

Controlling the Density of Amine Sites on Silica Surfaces Using Benzyl Spacers

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The synthesis and characterization of benzyl-spaced aminopropyl-functionalized mesoporous silica is reported by a method designed to reduce silanol–amine and amine–amine interactions. The new material is characterized by N_2 physisorption, thermogravimetric analysis, potentiometric titration, X-ray diffraction, FT-Raman spectroscopy, and ^{13}C and ^{29}Si solid-state NMR spectroscopy. The degree of clustering of the amines is studied by solid-state fluorescence spectroscopy of 1-pyrenecarboxylic acid bound to the deprotected benzyl-spaced aminosilica. The results obtained provide evidence of an amine loading comparable to traditional dense amine grafting approaches on SBA-15. Thermogravimetric analysis, FT-Raman spectroscopy, and ^{13}C solid-state NMR spectroscopy results show evidence that the protected imine can be quantitatively cleaved to yield the corresponding amine. As evidenced by fluorescence spectroscopy, the benzyl-spaced material is isolated enough to prevent excimer formation of the probe molecule, unlike aminopropyl-functionalized silica materials prepared by traditional grafting approaches.

Introduction

Traditionally, aminoalkyl-functionalized silica materials have been prepared by primarily two routes, the reaction of silica materials with organosilanes (grafting)¹ or the co-condensation of organosilanes with silicate precursors to create a functionalized silica gel (co-condensation).² These processes are most often used to create a material with a large loading of the alkoxy silane groups. Using a modified grafting technique, Tripp and co-workers elucidated a way to increase the reactivity of aminosilanes with the silica surface by adding an additional amine base.^{3,4} This method utilizes the additional amine to interact with the acidic silanols on the surface, thereby preventing or limiting the interactions of the amine groups of the silane with the surface silanols. The approach promotes the interaction of the silane end of the aminosilane with the surface, facilitating the grafting of a dense array of amines on the silica surface. As reported, Tripp was able to synthesize materials with amine loadings 1.7 times higher than the traditional direct grafting approach. Others, such as Shantz, Simanek, and co-workers, have reported the synthesis of dendritic aminosilicas as a way to increase amine loading.^{5,6} Recently, Luechinger et al. reported a synthesis of a mixture of aminopropyl and methyl groups on a mesoporous support. The reported amine loading was manipulated in a range of 0.2–2.7 mmol of NH_2/g of material.⁷

Utilizing the above methods, the creation of a final material with multiple types of amines is likely, with the presence of some isolated amines but the majority of the species being (a) hydrogen-bonded or (b) interacting with silanols (Figure 1). To

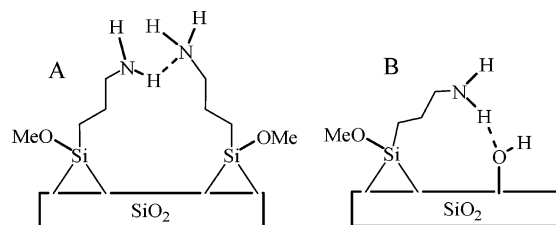


Figure 1. Multiple types of amine sites present on silica include (A) amine–amine and (B) amine–silanol interactions.

create truly well-defined functional materials, it is thus important to prevent these interactions by separating the amines and capping excess surface silanols. Many groups have attempted to synthesize aminosilicas in an effort to control the types of amine sites formed. For instance, Wulff et al. created spaced amines on silica by immobilizing a hydrolyzable template.^{8,9} This method led to amines spaced at specific distances apart at a low loading (<0.2 mmol of NH_2/g of material) but left silanols for possible amine interactions. Katz and Davis have synthesized aminosilicas by using a molecular imprinting approach to produce isolated amines.¹⁰ This method allowed immobilization of 1–3 spaced amine functionalities on silica. Again, the reported loading of the amine was <0.23 mmol of NH_2/g of material. Also, Bass and Katz reported the thermolytic synthesis of single-site aminosilicas by deprotecting a carbamate to the corresponding amine that produced a well-defined aminosilica.^{11,12} However, they reported a loading of only 0.25 mmol of NH_2/g of material. Our group recently developed a method of immobilizing a bulky tritylimine that could easily be deprotected to yield primary amines as a method to space surface-bound amine functionalities.^{13,14} After a few steps, the imine was removed by acid hydrolysis to reveal amines well-spaced from each other, with the average distance

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hypothesized to be similar to the size of a trityl group. This method reduced or eliminated amine–silanol and amine–amine interactions. This material has shown to be an excellent support for constrained-geometry Group 4 catalysts for ethylene polymerizations.^{15–19} Although the amine loading was roughly twice that of previously reported spacing methods (~0.4 mmol of NH₂/g of material), this method was deficient in amine loading compared to traditional methods (~1.2 mmol of NH₂/g of material).

