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Functionalization of Silica Surface Using Chan-Lam Coupling

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Functionalization of Silica Surface Using Chan-Lam Coupling

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In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

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by

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May 2014

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Keywords: Chan-Lam coupling, surface functionalization, silica gel, boronic acids

ABSTRACT

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by

George Appiah Kubi

The reaction of base-free Chan-Lam coupling was successfully used for functionalization of surface of mesoporous silica gel. Various aromatic, aliphatic, and heterocyclic compounds were immobilized by a copper-catalyzed reaction of corresponding boronic acids with surface amino groups at mild conditions. Obtained functionalized materials were mesoporous although their surface area decreased after immobilization. The reactivity of some surface functional groups was tested in their characteristic reactions.

DEDICATION

This work is dedicated to the ALMIGHTY GOD for being my help and my provider, Secondly my wife, Mrs. Hannah Appiah Kubi, my daughter, Janelle Appiah Kubi, for their support, understanding, and patience. Finally, to the larger family and friends for their prayers.

ACKNOWLEDGEMENTS

I will like to express my profound gratitude to Dr. Aleksey Vasiliev, my research advisor, for his able assistance, words of encouragements, patience, constructive criticisms, and professional contribution towards the success of this work. His availability, willingness, and the zeal towards the success of this work cannot be over emphasized and they are well appreciated. I want to thank my committee members- Dr. Ismail Kady and Dr. Ningfeng Zhao for their generous advice and assistance for making this dream a reality. Dr. Raymond Mohseni has been very instrumental towards the success of this work and I say thank you. My endless thanks go to my wife Mrs. Hannah Appiah Kubi for her physical and spiritual support, all my friends, course mates, and all members of Bread of Life Ministries. I want to say a big thanks to all faculty and staff of ETSU Chemistry Department. I will also like to thank ETSU Chemistry Department for providing me with resources to conduct this research work.

Most importantly, I thank the ALMIGHTY GOD for HIS provision.

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CHAPTER 1

INTRODUCTION

Functionalized Materials

There has been a tremendous breakthrough in the fields of nanotechnology and material chemistry over the past few decades. The process of modifying the surface of a material to achieve special physical, chemical, and biological characteristics that are different from the bulk of the original material is termed as surface modification. Modification is often done on solid materials; however, it is possible to find some examples of specific liquid surface modified materials. Surface modification can be conducted in different ways with the aim of altering a wide range of characteristics such as roughness,[1] hydrophilicity,[2] surface charge,[3] surface energy, biocompatibility[2,4] and reactivity.

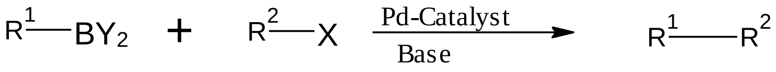
In surface modification sometimes specific chemical functional groups are introduced on the surface of the material and this is called surface functionalization. This technique has been employed in various fields for various reasons and various purposes. For example, in the medical field surface functionalization has been employed in creation of antimicrobial surfaces. The surfaces of such materials are coated with chemicals that may be toxic to microorganism.[5] Moreover, medicine and pharmacy widely use surface modified silica particles with bio-recognition molecules that may make a specific interaction with receptor sites of living systems. Surface modification technique has made it possible for a great number of research efforts to use the silica particles as carriers for drug or gene deliveries.[6-9] In addition, silica is also use as a surface coating material for many materials because of its stability, good biocompatibility and easy surface modification.[10] In the polymer industry, plasma processing technology has also successfully use surface functionalization technique to alter and to improve adhesion properties of the polymer surface prior to coating, painting, etc.

Silanol groups (Si–OH) on the silica surface can be used to introduce various functional groups by treating with organotrialkoxysilane ($RSi(OR)_3$) compounds.[11] In recent years silica particles have been represented as one of the most widely used porous material due to its several features such as (i) ease of preparation through hydrolysis condensation with comparatively low-priced precursors such as tetraethyl orthosilicate (TEOS) in the presence of an acid or a base, (ii) possibility to modify with various organosilane compounds, and (iii) its biocompatibility without showing acute toxicity.[12, 13]

Cross-Coupling Reactions

The formation of C-C, C-O, C-S, and C-N bond through catalytic cross coupling reactions have been extensively studied with the use of organic nucleophiles in the presence of some transition metals such as Ni, Pd, Cu, etc.[14]

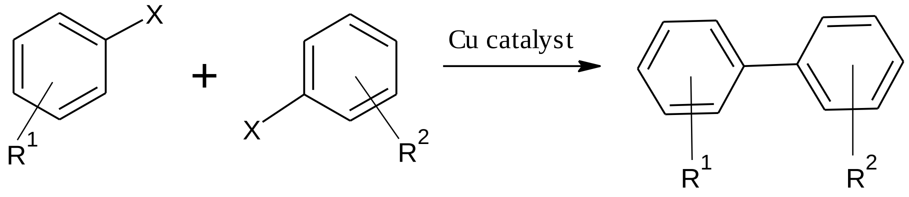
Suzuki cross coupling, named after Suzuki and Miyaura, the scientists who first found this useful reaction, has receive much attention in recent years because of its numerous applications in synthetic chemistry and biochemistry. The Suzuki cross coupling reaction proceeds as shown in Scheme 1. It involves the formation of C-C bond between organic halides and organoboron compounds with palladium catalyst.[15] Due to its mild reaction conditions, readily available reagents, and tolerance to a wide range of functional groups, the Suzuki cross coupling has a number of applications.[15, 16]



R^1 and R^2 = aryl or alkenyl; R^3 = alkyl; X = halide; Y = OH or OR^3

Scheme 1. Palladium catalyzed Suzuki-Miyaura cross-coupling reaction.

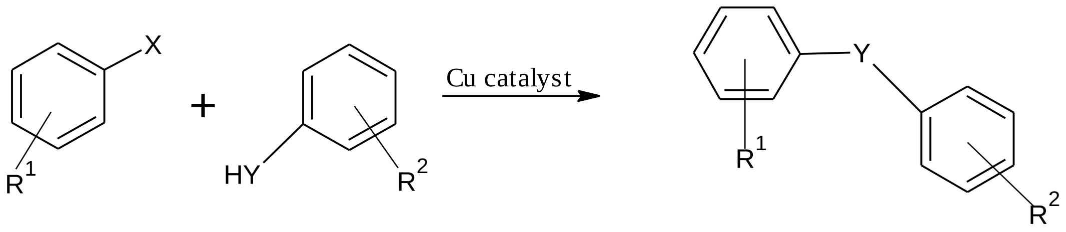
The C-C bond formation is not limited to Suzuki-Miyaura reaction. Ullman also succeeded in forming C-C bond using two aryl halides through a copper catalyst. The reaction proceeds as shown in Scheme 2.



X = Hal.; R^1 and R^2 = alkyl

Scheme 2. Copper catalyzed Ullman reaction

Subsequently, the Ullman type of reaction has led to the Ullman condensation reaction, which proceeds with the formation of C(aryl)-O, C(aryl)-N, or C-S bonds from aryl halides and phenols, anilines, and thiophenols derivatives through a copper catalyst.[17] The reaction proceeds as shown in Scheme 3 below.

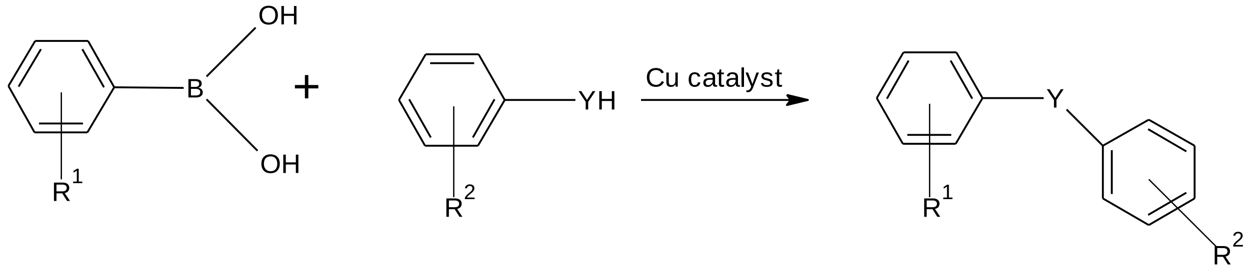


Y = O, NH, S; X=Hal.; R^1 and R^2 = alkyl

Scheme 3. Copper catalyzed Ullman condensation reaction

In 1998 Chan and co-workers originally discovered carbon(aryl)-oxygen bond formation.[18] A good yield was achieved when they reacted phenol with arylboronic acid (2-3 equiv) in the presence of stoichiometric amount of copper (II) acetate (1-2 equiv), and triethylamine (2-3 equiv) in dichloromethane at room temperature for one to two days to produce diaryl ether.[19] O-arylation was later optimized by Evans and co-workers in their expedient synthesis of thyroxine.[20] Decicco and co-workers were the first to successfully extend the intermolecular carbon(aryl)-oxygen cross-coupling to an intramolecular system for the synthesis of metalloprotease inhibitors.[21]

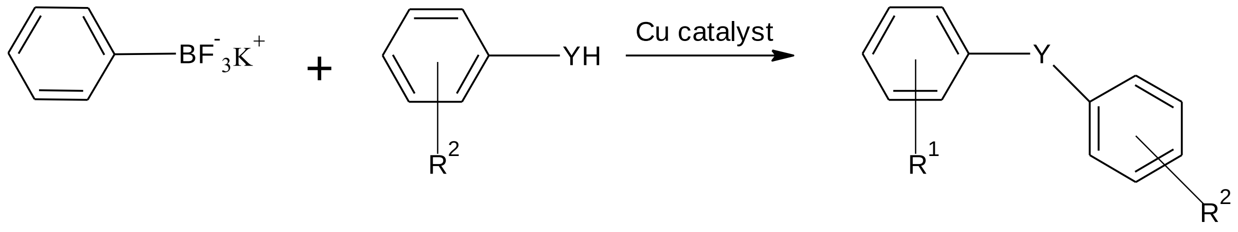
Chan, Evans, and Lam modified the Ullman condensation that involves the formation of carbon-oxygen, carbon-sulphur or carbon-nitrogen bonds using arylboronic acids with a phenol, thiophenol, or aniline derivatives. This reaction is also mediated by copper catalyst. It proceeds as shown in Scheme 4.[18, 22]



Y = NH, O; R^1 and R^2 = alkyl

Scheme 4. Copper catalyzed Cham-Evans-Lam coupling reaction.

