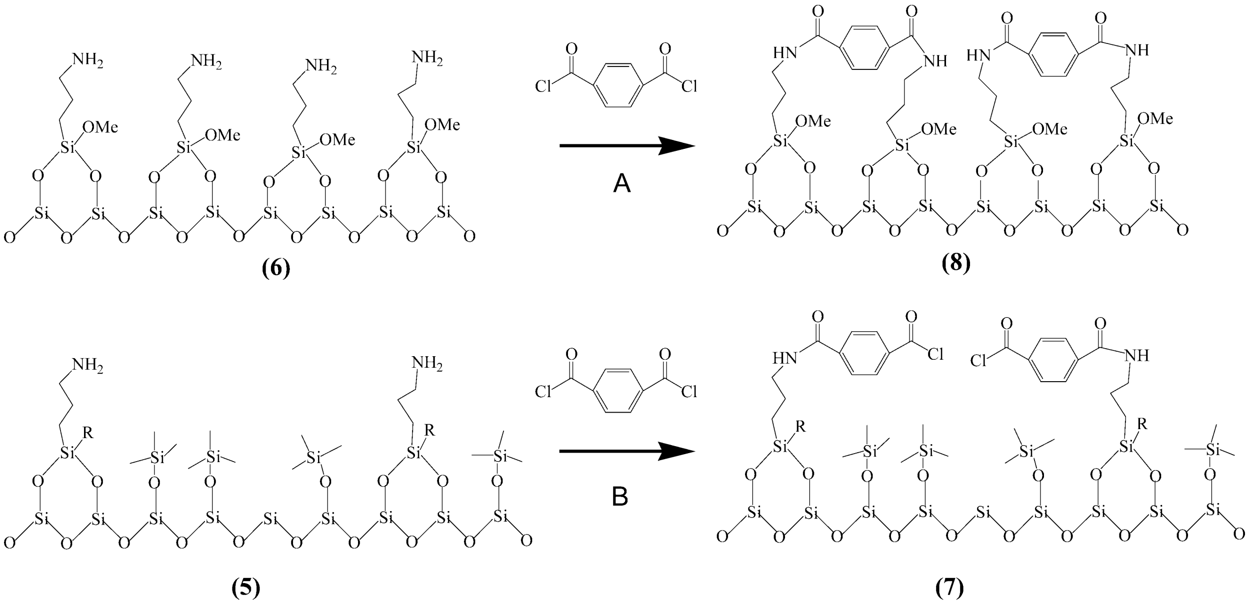
Figure 3. FT-Raman spectra of (A) SBA-15 functionalized with supported patterning agent (**2**), (B) material after hydrolysis (**4**), and (C) densely loaded APTMS-functionalized SBA-15 control material (**6**).

each time only marginally removing more trityl groups. However, the silica was degraded upon repeated exposure to acidic hydrolysis conditions. Using harsher conditions (i.e., higher acid concentration) in the hy-

Scheme 5



Scheme 6



drolysis resulted in the removal of the amine ligand from the surface, while also having an effect on the silica structure. Hence, the functionalized materials are subjected to the hydrolysis treatment at most twice, resulting in 93−95% removal of trityl groups by TGA.

One drawback of aminosilica materials prepared by traditional methods is the nonuniform reactivity imparted by the variety of types of amine sites on the surface. To probe the reactivity of the patterned amine surface, a control reaction was undertaken. Chlorodimethyl-(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane (Cp-silane) was reacted with the amine-functionalized surface to give the amidosilyl group shown in Scheme 5. This reaction was chosen because it has been previously studied on amine-functionalized silicas.[6] TGA shows the hydrolyzed amine functionalities react with the silane, giving nearly a quantitative yield (>99%). As reaction of Cp-silane with capped, amine-free SBA-15 results in no surface functionalization, it can be concluded that this functionalization occurs at the amine site as described in Scheme 5. It is important to note that this reaction results in substantially less than quantitative conversion when a traditional, densely loaded amine-functionalized silica is used (∼66% yield).[6] This may be attributed to either steric crowding of the amine groups or to the presence of some amines interacting with silanols on the surface. Hence, unlike traditional materials, the patterned amine material behaves as if it has a single type of amine site.