The main disadvantage of the previously reported^{18–12} amine-spacing methods is that the loading of the amine functionalities is greatly reduced on the support material, because amine spacing is controlled in part by keeping the total loading of amines low. When the amine concentration is kept low on the surface, the proximity of the individual amines to each other is limited statistically. However, when traditional silane grafting approaches are employed, a large amount of aminosilanes can be deposited on the surface via the reaction with silanols or siloxane bridges, allowing the pendant amines to group together on the surface close enough to interact with their nearest neighbor (which we describe here as “clustering”). It would thus be advantageous to maximize the amine loading on the surface while spacing the amine groups far enough apart in hopes of preventing the clustering of amines or the interaction of the amines with surface silanols. Previously, use of a trityl spacer allowed the creation of an aminosilica material with amines that were spaced far enough apart on the surface to allow for unique amine reactivity patterns.¹³ In comparison to traditional materials prepared by the grafting of simple, unprotected aminosilanes, the trityl-spaced amines behaved as if they were site-isolated. Quantitative stoichiometric transformations of the amine groups were possible with the trityl-spaced material but were generally not realized with the material prepared via traditional grafting techniques.^{13,16,17} The interesting fundamental question then becomes—how dense an array of amines can be made while still preparing sites that are chemically different from traditional, densely loaded aminosilica materials? Certainly, as the size of the protecting group is decreased and as the amines are more closely positioned together, at some point, the amines prepared by the imine-protected grafting route and the traditional unprotected grafting route should start to behave similarly. In this paper, we describe our initial efforts at probing this threshold. We present here a new benzyliminosilane [benzylidene-(3-trimethoxysilylpropyl)-amine], which when added to a silica surface followed by surface-capping reactions provides an aminopropyl-functionalized silica (benzyl-imine-spaced silica) with greater amine density than previously reported spacing methods,¹³ while providing some finite amount of surface spacing to help prevent amine–amine interactions that are indicative of amine clustering. Interestingly, we show that the benzyl-spaced aminosilica material has amines that are chemically different from a material that was prepared via traditional aminosilane grafting techniques, despite the fact that amine loadings are similar.

Experimental Procedures

Materials. The following chemicals were commercially available and used as received: redistilled benzaldehyde (Aldrich), Pluronic 123 (Aldrich), HCl (Fisher), tetraethylorthosilicate (Aldrich), 3-ami-

nopropyltrimethoxysilane (Aldrich), 1,1,1,3,3,3-hexamethyldisilazane (Aldrich), 0.1 N perchloric acid in acetic acid (LabChem, Inc.), glacial acetic acid (Fisher), methyl violet (Alfa Aesar), anhydrous toluene (Acros), anhydrous tetrahydrofuran (Aldrich), and 1-pyrene-carboxylic acid (Aldrich). Anhydrous dichloromethane and anhydrous hexanes were obtained from a packed bed solvent purification system utilizing columns of copper oxide catalyst and alumina (hexanes) or dual alumina columns (dichloromethane).²⁰ Anhydrous methanol (Acros) was further dried over 4-Å molecular sieves prior to use. All air- and moisture-sensitive compounds were transferred using standard vacuum line, Schlenk, or cannula techniques under dry, deoxygenated argon or in a drybox under a deoxygenated nitrogen atmosphere.

Synthesis of SBA-15. SBA-15 was synthesized similar to literature methods.²¹ To 561 g of DI H₂O, 18.0 g of EO-PO-EO block copolymer and 99.5 g of HCl was added and stirred overnight. To the micellar solution, 39.8 g of tetraethylorthosilicate was added and stirred for 5 min. The solution was stirred for 20 h at 35 °C. To swell the pores, a temperature treatment of 80 °C for 24 h was applied. The resulting solid was filtered with copious amounts of distilled H₂O and dried overnight at 60 °C. 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. Approximately 11 g of SBA-15 was synthesized with this method. Prior to use, the SBA-15 was dried under vacuum at 200 °C for 3 h and stored in a N₂ drybox.

Synthesis of Densely Loaded Amine-Functionalized SBA-15. Excess 3-aminopropyltrimethoxysilane (1.0 g, 5.58 mmol) 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 50 °C overnight, and then stored in a drybox. TGA showed that 1.21 mmol/g of material of 3-aminopropyltrimethoxysilane (APTMS) was immobilized on the SBA-15.