Copper mediated reaction of potassium aryltrifluoroborates and phenols or phenol derivatives has been studied by Batey.[23] The reaction proceeds as shown in Scheme 5.



Y = O; R^1 and R^2 =alkyl

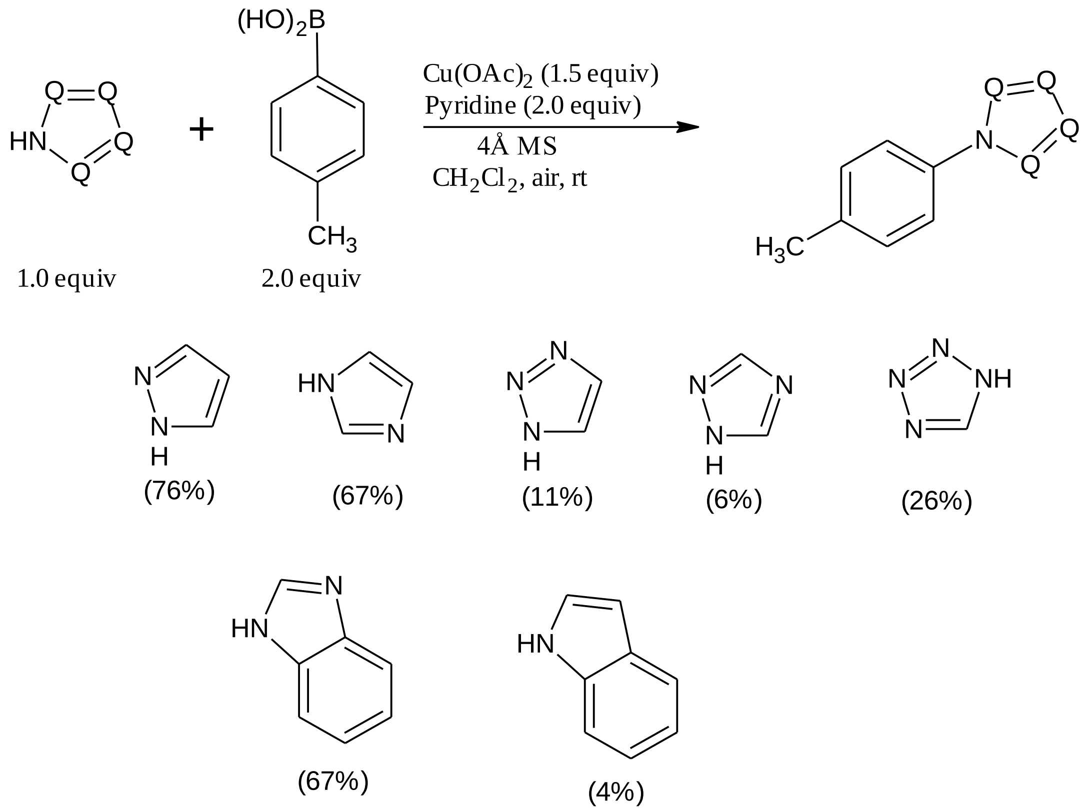
Scheme 5. Base free copper catalyzed Batey cross-coupling reaction

In addition to that, Guy and co-workers also introduced the C-S cross coupling reactions of electron rich alkylthiols.[24] It was necessary to carry out the reaction under reflux in argon atmosphere with *N*,*N*-dimethylformamide. This suppresses the formation of disulfide bonds. Arylation of cyclic thiolurea at the sulfur has also been achieved by using phenylboronic acid, copper (II) acetate, and 1,10-phenanthroline.[25] Microwave irradiations and dichloroethane solvent have shorten the reaction time considerably.

Carbon-Nitrogen Cross-Coupling

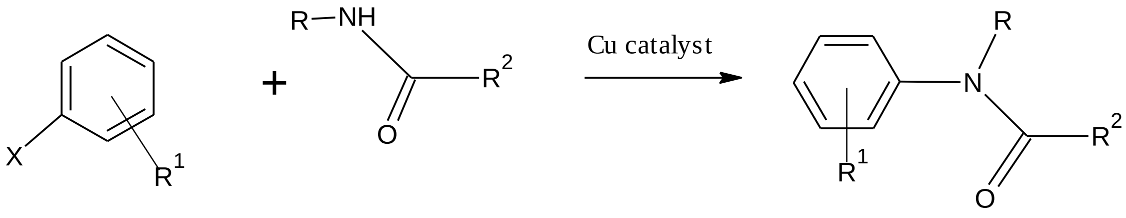
One of the most interesting cross coupling reactions is the Chan-Lam reaction that involves the formation of C-N bond by coupling substituted arylboronic acids to aliphatic and aromatic amines as well as amides in the presence of a base and copper acetate as catalyst. The reaction proceeds at room temperature for 18-65 hours producing an N-arylated product. Lam and co-workers extended the original scope of copper-mediated carbon–nitrogen bond formation to a variety of aromatic heterocycles. Imidazole, pyrazole, triazoles, tetrazole, benzimidazole, and indazole can be used as N-containing nucleophiles.[22] For example, azole compounds can be N-arylated with two equivalents of *p*-tolylboronic acid under typical conditions (shown in Scheme 6). Electron-poor azoles such as triazole, tetrazole, and indole gave low yields, whereas pyrazoles and imidazoles were more reactive. The parent pyrrole and indole also gave poor yields. However, it was later reported that N-arylation proceeded with good yields with pyrroles and indoles containing a chelating aldehyde, ketone or ester located in α-position to the -NH group.[26,27]

In addition to that, there are other modifications of the Ullman type of coupling. For example, Goldberg first studied the C(aryl)-N bond formation from amides and aryl halides using copper catalyst.[28] The reaction proceeds as shown in Scheme 7 below.



Q = CH or N

Scheme 6. Copper catalyzed N-arylation of azole compounds and corresponding yields of the products



R, R^1 and R^2 = alkyl; X = Hal.

Scheme 7. Copper catalyzed Goldberg cross-coupling reaction

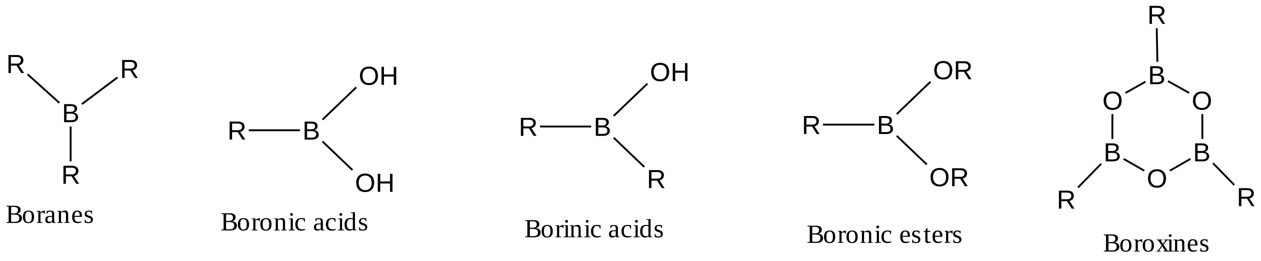
Two major advantages of the copper-catalyzed carbon–nitrogen bond formation using boronic acids are its tolerance to wide range of functional groups and its success on a broad spectrum of substrates because of the mildness and efficiency of the reaction conditions.[19]

Amines, amides, and N-heterocyclic compounds are reactive to alkyl and vinyl boronic acids.[29-31] Raghuvanshi demonstrated that Ni complex of 2,2'-bipyridyl ligand in a strong basic medium can also be used instead of the copper catalyst to achieve high yield in this synthesis.[32] Studies showed that carbon–nitrogen (e.g. aryl–heteroaryls) products can be used extensively as building blocks for biologically active compounds. However, carbon–nitrogen linked polyindazoles, polybenzimidazoles, and polybenztriazoles are in theory similar to polyanilines but have not been deeply explored as organic conductors in materials science.[19] Buchwald–Hartwig in late 1990's succeeded in carbon(aryl)-nitrogen bond formation using aryl halides and primary or secondary amines catalyzed by palladium compounds and a strong base.[33,34] The limitation of Buchwald–Hartwig palladium-catalyzed N-arylation chemistry with aryl halides was that it did not work for the N-arylation of several azoles such as imidazoles and some heterocycles such as quinazolinediones.[35]

Further studies show that aryl donors in cross coupling reaction are not limited to aryl halides as indicated in cases of Suzuki-Miyaura, Ullman, and Goldberg. However, Chan and co-workers, Evans and co-workers, Guy and co-workers, and Lam demonstrated the effectiveness of arylboronic acids as arylating agents. Furthermore, Batey has also shown that it is also effective to use potassium aryltrifluoroborates as arylating agent. There are other aryl donors in cross coupling reactions. For example, iodonium salts, siloxanes, stannanes, plumbanes, and bismuthate can be used as aryl donors.[14] However, due to the exceptional reactivity of amino groups with boronic acids in cross coupling reactions, it was interesting to investigate N-arylation on solid support using boronic acids and this will occupy the center-stage in this research.