Site isolation was probed by contacting the amine-functionalized materials with a diacid chloride, terephthaloyl chloride. The acid chloride functionality readily reacts with an immobilized amine ligand to form an amide. If the amine functionalities are not sufficiently isolated, both acid chloride functionalities on the probe molecule can react to make two amide bonds (Scheme 6A). In contrast, for isolated amines only one acid chloride functionality should react, leaving one acid chloride functionality and making one amide bond (Scheme 6B). Both solids **5** and **6** were contacted with 0.35 equiv of terephthaloyl chloride in dichloromethane. Only 0.35 equiv was used, as opposed to a full equivalent or excess, so that it is theoretically possible to consume all the acid chloride groups if the amines are densely loaded.[10] The resulting materials were characterized by FT-Raman spectroscopy. Figure 4 shows the important region of the Raman spectrum of solid **7** (A) and solid **8** (B) after reaction with the diacid chloride (1550−1750 cm^{-1}). The peak corresponding to the amide $\nu_{C=O}$ vibration is seen at 1610 cm^{-1}.[10] The vibration from the acid $\nu_{C=O}$ vibration is seen at 1710 cm^{-1}.[10] As seen in the spectra, the reaction of the diacid chloride with the nonpatterned, amine-functionalized solid results in the complete loss of the acid chloride functionality. This suggests that both functionalities on the probe molecule react with surface amine ligands. As such, the amine ligands are relatively densely packed and nonisolated. However, the presence of the acid and the amide in solid

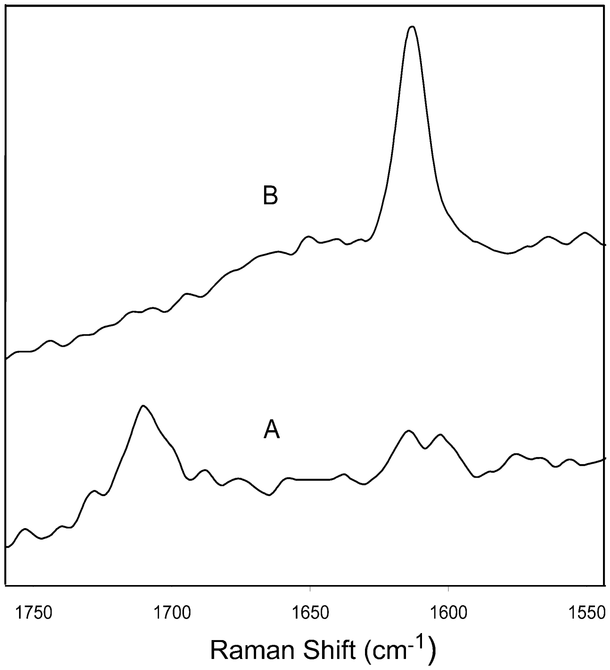


Figure 4. FT-Raman spectra of (A) patterned amine-functionalized SBA-15 contacted with the diacid chloride probe molecule (**7**) and (B) densely loaded APTMS-functionalized SBA-15 reacted with diacid chloride probe molecule (**8**).

7 suggests the amine ligands are *on average* sufficiently spaced on the surface so that the probe molecule cannot react with more than one ligand. While this does not prove that all the amines are isolated, it clearly shows that the patterned material is substantially different from traditional aminosilicas and suggests that the amine ligands may be isolated by a minimum distance of 7−8 Å.

Summary

All of these results, when taken together, support the presence of a well-defined, amine-functionalized surface with site-isolated amine groups. The evolution of the organic functional groups can be easily tracked using ^{13}C NMR and Raman spectroscopy and all of the relevant groups can be identified by one or both of the techniques. Reactivity studies with the Cp-silane and diacid chloride probe molecules illustrate that the amines are effective foundations for subsequent synthesis on the solid surface and that the amine groups behave as if they are isolated compared to aminosilica materials prepared by traditional methods. The method appears to be versatile in that the minimum spacing between the amines can theoretically be controlled by proper design of the patterning molecule. For instance, one can imagine using other patterning molecules such as one derived from 3,3,3-trifluorenylpropanal (instead of 3,3,3-triphenylpropanal) to increase the spacing. It is expected that these new materials will allow for the synthesis of well-defined, single-site organometallics and other catalysts with nanostructured active sites previously unattainable using current synthetic methods. Furthermore, materials of this type may have applications in molecular recognition and chemical sensing. The materials are currently being evaluated in our laboratory along these lines.

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