Synthesis of Benzylidene-(3-trimethoxysilylpropyl)-amine Spacer. Benzaldehyde (0.60 g, 5.65 mmol) was refluxed with APTMS (1.02 g, 5.69 mmol) in dry toluene using a 100 mL roundbottom flask equipped with a Dean–Stark trap for 24 h. The toluene was removed in vacuo. The excess APTMS was removed under vacuum at 90 °C overnight. NMR data: ¹H NMR (400 MHz, CD₃OD) δ, 0.70 (2 H), 1.83 (2H), 3.57 (9 H), 3.61 (2 H), 7.40 (3 H), 7.72 (2 H), 8.27 (1 H).

Synthesis of SBA-15 Functionalized with the Benzylimine Spacer. The benzylimine spacer (1.0 g, 3.74 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 50 °C overnight, and then stored in a drybox.

Silanol-Capping Reaction. The capping synthesis was carried out by contacting a large excess of hexamethyldisilazane (HMDS) with the benzylimine-spaced SBA-15 in anhydrous hexanes 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 50 °C overnight, and then stored in a drybox.

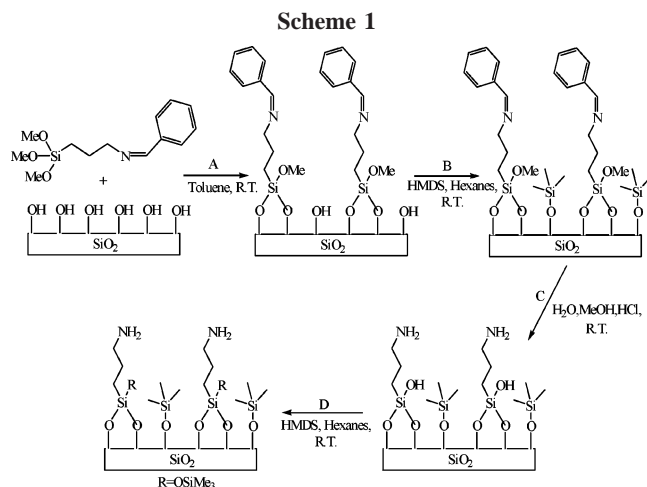
Hydrolysis. The capped benzylimine SBA-15 (0.6 g) was added to 60 g of a 1:1:1 solution of H₂O/MeOH/HCl (38 wt %). The mixture was stirred in air at room temperature for 6 h. The solid was collected via filtration, washed with copious amounts of DI water, anhydrous methanol, and anhydrous THF, and then dried under vacuum at 50 °C overnight.

Second Silanol Capping. The hydrolyzed amine-functionalized SBA-15, excess HMDS, and anhydrous hexanes were mixed and stirred 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 50 °C overnight, and then stored in a drybox.

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Loading of Fluorescent Probe Molecule on Amino-propyl-Functionalized SBA-15 Materials. A slight excess of 1-pyrene-carboxylic acid was added to 500 mg of densely loaded or hydrolyzed, benzyl-spaced aminosilica in anhydrous toluene in a nitrogen drybox. The solution was brought to reflux for 24 h after the nitrogen was replaced with argon. The solid was washed with copious amounts of anhydrous toluene and anhydrous THF to remove any physisorbed acid. The material was dried at 60 °C at a pressure of 6 mTorr.

Material Characterization. The XRD patterns were collected on a PAN analytical X'Pert Pro powder X-ray diffractometer using Cu K α radiation and a PW3011 proportional detector with a parallel plate collimator. Scanning electron microscopy (SEM) images were captured on a Hitachi S800 field emission gun (FEG) SEM. Cross-polarization magic angle spinning (CP-MAS) NMR spectra were collected on a Bruker DSX 300-MHz instrument. Samples were packed in 7-mm zirconia rotors in a nitrogen drybox and spun at 5 kHz. Typical ¹³C CP-MAS parameters were 3000 scans, a 90° pulse length of 4 μ s, and recycle times of 4 s. Typical ²⁹Si CP-MAS parameters were 5000 scans, a 90° pulse length of 5 μ s, and recycle times of 5 s. FT-Raman spectra were obtained on a Bruker FRA-106. At least 1024 scans were collected for each spectrum, with a resolution of 2–4 cm⁻¹. FT-IR spectra were collected on a Bruker IFS 66v/S spectrometer with an aperture setting of 9 mm and a scanning velocity of 3.0 kHz. Thermogravimetric analysis (TGA) was performed on a Netzsch STA409. Samples were heated under air from 30 to 900 °C at a rate of 10 °C/min. The organic loading was measured by determining the weight loss from 200 to 650 °C. The organic loading was determined by assuming two methoxy linkages to the surface before hydrolysis and three methoxy linkages after. For the traditional amine-functionalized SBA-15, two methoxy linkages were assumed. Nitrogen physisorption measurements were conducted on a Micromeritics ASAP 2010 at 77 K. SBA-15 samples were pretreated by heating under vacuum at 150 °C for 24 h. Organic-loaded samples were pretreated by heating at 75 °C under vacuum for 24 h. Nonaqueous potentiometric titrations were carried out in 30 mL of glacial acetic acid with 50–300 mg of aminosilica. The aminosilica was titrated with 10–100 μ L aliquots of 0.1 N perchloric acid in acetic acid. Fluorescence experiments were collected at Oak Ridge National Laboratories on a Jobin Yvon FluoroMax -P spectrometer. The continuous light source was a 150-W ozone-free xenon arc lamp. The samples were studied under vacuum with slits set to 1 nm.