Boronic Acids

Boronic acids are substituted boric acids containing carbon-boron bond. They belong to a larger class of compounds called organoboranes. They have trigonal and fairly coplanar geometry with the aryl group. However, they can assume a perpendicular geometry to the aryl group if there are bulky substituents at the ortho positions of the aryl group due to steric interactions.[36] Some examples of organoboron compounds are shown in Figure 1.



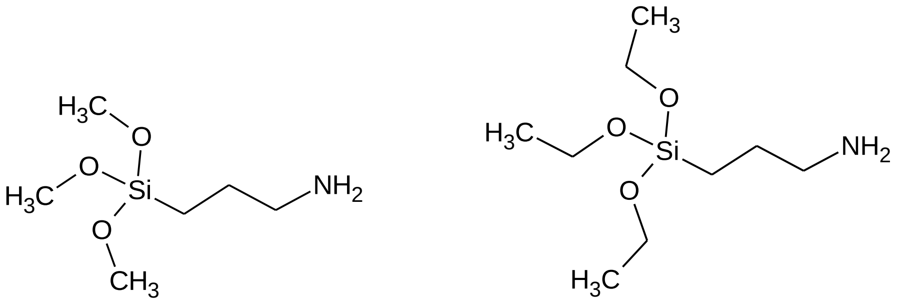
Boranes Boronic acids Borinic acids Boronic esters Boroxines

Figure 1. Examples of organoboron compounds.

Boronic acids are trivalent compounds containing alkyl, alkenyl, alkynyl, or aryl substituent and two hydroxyl groups to fill the empty orbitals of the boron atom.[36] They act as both Bronsted-Lowry and Lewis acids. The nature of the substituent directly bonded to the boron determines their reactivity, specifically the type of carbon directly bonded to the boron.[36] In cross coupling reactions, boronic acids act as electrophiles to react with the nucleophilic heteroatoms. As indicated, boronic acids have special reaction affinity for amino groups. (3-Aminopropyl)trimethoxysilane (APTMS) and (3-aminopropyl)triethoxysilane (APTES) are examples of compounds with amino groups among many others.

Organosubstituted Trialkoxysilanes

There are many organotrialkoxysilane molecules for the modification of silica surfaces. However, (3-aminopropyl)trimethoxysilane (APTMS) and (3-aminopropyl)triethoxysilane (APTES) are widely used by many researchers. The alkoxy groups on the APTES and APTMS are hydrolysable and it is important to carry out such surface modification reactions under anhydrous conditions. Structures of APTES and APTMS are shown in Figure 2.



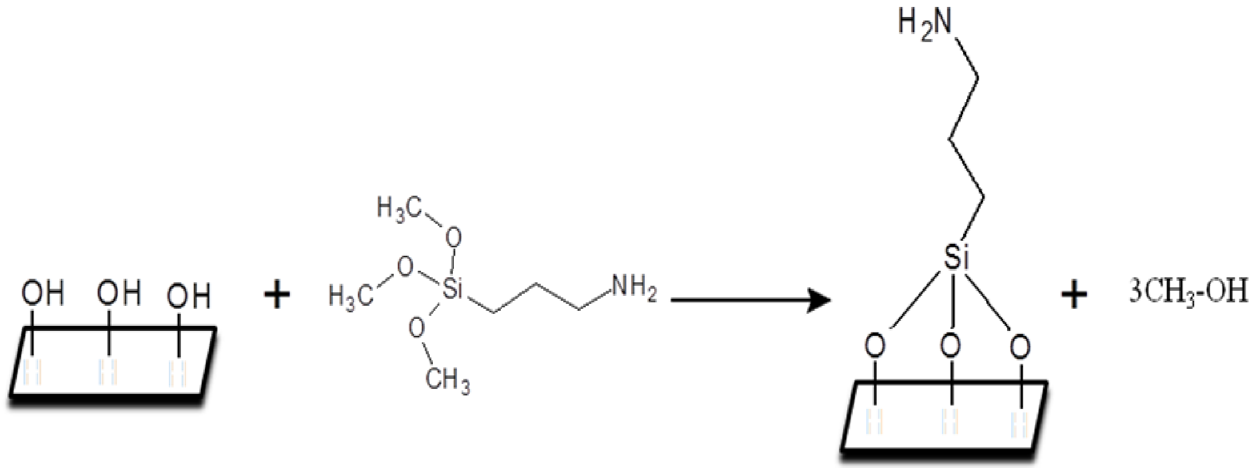
(3-Aminopropyl)trimethoxysilane (APTMS)

(3-Aminopropyl)triethoxysilane (APTES)

Figure 2. Structures of APTMS and APTES

Organotrialkoxysilanes produce silanol groups by hydrolysis. They can be condensed with surface Si–OH group to form stable siloxane bond, Si–O–Si, for surface modification. However, they can also undergo self-condensation to form gel or oily oligomers that precipitate within few hours in the presence of acid or base catalysts.[37] In spite of this, there is an issue as to whether to use the large excess amount of organotrialkoxysilane to maximize the coverage of silica surface or to use a minimum quantity to prevent the formation of any unwanted self-condensed side products.[37] Repetition of centrifugation or redispersion process can help to remove the self-condensation by-product because the actual size of self-condensed products are very small in comparison to the size of SiO_2 particle.[37] Therefore, there is a possibility that these self-condensed products further condense with silanol, Si–OH, groups on the silica surface, resulting in a thick coating layer instead of generating a monolayer.[37]

The thick coating layer of organotrialkoxysilane has the advantage of giving more reactive functional groups for further reaction. However, precise control of the number of surface functional groups cannot be achieved in a reproducible and reliable fashion.[37] The amino groups enhance miscibility and dispersibility and also serve as precursors for the linkage of other functional groups to the surface.[38] For the reaction mechanism, it has been suggested as through the interaction of the amino groups and the silica surface, Si-OH group in an anhydrous condition[39-42] through self-catalytic of the amino groups of APTMS in a polar alcoholic media.[43] At neutral pH, organotrialkoxysilanes cause rapid condensation with Si-OH groups to form insoluble gels.[38] Silica gel surface functionalization reaction is shown in Scheme 8.



Silica gel APTMS Amino-functionalized surface

Scheme 8. Surface functionalization of silica gel.

Several attempts have been made to arylate nitrogen containing compounds in heterogeneous conditions. The reaction was studied with heterogeneous copper catalyst immobilized on silica gel material.[44] However, the catalyst was sufficiently active to arylate N-heterocyclic compounds and benzylamines only at higher temperatures. It was successful to obtain N-aryl compounds in the presence of copper catalyst at solid-phase synthesis. Imidazole and benzimidazole were immobilized on a polymer support, arylated with 4-methylphenylboronic acid, and the products removed from the polymer support. Microwave irradiation increased the reaction rate.[45] It has been demonstrated that solid-phase methodology of N-arylation of sulfonamides and aliphatic amines is very effective.[46, 48]

Earlier publications report Chan-Lam coupling reaction in the presence of a base. Quach and Bartey showed that it was possible to achieve high yield even in base-free medium.[48] The reaction proceeded with $PhBF_3^-K^+$ as arylating agent at room temperature while $PhB(OH)_2$ required mild heating. A possibility to use large variety of boronic acids containing various functional groups can be a novel approach to the synthesis of functionalized materials.

Research Objectives

1. To compare reactivity of boronic acids with different subtituients to surface amino groups.
2. To study the effect of surface modification on porosity.
3. To develop a new efficient method of surface functionalization by base free catalytic Chan-Lam coupling.
4. To test the reactivity of introduced functional groups in their typical organic reactions.

CHAPTER 2

EXPERIMENTAL

Chemicals and Reagents

Some chemicals that were used for the synthetic reactions are listed in Table 1.

Table 1. List of Chemicals used for the various syntheses

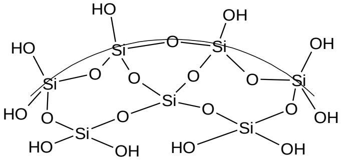
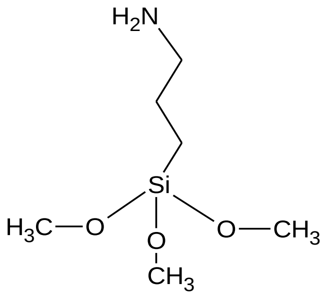
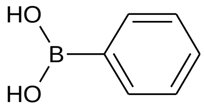
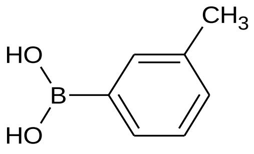
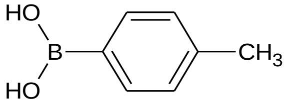
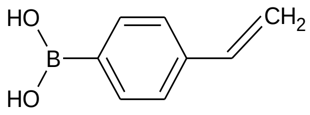
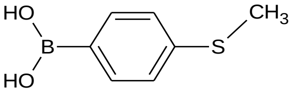
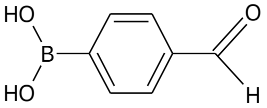
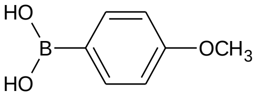
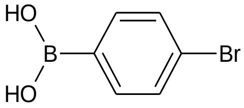
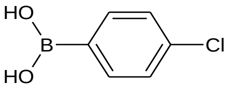
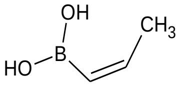
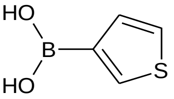
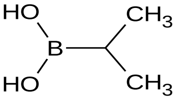
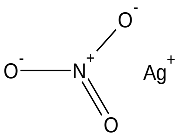
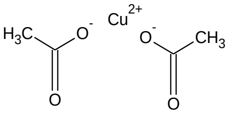
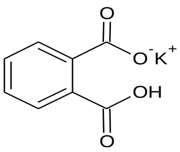
Name	Structure	Characteristics	Manufacturer
Silica gel		100-200 µm Pore size 60 Å Solid particles	EcoChrom Eschwege, Germany
(3-Aminopropyl)-trimethoxysilane		97% pure m.p: 91-92 ^{o}C	Sigma-Aldrich St. Louis, MO
Phenylboronic acid		95% pure m.p: 216-219 ^{o}C	Sigma-Aldrich St. Louis, MO
m-Tolylboronic acid		≥97% pure m.p: 160-162 ^{o}C	Sigma-Aldrich St. Louis, MO
p-Tolylboronic acid		97% pure m.p: 256-263 ^{o}C	Sigma-Aldrich St. Louis, MO
4-Vinylphenylboronic acid		≥95% pure m.p: 190-193 ^{o}C	Sigma-Aldrich St. Louis, MO

Table 1 (continued)

4-(Methylthio)phenylboronic acid		≥95% pure m.p: 210-214 ^{o}C	Sigma-Aldrich St. Louis, MO
4-Formylphenylboronic acid		≥95% pure m.p: 237-242 ^{o}C	Sigma-Aldrich St. Louis, MO
4-Methoxyphenylboronic acid		≥95% pure m.p: 209 ^{o}C	Sigma-Aldrich St. Louis, MO
4-Bromophenylboronic acid		≥95% pure m.p: 284-288 ^{o}C	Sigma-Aldrich St. Louis, MO
4-Chlorophenylboronic acid		≥95% pure m.p: 284-289 ^{o}C	Sigma-Aldrich St. Louis, MO
cis-Propenylboronic acid		≥95% pure m.p: 65-70 ^{o}C	Sigma-Aldrich St. Louis, MO
3-Thienylboronic acid		≥95% pure m.p: 164-169 ^{o}C	Sigma-Aldrich St. Louis, MO
Isopropylboronic acids		≥95% pure m.p: 95-100 ^{o}C	Sigma-Aldrich St. Louis, MO
Silver Nitrate		99+% pure m.p: 212 ^{o}C	Sigma-Aldrich St. Louis, MO
Cupric Acetate		99.7 % pure	Mallinckrodt Paris, KY
Potassium Hydrogen Phthalate		99.98 % pure	Fischer Scientific Fair Lawn, NJ

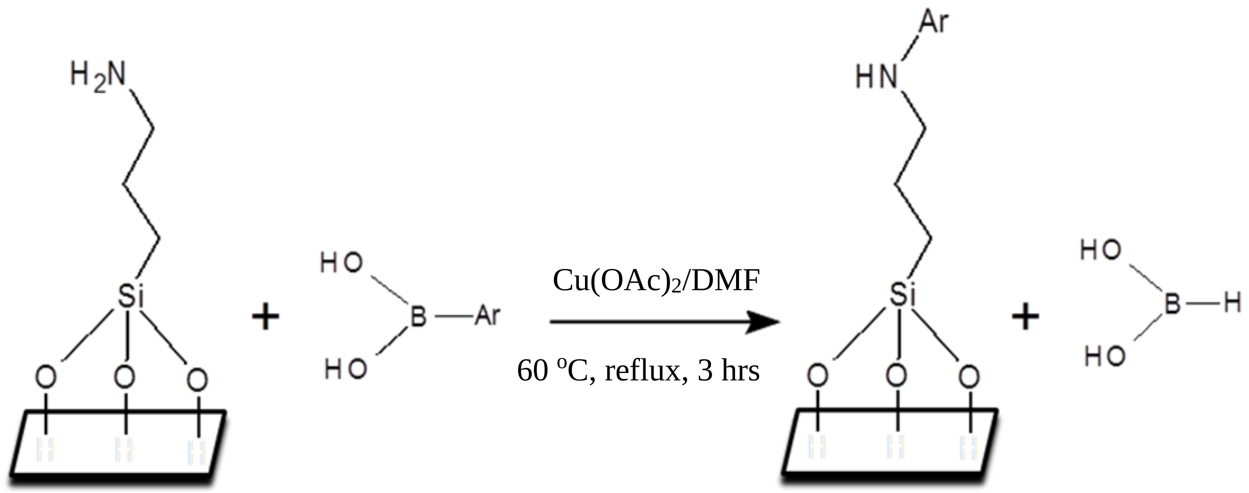
Other solvents and reagents include: *N*,*N*-dimethylformamide, tetrahydrofuran, chloroform, acetic acid, nitric acid, sodium bicarbonate, acetone, ammonium hydroxide, carbon tetrachloride, sodium hydroxide, hydrochloric acid, and diethyl ether.

Surface Modification of Silica Gel with (3-Aminopropyl)trimethoxysilane (APTMS)

A 40 g of APTMS was dissolved in 500 mL of toluene in a 1000 mL flask. A 200 g of silica gel was dispersed in the mixture. It was then thoroughly shaken and stirred continuously for 24 hours using a magnetic stirrer at 80-90 ^{o}C. The reaction mixture was taken off the heat source and allowed to cool gradually to room temperature. It was then filtered using gravity filtration and washed consecutively with 200 mL of acetone and 50 mL of diethyl ether. The product was allowed to dry in air overnight. The reaction of surface modification of silica gel is shown in Scheme 8.

General Synthetic Procedure for N-Arylation

A mass equivalent of 1.64 mmol of the boronic acid was dissolved in 4 mL of 0.04 M copper acetate in DMF solution. The mixture was then transferred into a 100 mL flask with 35 mL of chloroform. It was then stirred for 3 minutes and 1.8 g of amino-functionalized silica gel was added. The composite mixture was stirred with a magnetic stirrer and refluxed continuously for 3 hours. The mixture was taken off the heat source and allowed to cool to room temperature. It was then filtered using vacuum filtration and washed twice with 5 mL portions of chloroform. It was again washed consecutively with 30 mL of 50% acetic acid solution, followed by distilled water until it tested negative to acid, followed by 0.1M $NaHCO_3$, followed by distilled water till tested negative to base. It was then finally washed with 20 mL of acetone and allowed to dry overnight. The N-arylation reaction is shown in Scheme 9.



Amino-functionalized silica gel

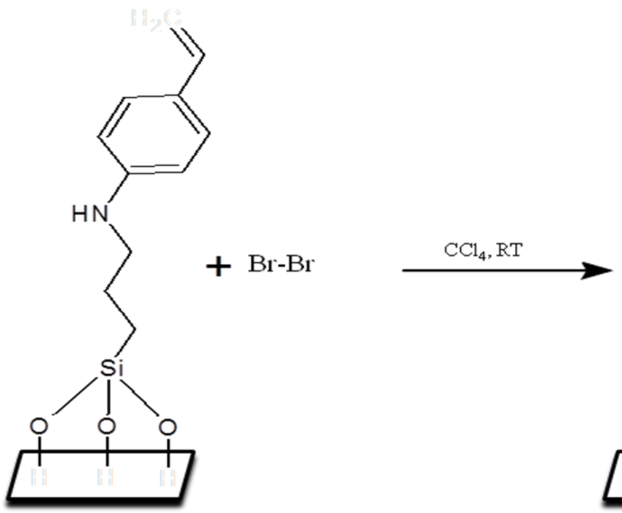
N-arylamino-functionalized silica gel

Scheme 9. N-arylation of amino-functionalized silica gel.