Results and Discussion

The benzylimine spacer was chosen in an attempt to produce an aminosilica with an organic loading approaching those achieved using traditional synthetic methods, while preventing amine–silanol interactions. The advantage of the imine functionality is that it can be easily transformed into a primary amine. This benzyl-spaced aminosilica synthesis is shown in Scheme 1. The benzylimine silane was synthesized by a condensation

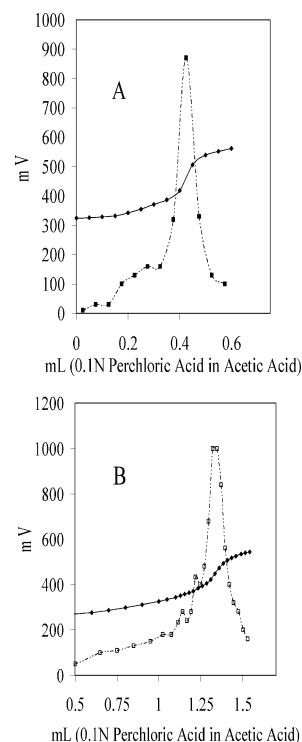


Figure 2. (A) Nonaqueous potentiometric titration of benzylimine loaded on SBA-15 and (B) the material after hydrolysis and base wash. The derivative of the potential with respect to the volume added is plotted on each graph to identify the equivalence point.

reaction between benzaldehyde and 3-aminopropyltrimethoxysilane using a Dean–Stark trap. The synthesized benzylimine spacer was added to calcined SBA-15 (A). To prevent possible amine–silanol interactions in later steps, the unreacted silanols were capped with the well-known silylating agent HMDS (B).^{22,23} In the third step, the imine was converted to the amine by acid hydrolysis (C). Finally, the surface was reacted with HMDS an additional time to ensure all accessible silanols were capped after the acidic solution was added (D).

The organic loading on SBA-15 was determined by TGA. The organic loading of the benzylimine on SBA-15 was 0.98 mmol of N=C/g of material. After the hydrolysis step, the amine loading was estimated to be 0.99 mmol of NH₂/g of material. This is consistent with the hypothesis that the imine functionalities were completely removed from the support material. Spectroscopic evidence presented later confirms this assumption. The organic loading was determined by assuming two methoxy linkages to the surface before hydrolysis and three methoxy linkages after. As a comparison material, traditional densely loaded amino-propyl-functionalized SBA-15 gave a loading of 1.21 mmol of NH₂/g of material. This indicates that the benzyl-spaced aminosilica approaches the loading of traditional dense aminosilicas.

To confirm the TGA experiments, nonaqueous potentiometric titrations were performed. The imine was titrated to approximately 0.99 mmol of N=C/g of material (Figure 2A). The material was then contacted with an acid solution to hydrolyze the imine species and to remove the benzyl-protecting group. A base wash was then performed with ammonium hydroxide in water to remove any excess acid after the hydrolysis step.²⁴ After this wash, the material was dried with heat under vacuum to remove any

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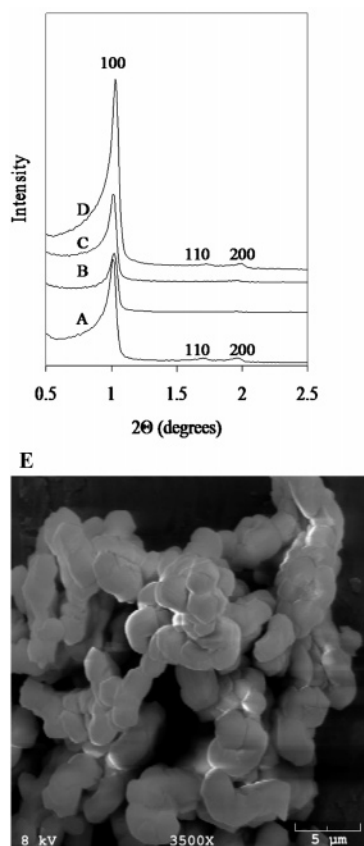


Figure 3. Powder X-ray diffraction patterns for the (A) calcined SBA-15, (B) benzylimine-loaded SBA-15, (C) capped benzylimine SBA-15, and (D) hydrolyzed to amino-functionalized SBA-15 and (E) SEM image of calcined SBA-15 particles.

remaining ammonia. The hydrolyzed material was titrated to 0.95 mmol of NH_2/g of material (Figure 2B). As a comparison, titration experiments were performed right after the hydrolysis. The amines were most likely protonated by HCl in this case, leading to a titration of only 50–70% of the amines.

X-ray diffraction patterns were collected for the materials after various steps of functionalization. In the calcined SBA-15 material (Figure 3A), three well-resolved peaks that correspond to the (100), (110), and (200) reflections were noted. The peaks were attributed to a well-defined 2D-hexagonal mesostructure ($p6mm$).²¹ A d spacing of 90 Å was determined from this material, corresponding to 104 Å for the unit-cell parameter. However, as shown in Figure 3B, after functionalization with the benzylimine spacer, only one peak can be seen (100). The decrease of the (110) and (200) peaks is common for silanated silica frameworks.^{25,26} After the hydrolysis step, all of the peaks corresponding to a well-defined 2D-hexagonal structure reappeared. This indicates that the hydrolysis step is not so harsh as to disrupt the order of the mesoporous silica framework. Also, it shows that the loss of the benzylimine functionalities results in a material very similar in its mesostructure to calcined SBA-15. Included in Figure 3E is an SEM image of the calcined SBA-15 particles used as the support material in this work. The particles have a range of sizes of approximately 1–5 μm in diameter.

The pore diameter and surface area of the material was tracked in each step by nitrogen physisorption (Table 1). The calcined SBA-15 gave a BET surface area of 930 m^2/g and a pore diameter

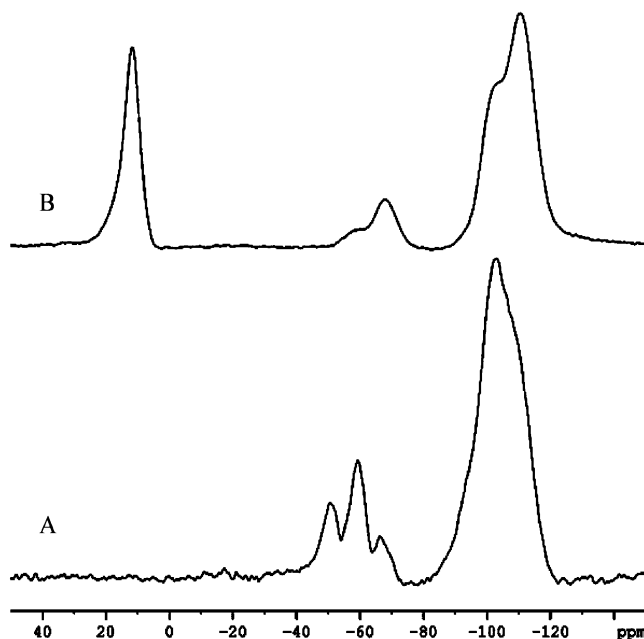


Figure 4. ^{29}Si CP-MAS NMR spectra for (A) benzylimine-spaced SBA-15 and (B) the material after hydrolysis.

Table 1. N_2 Physisorption Data for SBA-15 after Various Stages of the Benzylimine Functionalization Process

nitrogen physisorption results at 77 K		
sample	average pore diameter (Å)	BET surface area (m^2/g SiO_2)
SBA-15	65	930
benzylimine-patterned SBA-15	48	280
capped benzylimine SBA-15	48	272
material after hydrolysis	63	510

of 65 Å determined from the BJH adsorption curve. The BET surface area presented reflects both mesopores (that are accessible to the bulky silane) and micropores (that become blocked by the silane treatment), because of the SBA-15 synthesis procedure used.^{27–29} After contact with the benzylimine-patterning agent, the surface area and mesopore diameter were reduced, indicating the reaction of the benzylimine spacer within the mesoporous silica material. After hydrolysis, the pore diameter returned to a similar size relative to the calcined SBA-15.