Test Reactions

Bromination of 4-Vinylphenyl- and cis-Propenyl-functionalized Silica Gel

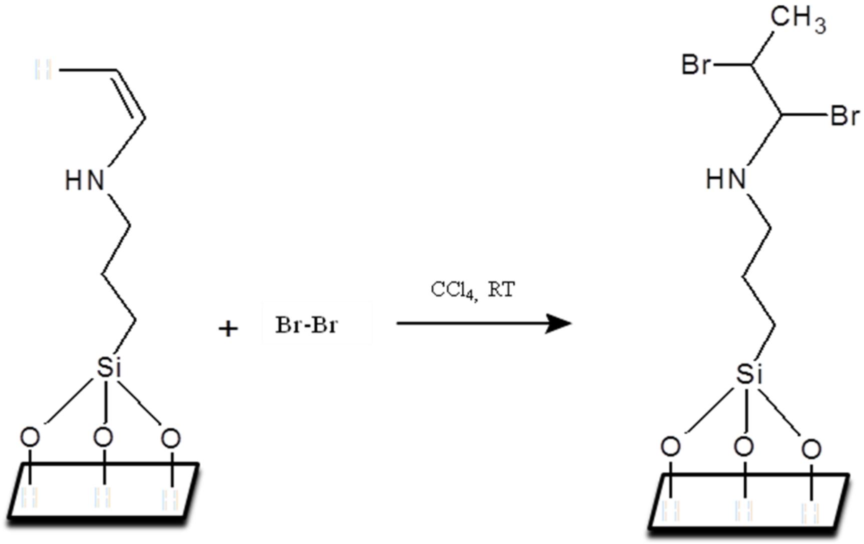
A 0.50 g of 4-vinylphenyl- and 0.50 g of cis-propenyl-functionalized silica gel were dried at 120 °C under vacuum for 1.5 hours. A solution of bromine (1 wt.%) in tetrachloromethane (CCl_4) was prepared. Degassed samples of 0.465 g of 4-vinylphenyl- and 0.452 g of cis-propenyl-functionalized silica gel were dispersed in 10 mL CCl_4 in two separate 50 mL flasks. A 1.0 g and 2.5 g of bromine in CCl_4 solution (1wt.%) were added to the dispersed 4-vinylphenyl- and cis-propenyl-functionalized silica gel respectively. They were stirred continuously overnight with a magnetic stirrer. The dispersions were then vacuum filtered and washed with two portions of 10 mL CCl_4 and allowed to dry in air for 12 hours. The bromination reactions of 4-vinylphenyl- and cis-propenyl-functionalized silica gel are shown in Scheme 10 and Scheme 11 respectively.



4-Vinylphenyl-functionalized silica gel

N-[4-(1,2-dibromoethyl)phenyl]-functionalized silica gel

Scheme 10. Bromine addition to 4-vinylphenyl-functionalized silica gel



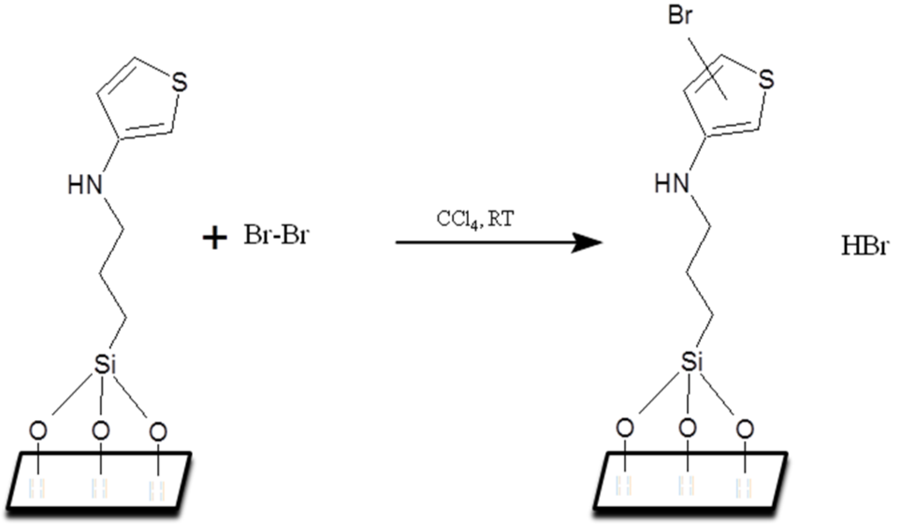
cis-Propenyl-functionalized silica gel

N-(1,2-dibromopropyl)-functionalized silica gel

Scheme 11. Bromine addition to cis-propenyl-functionalized silica gel

Bromination of 3-Thienyl-functionalized Silica Gel

A 0.640 g of 3-thienyl-functionalized silica gel was dried at 120 °C under vacuum for 1.5 hours. After drying, a 0.602 g of the dried sample was dispersed in 10 mL CCl_4 in a 50 mL flask. To this dispersion, 2 mL of bromine in CCl_4 (1 wt. %) was added. It was covered and stirred overnight. The product was filtered and washed with two portions of 10 mL CCl_4 and allowed to dry in air for 5 hours. The substitution reaction of 3-thienyl-functionalized silica gel with bromine is shown in Scheme 12.



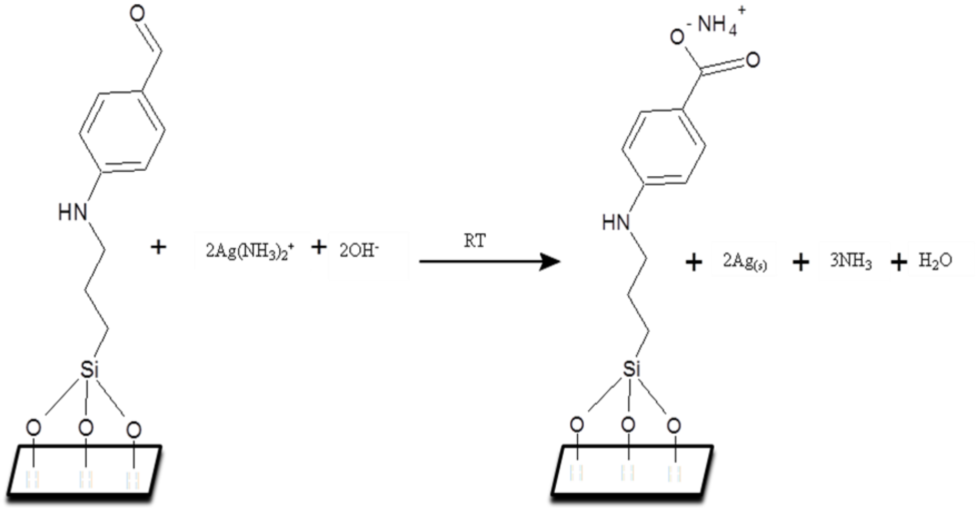
3-Thienyl-functionalized silica gel

Bromo-substituted 3-thienyl-functionalized silica gel

Scheme 12. Bromination of 3-thienyl-functionalized silica gel

Oxidation of 4- Formylphenyl-functionalized Silica Gel by Silver Complex

A 1 wt. % solution of silver nitrate ($AgNO_3$) in ammonia was prepared by dissolving 0.050 g of $AgNO_3$ in 4.950 g of ammonium hydroxide (NH_4OH). A 0.420 g of 4-formylphenyl-functionalized silica gel was dispersed in 9.0 mL of NH_4OH in a flask. A 1.5 mL of $AgNO_3/NH_3$ solution (1 wt.%) was added to the dispersion and the mixture was covered. The mixture was stirred overnight with a magnetic stirrer. The product was filtered and washed with two portions of 10 mL NH_4OH and dried in air. The oxidation reaction of 4-formylphenyl-functionalized silica gel is shown in Scheme 13.



4-Formylphenyl-functionalized silica gel

N-[4-carboxylate)phenyl]-functionalized silica gel

Scheme 13. Oxidation of 4-formylphenyl-functionalized silica gel surface.

Characterization

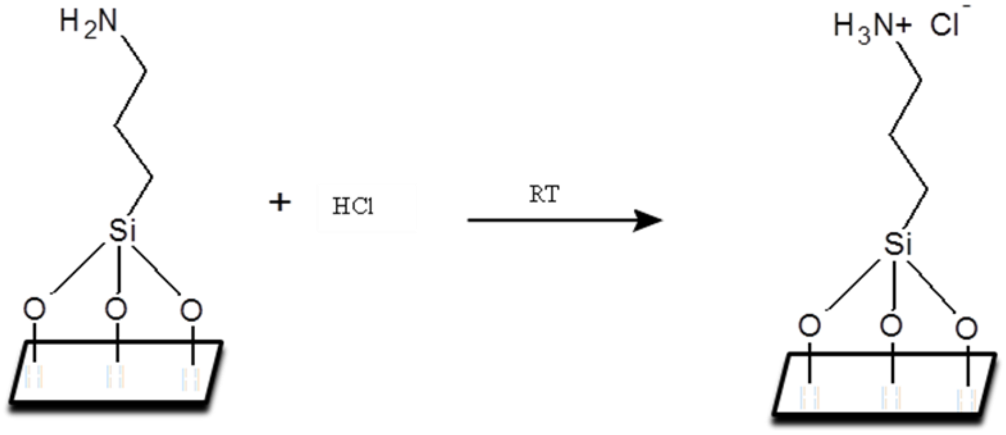
Quantitative Analysis of Amino Groups on Amino-modified Silica Material

The amount of amino groups on the surface of sample **2** was determined by reverse titration with standardized HCl and NaOH. A 1.0 g of sample **2** was dispersed in 23 mL of 0.0848 M HCl and stirred at room temperature for 30 minute (Scheme 14). The mixture was gravity filtered and the filtrate titrated with a 0.1053 M NaOH.