^{29}Si CP-MAS NMR spectra are shown in Figure 4 for the benzylimine-functionalized SBA-15 (A) and the material after hydrolysis (B). The spectrum of the benzylimine functionalized SBA-15 (A) shows the Q^2 , Q^3 , and Q^4 silicon resonances between -90 and -110 ppm.³⁰ Also, three distinct peaks at -51 , -60 , and -66 ppm correspond to the alkyl linkages to the surface created by the reaction of 1, 2, or 3 methoxy groups, respectively.^{13,31} Although cross-polarization experiments are not strictly quantitative, assuming all of the silicon atoms in the silane cross-polarize with roughly similar efficiencies, it appears that the majority of the silanes react to the surface by two methoxy groups. This interpretation is consistent with TGA and titration results. After the hydrolysis step, mainly Q^3 and Q^4 silicon resonances are seen between -100 and -111 ppm. Also, the spectrum may be interpreted as being consistent with mainly

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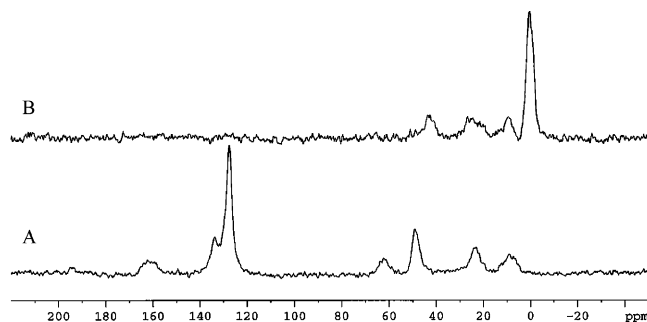


Figure 5. ^{13}C CP-MAS NMR spectra for (A) benzylimine-spaced SBA-15 and (B) the material after hydrolysis.

Table 2. ^{13}C CP-MAS NMR Chemical Shifts for SBA-15 Functionalized with (A) the Benzylimine Moiety and (B) the Same Material after Hydrolysis

A		B	
assignment	resonance (ppm)	assignment	resonance (ppm)
–Si–CH ₂ –	9	–Si–CH ₃	0
–Si–CH ₂ –CH ₂ –	24	–Si–CH ₂ –	9
–Si–OCH ₃	49	–Si–CH ₂ –CH ₂ –	27
–CH ₂ –CH ₂ –N=	62	–CH ₂ –CH ₂ –NH ₂	43
aromatic carbons	129		
–CH=N–	162		

three methoxy groups reacting with the surface. The resonance of the trimethylsilyl groups derived from capped silanols can also be seen at 12 ppm.

Solid-state ^{13}C CP-MAS spectra are shown in Figure 5. The functionalized material was analyzed after the addition of the benzylimine to the SBA-15 (A) and after the removal of the imine functionalities by hydrolysis (B). With the benzylimine spacer loaded on SBA-15, the spectrum shows all of the peaks expected. The aromatic carbons are located at 134 and 127 ppm. The imine carbon is located at 162 ppm. After hydrolysis, both the aromatic and imine carbon peaks disappeared. This indicates that the hydrolysis transformed the imines to primary amines. Also, it is noted that the carbon next to the imine shifts from 62 to 43 ppm after hydrolysis. Overall, the spectrum of the deprotected aminopropyl-functionalized SBA-15 after hydrolysis resembles that of aminopropyl silicas prepared by traditional grafting techniques.^{13,32} As seen in the ^{13}C CP-MAS NMR spectrum, residual methoxy groups at 50 ppm are removed after hydrolysis, indicating that the silanes are bonded by mostly three linkages after hydrolysis. The very large peak at 0 ppm is the result of trimethylsilyl groups left by the use of HMDS as a silanol-capping agent. All of the peak assignments are collected in Table 2.

As shown in Figure 6, FT-Raman spectroscopy was used as a complimentary technique to ^{13}C CP-MAS NMR to track the changes before (A) and after (B) imine hydrolysis. The main peaks of interest are those that involve only the benzylimine spacer. For instance, the spectrum (A) has three distinct transitions corresponding to the aromatic C–H ($\nu_{\text{aromatic C-H}} = 3100 \text{ cm}^{-1}$), C=N ($\nu_{\text{C=N}} = 1640 \text{ cm}^{-1}$), and C=C ($\nu_{\text{C=C}} = 1601 \text{ cm}^{-1}$) stretches. After hydrolysis, these three bands are absent from the spectrum (B). The only band remaining is the broad stretch from the aliphatic C–H ($\nu_{\text{C-H}} = 3100 \text{ cm}^{-1}$) that is seen in both A and B. After hydrolysis, the N–H stretch is not visible in the spectrum. Nonetheless, the presence of amines has been verified by potentiometric titration (vide supra). The complete removal

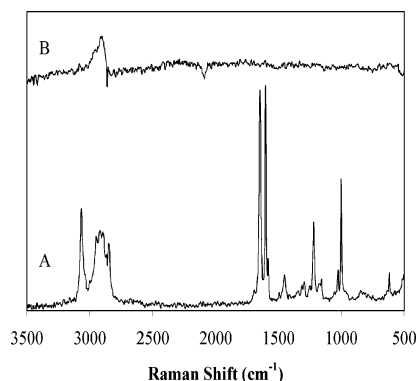


Figure 6. FT-Raman spectra of (A) benzylimine-spaced SBA-15 and (B) the material after hydrolysis.

of the aromatic C–H bands is different from our previously reported amine-spacing techniques, which show only a reduction in aromatic peak intensities rather than removal.¹³ The residual aromatic C–H bands in previously reported syntheses may be a consequence of the synthetic method employed and the relative size of the organic spacers. The previously reported silane synthesis¹³ involved mixing a 3,3,3-triphenyl-propionaldehyde and 3-aminopropyltrimethoxysilane in anhydrous methanol. The methanol was used to inhibit the polymerization of the silanes that could be caused by water formed in the reaction. In this paper, we utilized a Dean–Stark trap to remove the water generated by the reaction. Also, the trityl group is much bulkier and less soluble than the benzyl functionality. Hence, the smaller benzyl-capped materials are expected to be more easily hydrolyzed, and after hydrolysis, it is expected that the benzyl functionalities will be removed from the pores more easily, resulting in a lack of aromatic C–H bands in FT-Raman experiments.

The proximity of the amine groups (degree of clustering) was studied by steady-state fluorescence emission experiments.^{10,33,34} The hydrolyzed benzyl-spaced SBA-15 material was contacted with 1-pyrenecarboxylic acid, carefully washed, and then dried under vacuum. To ensure that the pyrene species were associated with the amine groups on the surface, bare SBA-15 was also contacted with 1-pyrenecarboxylic acid, washed, and dried in the same manner. TGA data indicated that only a trace of pyrene moieties remained on the bare silica surface (<0.04 mmol/g or ~10% of the pyrene loading on the aminosilica materials), indicating that majority of the pyrene species are associated with surface aminopropyl groups. The fluorescence spectrum of the pyrene-loaded benzyl-spaced material is shown in Figure 7A. Monomer emission was strongly detected by this technique. However, when the same experiment was performed on densely loaded aminopropyl-functionalized silica, the spectrum (B) shows strong excimer emission.¹⁰ This indicates that the benzyl-spaced amines are separated far enough to prevent excimer formation. The dense material, on the other hand, has amines positioned close enough to allow for this formation (Scheme 2; acid-base interactions are shown, although this is not conclusively known to be the means by which the amines interact with the pyrene acid). This result is somewhat surprising, because it might be surmised that the materials should be very similar in amine distribution because of their roughly similar loadings. It is suggested that this observation is a consequence of the synthetic method used, where the benzyl-spacing methodology prevents

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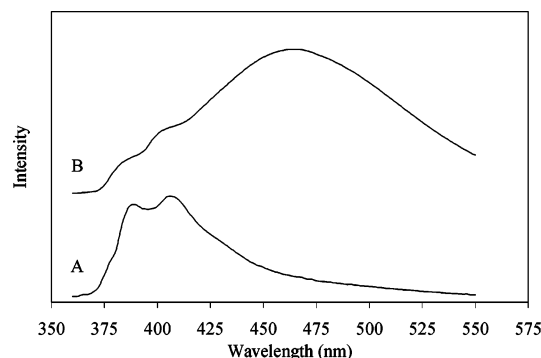


Figure 7. Fluorescence emission spectra of 1-pyrenecarboxylic acid loaded on (A) benzyl-spaced aminosilica and (B) densely functionalized aminosilica. The solid materials were excited at 330 nm. Arbitrary units were used for the fluorescence intensity.