A 0.4167 M of potassium hydrogen phthalate was prepared according to the method[49] and was subsequently used to standardize the NaOH solution.

Elemental Analysis

The contents of carbon, nitrogen, and bromine were calculated from elemental analysis conducted by Robertson Microlit Laboratories (Ledgewood, NJ).



Scheme 14. Reaction of amino groups with HCl

Porosity Measurements

A clean glass tube was filled with the sample of material (0.1–0.4 g) and degassed at 120 °C under vacuum for 3 hours. Their porous characteristics were analyzed with Quantachrome Nova 2200e porosimeter (Boynton Beach, FL). The surface areas were calculated with the Brunauer–Emmett–Teller **(**BET) method, whereas the pore volume and pore size distribution were also calculated with Barrett-Joyner-Halenda (BJH) method.

FT-IR Analysis of Amino-modified and Phenyl-functionalized Silica Materials

FT-IR spectra were obtained for pellets in KBr using a Mattson Genesis II spectrometer (Madison, WI).

Thermal Analysis

Phenyl-functionalized silica gel was studied by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). DSC determines how much energy is required to heat a pan containing a sample compared to an empty reference pan as a function of temperature. TGA measures the weight change of a sample versus temperature. These two thermal analyses were conducted by Robertson Microlit Laboratories (Ledgewood, NJ).

Atomic Absorption Spectroscopy

Quantitative analysis of reduced silver was done using AA-6300 atomic absorption spectrophotometer from Schimadzu Scientific Instruments Inc. (Kyoto, Japan)

A 0.1 g of reacted sample was dispersed in 10 mL of concentrated HNO_3. The mixture was stirred for 2 hours. The mixture was filtered and washed with two portions of 10 mL HNO_3 (making a total volume of 30 mL). To the filtrate, 80 mL of HNO_3 was added and transferred to a flask containing 110 mL of distilled water. This made a total volume of 220 mL. Standard solutions of 1 ppm, 2 ppm, 3 ppm, and 4 ppm of $AgNO_3$ were prepared for the purposes of calibration.

CHAPTER 3

RESULTS AND DISCUSSION

Synthesis

Aminopropyl-modified Silica Gel

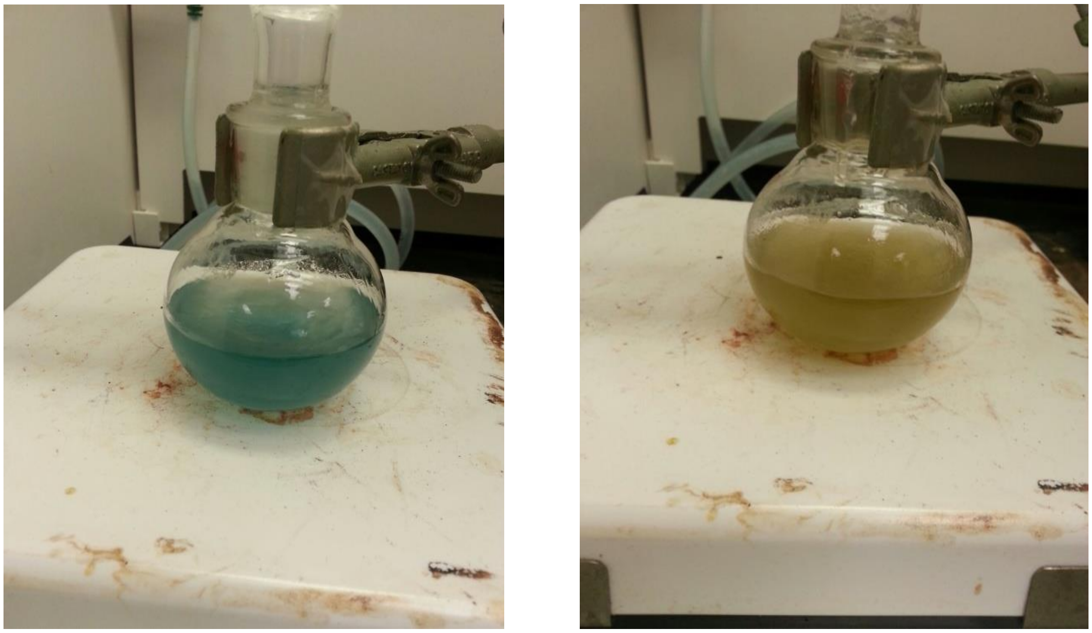
After the modification of silica gel with APTMS, the white solid particles turned creamy color. Calculations from elemental analysis data showed that 0.97 mmol/g of amino groups were grafted on the surface of the silica gel, which corresponds to surface density of 1.57 molecules/nm^2.

Quantitative Analysis of Amino Groups on Amino-modified Silica Material

After dispersing 1 g of amino-modified silica material in 23 mL of 0.0848 M HCl, a result obtained by titration of unreacted HCl with NaOH showed 0.993 mmol of HCl. Hence, 0.9574 mmol of amino groups reacted with the HCl.

Functionalized Materials

During the syntheses the initially blue solution gradually changed color to yellow (Figure 3). This was observed for all the boronic acids used. However, with the 3-thienylboronic acid synthesis, the mixture was initially blue and gradually turned brown. The brown color intensified with time. In all the syntheses, nine arylboronic acids containing various substituents, one heterocyclic boronic acid and two aliphatic boronic acids reacted with the amino groups in sample **2**. The extent of reaction was calculated using data from elemental analysis (Table 2). As revealed by increase of C/N ratio, all boronic acids reacted with **2.** The degree of immobilization varied depending on the nature and size of substituent. Non-substituted phenylboronic acid (sample **3**) reacted to a largest extent with the amino groups (fraction of amino groups reacted 0.3). Among the substituted phenylboronic acids, 4-halophenylboronic acids were the most reactive whilst p-tolylboronic acid was less reactive (fraction of amino groups reacted 0.10). Aliphatic boronic acids (samples **13** and **14**) were also very reactive with the amino groups. Figure 3 shows visual evidence of the synthesis.



(a) Start of the synthesis (b) End of the synthesis

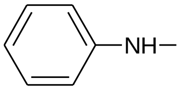
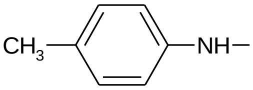
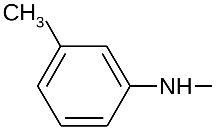
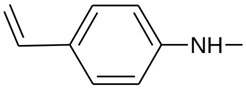
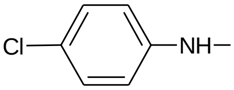
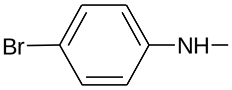
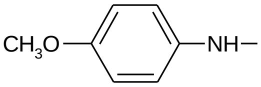
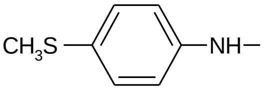
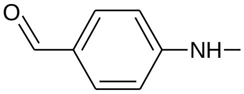
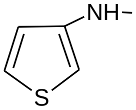
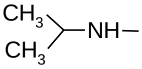
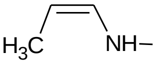
Figure 3. Reaction mixture at the start and the end of the synthesis

Characterization

Porous Structure of the Materials.

Functionalization of the silica surface significantly changed the porous structure of silica gel. All functionalized silica materials had reduced surface areas and pore volumes compared to unmodified silica gel (Table 2). It can be seen from the table that among the functionalized silica materials **12** recorded the largest surface area (372 m^2/g) whilst **7** had the lowest surface area (352 m^2/g). Sample **14** also showed very high pore volume (0.651 cm^3/g); however, **5** recorded the least pore volume (0.464 cm^3/g). Pore size distribution showed that the modification mostly affected large pores (>25 Å).

Table 2. Characteristics of the functionalized silica gels

#	Functional group	C/N ratio	Fraction of NH_2 groups reacted	Surface density, molecules/nm^2	S_{BET}, m^2/g	Pore volume, cm^3/g	Average pore radius, Å
1	None	-	-	-	457	0.748	33.1
2	NH_2-	3.1	-	1.57	371	0.653	33.1
3		4.8	0.30	1.16	362	0.640	22.8
4		3.7	0.10	0.16	365	0.563	22.9
5		3.9	0.13	0.22	355	0.464	22.9
6		3.9	0.11	0.16	365	0.643	22.8
7		4.1	0.18	0.30	352	0.616	22.9
8		4.3	0.23	0.38	358	0.613	22.9
9		3.8	0.11	0.18	365	0.554	22.9
10		3.7	0.10	0.16	357	0.632	22.9
11		3.8	0.11	0.18	353	0.562	22.9
12		3.6	0.15	0.24	372	0.550	22.9
13		3.6	0.20	0.33	358	0.639	22.7
14		3.6	0.29	0.49	360	0.651	22.8

Changes in the pore volume correlated with the substituent size: it was the highest for bulky 3-methylphenyl substituent while smaller phenyl, isopropyl, and *cis*-propenyl substituents affected this characteristic in much lesser degree. Adsorption isotherms of the samples proved that all modified samples were mesoporous (Figure 4).

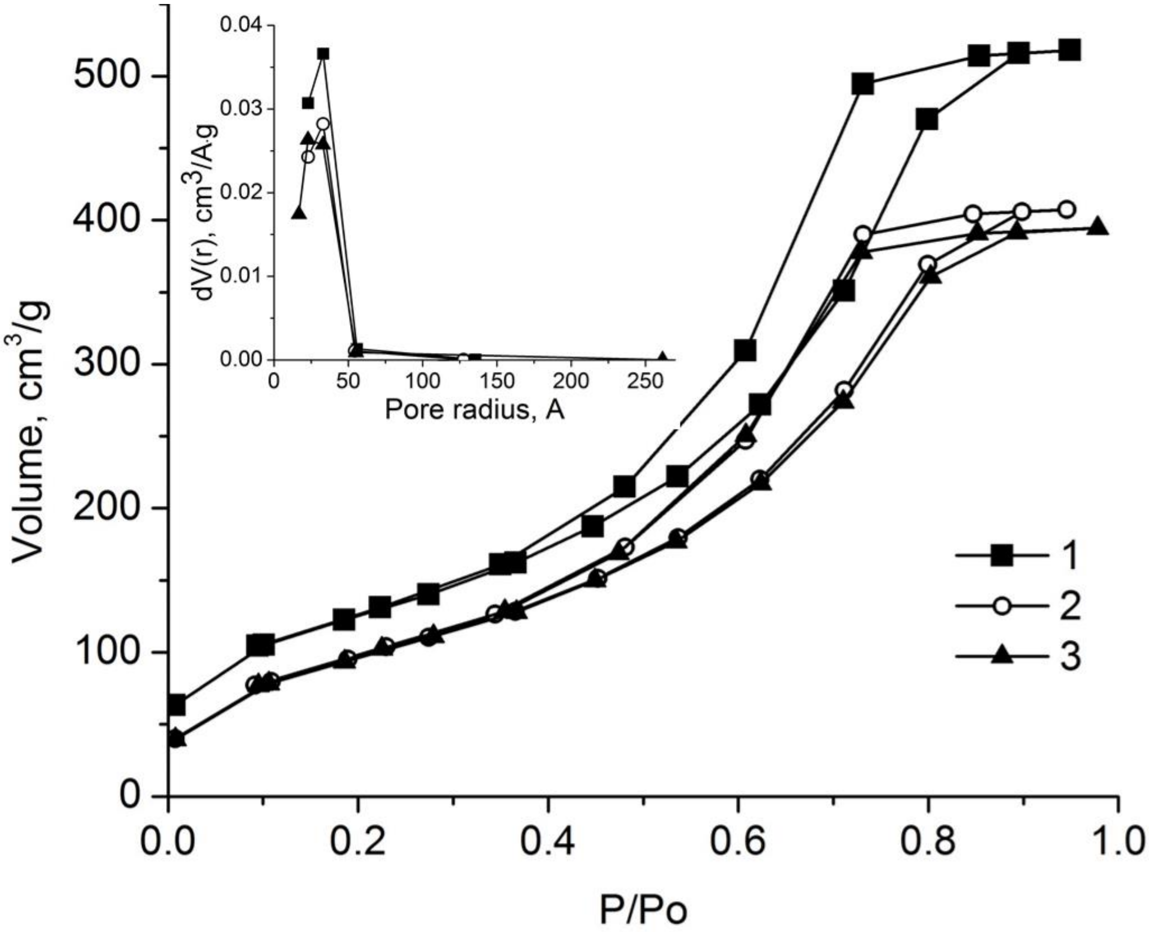


Figure 4. Nitrogen adsorption isotherms and pore size distributions of samples

FT-IR Analysis of Amino-modified and Phenyl-functionalized Silica Materials

A weak shoulder at 3050 cm^{-1} was detected in the spectrum of sample **3.** This corresponds to C(Ar)-H vibrations. This shoulder was not present in the spectrum of sample **2** (Figure 5).

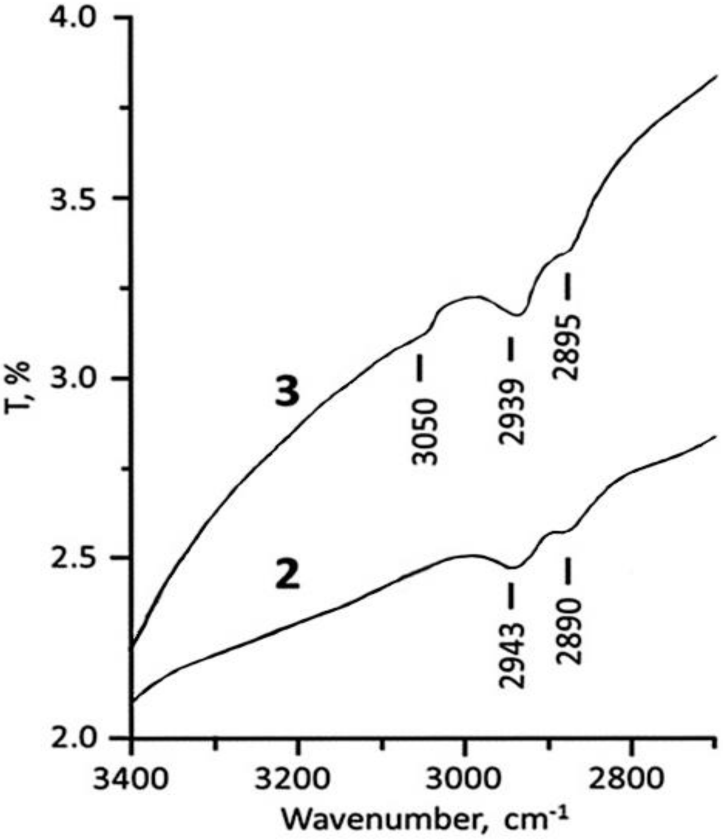


Figure 5. FT-IR spectra of samples **2** and **3**.

DSC Analysis of Phenyl-functionalized Silica Gel

Differential Scanning Calorimetry (DSC) thermogram obtained for sample **3** showed five endothermic peaks and two exothermic peaks (Figure 6 a). The temperatures (°C) and thermal effects (ΔH, J/g) of these thermal events are: 205 (7.13), 207 (4.05), 223 (41.3), 226 (12.15), 300 (37.36), 513 (-29.6) and 539 (-59.9).

TGA Analysis of Phenyl-functionalized Silica Gel

Thermogravimetric analysis (TGA) of sample **3** also shows that upon heating the sample to 700 ^{o}C the sample lost a total weight of 9.4 % (Figure 6 b). The sample lost 2.0 % of its weight between 25 to 200 ^{o}C and 7.4 wt.% above 200 ^{o}C.