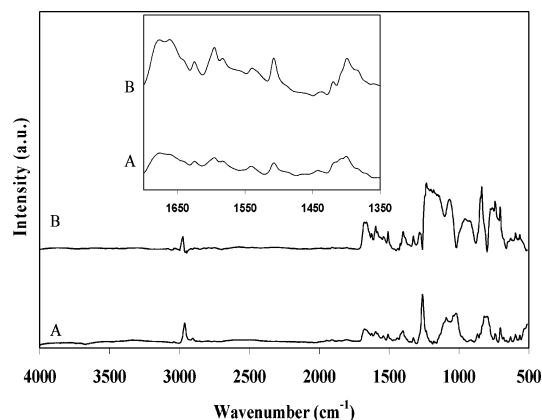
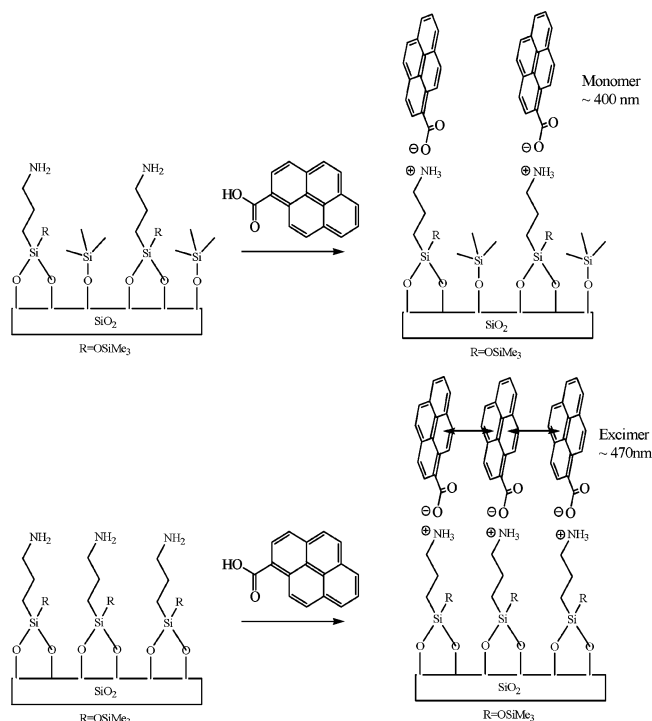


Figure 8. FT-IR spectra for (A) 1-pyrenecarboxylic acid and (B) 1-pyrenecarboxylic acid reacted with amine-functionalized SBA-15.

Scheme 2



the aminosilanes from being deposited on the surface in very close proximity to each other, perhaps by inhibiting the clustering of the free amines during the grafting process. FT-IR experiments indicate that the interaction between the probe molecule and the amine scaffold may occur via an acid–base or hydrogen-bonding interaction, because of the lack of amide stretches in the spectrum of the pyrene-functionalized solid (Figure 8). TGA experiments on traditionally prepared aminosilica SBA-15 loaded with 1-pyrenecarboxylic acid indicated that 34% of the amine sites could be bound with the acid probe molecule (for a loading of 0.41 mmol of pyrene/g of silica). Similarly, the benzyl-spaced material loaded with 1-pyrenecarboxylic acid resulted in 37% amine coverage with the probe molecule (for a loading of 0.37 mmol of pyrene/g of silica). The TGA results indicate that the loadings of the acid probe molecule are comparable on the two materials.

The benzyl-spaced aminosilica synthesized here can be used to better understand the role of isolated amines versus amine pairs or clusters for a variety of different applications including catalysis, adsorption, and separation. For instance, as previously mentioned, our group has shown the importance of spacing the amines for an enhancement in catalytic productivity for the polymerization of ethylene using Group 4 constrained-geometry catalysts (CGCs).^{15–19} The presented synthesis adds a new type of aminosilica material to the repertoire of material designers, one with a relatively dense array of amines that are potentially slightly spaced relative to each other. Data from fluorescence experiments imply that the amines on the surface of the benzyl-spaced aminosilica are chemically different from those on a traditional, densely loaded aminosilica material. Currently, the threshold between monomer and excimer formation in fluorescence characterization of a variety of differently “spaced” amine-functionalized silica materials is being probed, and these results will be reported in a future publication.

Conclusions

The results presented show the synthesis of an aminopropyl-silica material with high amine loading yet some evidence of limited amine-spacing relative to aminopropyl-silicas made via traditional grafting techniques. ²⁹Si CP-MAS NMR and N₂ physisorption data confirm functionalization within the mesopores. XRD data provide evidence that the functionalization steps leave the 2D-hexagonal mesoporous framework undisturbed. All of the data together support the preparation of a well-defined aminopropyl-functionalized silica. Site isolation was probed by fluorescence emission techniques. These results indicate that the benzyl-spaced amines are positioned far enough apart as to prevent excimer formation. The degree of site isolation in aminosilica materials continues to be a topic of study in our laboratory.

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