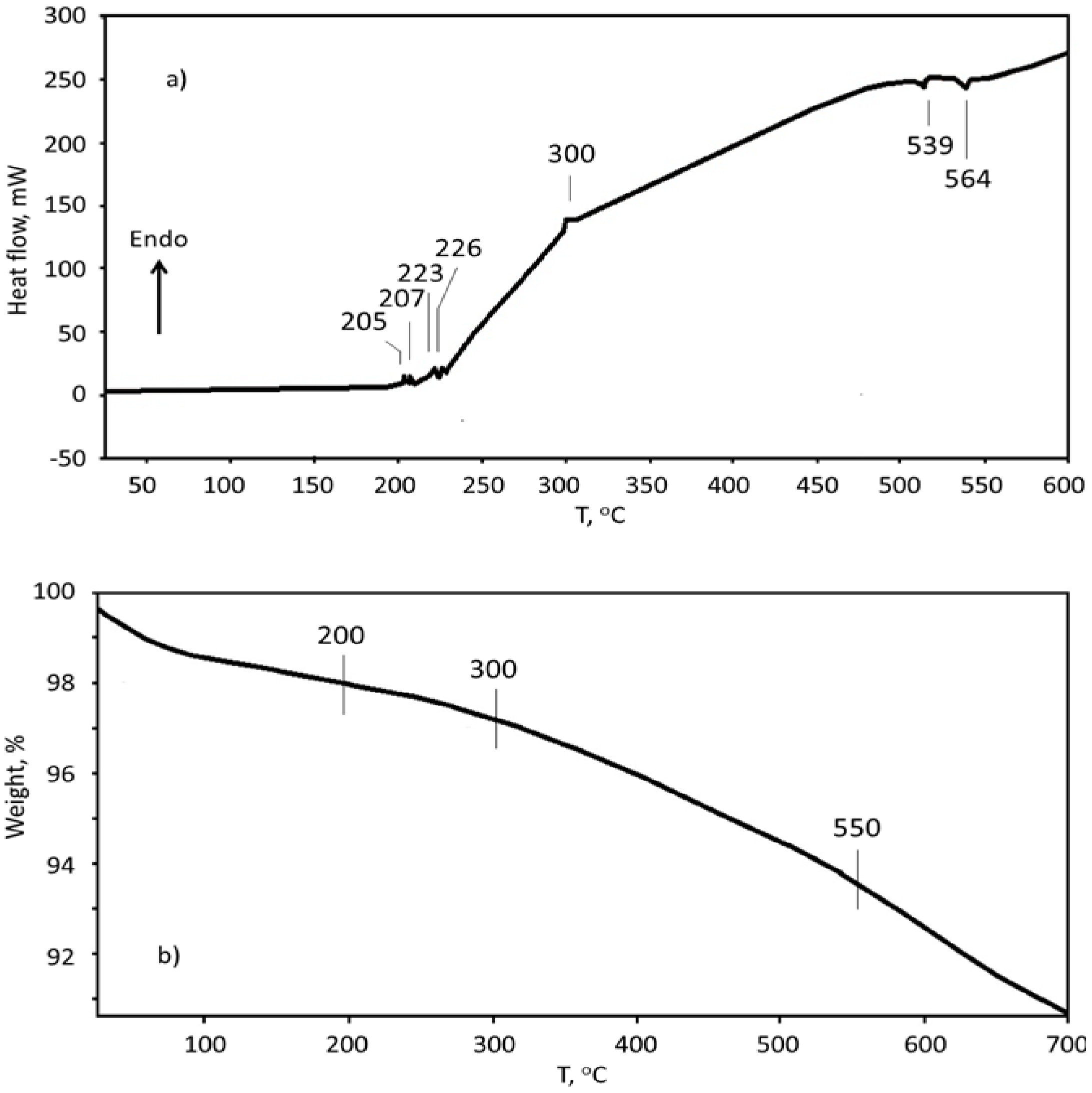


Figure 6. DSC (a) and TGA (b) thermograms of phenyl-functionalized silica gel

Test Reactions

Some characteristic organic reactions were conducted to ascertain the extent of success of the surface functionalization of the silica gel. Alkenyl-functionalized silica materials (samples **6** and **14**) were tested with bromine addition reaction and 3-thienyl-functionalized silica material (sample **12**) was tested with electrophilic substitution reaction with bromine. Furthermore, formyl-functionalized silica material (sample **11**) was also oxidized with Tollen’s reagent.

Addition of Bromine

The samples **6** and **14** demonstrated high reactivity to the molecular bromine. The solution decolorized within 1 minute that showed fast diffusion of Br_2 molecules to the reaction sites. Contents of bromine in the products were 1.84% and 3.08%, respectively. This corresponds to the yields of 100% for **6** and 67% for **14** in respect to the contents of alkenyl groups. Introduction of two bromine atoms on the surface molecules significantly decreased BET surface areas from 365 to 304 m^2/g (sample **6**) and from 360 to 301 m^2/g (sample **14**).

Electrophilic Substitution with Bromine

Sample **12** was tested in the reaction of electrophilic substitution with bromine. This reaction is known to be about 10^9 times faster for electron-rich thiophene ring than for non-substituted benzene ring.[50] The solution quickly decolorized. The content of bromine in **12** after substitution was 3.47%. Considering molar content of thienyl groups, it is evident that polybromination of the ring took place. It was not surprising because the presence of electron-donating –NH substituent on the thiophene ring should significantly increase its reactivity. The surface area of the sample **12** decreased from 372 to 330 m^2/g after bromination.

Oxidation of 4-Formylphenyl-functionalized Silica Gel with Tollen’s Reagent

The amount of formyl groups on the functionalized silica gel that were oxidized was calculated from data obtained by atomic absorption spectroscopy analysis of reduced silver.

Sample **11** was oxidized by silver-ammonia solution. The reaction effectiveness was determined from the amount of metallic silver precipitated on the product. It was found that content of Ag was 0.043 mmol/g that corresponds to 20% yield. BET surface area after oxidation decreased from 353 to 325 m^2/g. Data obtained from atomic absorption spectroscopy of dissolved Ag are shown in Table 3 and its corresponding calibration curve in Figure 7.

Table 3. Data from the atomic absorption spectrophotometry analysis of silver

Concentration (ppm)	Absorbance
1	0.0416
2	0.0736
3	0.1176
4	0.1422
Analyte	0.0808

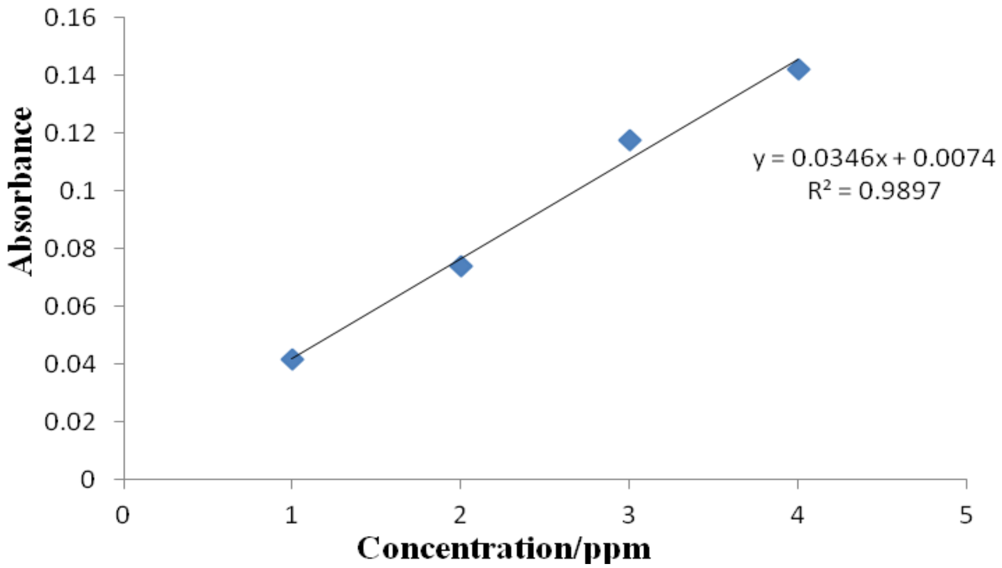


Figure 7. A plot of calibration curve for silver analysis.

Discussion

Synthesis

As mentioned, the reaction mixture changed color from bluish green at the start of the reaction to yellow. This may be due to a change in oxidation state of copper that is characteristic of Chan-Lam coupling mechanism

Calculated results from both elemental analysis and titration showed that amino modification of the silica gel was successful. Data from titration showed that 0.9574 mmol/g of amino groups was immobilized on the silica gel. This value is in good agreement with results calculated from elemental analysis (0.97 mmol/g of amino groups).

As indicated, the results obtained from elemental analysis data (Table 2) reveal that all the boronic acids reacted with the amino groups. The reactivity varied depending on the nature and size of substituent. It should be noted that the yield in this reaction depends on not only relative reactivity of boronic acids but also steric hindrances in mesopores. Smaller molecules of isopropylboronic acid and *cis*-propenylboronic acid may reach the reaction sites easier hence comparatively higher fractions of amino groups reacted with them. (0.2 and 0.29 respectively)

Characterization

Determination of the presence of aryl group in the samples using FT-IR spectroscopy was difficult due to low contents of these groups and as a result, very weak characteristic peaks. A weak shoulder at 3050 cm^{-1} on the spectrum of sample **3** (Figure 5) corresponds to C(Ar)-H vibrations. This characteristic peak was absent on the spectrum of sample **2** (Figure 5). This gave a clear indication that the arylation was successful.

Having heated the sample from 25 to 600 ^{o}C showed five endothermic peaks and two exothermic peaks. Decomposition at peak 300 °C is characteristic of 3-aminopropyl groups on the surface.[51] Other peaks at lower temperature are not present in thermograms of 3-aminopropyl-functionalized silica gel and these endothermic peaks can be attributed to decomposition of N-phenyl-3-aminopropyl groups. The step starting at 200 °C is typical for glass transition effect. However, considering gradual loss of weight at this temperature, it is more probably that this effect occurred due to loss of organic phase and, as a result, changing of the material heat capacity.

TGA analysis revealed that the sample lost 2.0 wt.% between 25 and 200 ^{o}C that could be attributed to desorption of gases and partial dehydroxylation of silica gel. Organic phase is stable within this temperature range. However, above 200 ^{o}C, the organic component grafted on the silica surface begun to decompose and resulted in a weight loss of 7.4%, which is in good agreement with data from elemental analysis on C, H, and N (5.19%; 1.40% and 1.29%, respectively) corresponding to a total amount of organic phase 7.88%

Test Reactions

Results from all the test reactions point to the success of the functionalization. Bromination of **6** and **14** that gave 100% and 67% yield can be attributed to a high reactivity of double bonds towards bromine. Comparing **6** and **14**, the π-electrons in the aromatic ring (sample **6**) also increased the electron density of the vinyl substituent subsequently increasing its reactivity towards bromine resulting in 100 % yield where as **14** do not have the aromatic ring, which resulted in 67 % yield. Bulkier bromine groups also decreased the surface area of the functionalized silica gel.

The electrophilic substitution reaction of bromine and thiophene also showed polybromination of the thiophene ring contrary to monobromination as expected. The –NH group increased its electron density thereby increasing its reactivity towards bromine. Again, bulkier bromine groups reduced the surface area of the functionalized silica gel.

Oxidation of formyl groups by silver was also successful even though it proceeded with a 20 % yield. The decrease of surface area in this case occurred due to not only transformation of CHO groups into bigger COOH groups but also formation of silver aggregates in the pores.

CHAPTER 4

CONCLUSION

A new efficient method of surface functionalization by the Chan-Lam coupling was successfuly developed. Reactivity of boronic acids depended on the substituent nature and steric hindrances. Obtained functionalized materials were mesoporous though their surface areas and pore volumes decreased after the functionalization. Immobilized functional groups demonstrated high reactivity in their typical reactions under mild conditions. In spite of the succeful application of this method to functionalize silica gel, it can not be applied for introducing functional groups that are reactive to boronic acids in the synthesis conditions, i.e., OH, NH_2 or COOH.

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