1-1-1996

Synthesis and Characterization of Bifunctional Silica Gel Surfaces

Alufelwi Maxwell Tshavhungwe

Eastern Illinois University

This research is a product of the graduate program in Chemistry at Eastern Illinois University. Find out more about the program.

Recommended Citation

http://thekeep.eiu.edu/theses/1857

This Thesis is brought to you for free and open access by the Student Theses & Publications at The Keep. It has been accepted for inclusion in Masters Theses by an authorized administrator of The Keep. For more information, please contact tabruns@eiu.edu.
THESIS REPRODUCTION CERTIFICATE

TO: Graduate Degree Candidates (who have written formal theses)

SUBJECT: Permission to Reproduce Theses

The University Library is receiving a number of requests from other institutions asking permission to reproduce dissertations for inclusion in their library holdings. Although no copyright laws are involved, we feel that professional courtesy demands that permission be obtained from the author before we allow theses to be copied.

PLEASE SIGN ONE OF THE FOLLOWING STATEMENTS:

Booth Library of Eastern Illinois University has my permission to lend my thesis to a reputable college or university for the purpose of copying it for inclusion in that institution's library or research holdings.

I respectfully request Booth Library of Eastern Illinois University not allow my thesis to be reproduced because:

____________________________________________________________

____________________________________________________________

____________________________________________________________

____________________________________________________________

____________________________________________________________

Author ____________________________ Date ________________

08.26.96
SYNTHESIS AND CHARACTERIZATION OF

BIFUNCTIONAL SILICA GEL SURFACES

(TITLE)

BY

ALUFELWI MAXWELL TSHAVHUNGWE

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTERS OF SCIENCE IN CHEMISTRY

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1996

YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
THIS PART OF THE GRADUATE DEGREE CITED ABOVE

[Signatures]

DATE

DATE
THESIS

Synthesis and Characterization of Bifunctional Silica Gel Surfaces

by

Alufelwi Maxwell Tshavhungwe

Research Advisor: Dr. Jonathan P. Blitz

Submitted: July 31, 1996

Oral defense: August 14, 1996

Thesis Committee:

Dr. Jonathan P. Blitz (Advisor) 8/21/96

Dr. Richard L. Keiter 8/26/96

Dr. Mark E. McGuire 8-21-96

Dr. Daniel J. Sheeran 8/21/96
ABSTRACT

Bifunctional silica surfaces consisting of various combinations of the following organofunctional silanes were synthesized and characterized using diffuse reflectance infrared spectroscopy: hexamethyldisilazane, octyldimethylmethoxysilane, phenyldimethylmethoxysilane, (3-aminopropyl)-dimethylmethoxysilane, (2-cyanoethyl)triethoxysilane, and trimethylmethoxysilane.

The relative amounts of organosilanes loaded on a silica surface were obtained from band area ratios of IR bands. Ratios of organosilanes bonded to the same silica surface were calculated from normalized band areas of the isolated silanol peak. In reactions in which surface coverage was incomplete, the relative amount of inaccessible silanols was determined from the band area ratio of the silanol peak. Comparisons of organosilane loading when reactions were done in one and two steps were also made. It was found that for reactions which are incomplete when the second organosilane is a relatively bulky group, better surface coverage is obtained when silylation reactions are done using a mixture of organosilanes.
DEDICATION

In memory of my Dad.
ACKNOWLEDGEMENTS

Special thanks to my wife, my son and two daughters, my mom and other members of the family for their encouragement and unwavering moral support.

I wish to extend my sincerest gratitude and thanks to Dr Jonathan P. Blitz, my research director, for his expert guidance and assistance during the entire research.

I would like to thank members of the thesis committee - Drs Richard L. Keiter, Mark E. McGuire and Daniel J. Sheeran - for their constructive critique of the thesis.

The support provided by the following organizations is highly appreciated:

Eastern Illinois University Faculty Research Fund for funding the research described herein.

The South African Education Program, a scholarship program administered by the Institute of International Education and funded by the United States Agency of International Development, for awarding a scholarship to me.

Eastern Illinois University's International Student Services Program for providing tuition waiver.

Finally, I would like to thank Chemistry Faculty and
Staff at EIU, and other members of Dr Blitz's research group for making my stay at Eastern a memorable one.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>i</td>
</tr>
<tr>
<td>Dedication</td>
<td>ii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iii</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>v</td>
</tr>
<tr>
<td>List of Figures</td>
<td>viii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xi</td>
</tr>
<tr>
<td>1 Introduction and background</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Surface modification reactions</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1 The nature of silica surface</td>
<td>2</td>
</tr>
<tr>
<td>1.2.2 Silylating agents</td>
<td>3</td>
</tr>
<tr>
<td>1.2.3 Silylation reactions</td>
<td>5</td>
</tr>
<tr>
<td>1.2.4 Amine catalysis</td>
<td>8</td>
</tr>
<tr>
<td>1.2.5 Steric hindrance</td>
<td>9</td>
</tr>
<tr>
<td>1.3 Potential utility of mixed functional silica surfaces</td>
<td>9</td>
</tr>
<tr>
<td>1.4 Characterization of silica surfaces</td>
<td>15</td>
</tr>
<tr>
<td>1.5 Purpose of this study</td>
<td>19</td>
</tr>
<tr>
<td>2 Experimental section</td>
<td>21</td>
</tr>
</tbody>
</table>
2.1 Introduction ................................... 21
2.2 Materials ...................................... 21
2.3 Instrumentation ............................... 22
2.4 General considerations ......................... 22
   2.4.1 Synthesis .................................. 23
   2.4.2 Characterization .......................... 26
2.5 Procedures ..................................... 27
   2.5.1 Synthesis of monofunctional silica surfaces ...................... 27
   2.5.2 Synthesis of bifunctional silica surfaces ......................... 28
   2.5.3 Reaction of HMDS and PDES with silica in one step .......... 29

3 Results and discussion .............................. 30
3.1 Monofunctional silica .......................... 30
3.2 Bifunctional silica ............................ 48
3.3 Investigation of the lack of a complete reaction .................. 73
3.4 Comparison of one-step and two-step reaction .................. 79
3.5 Conclusions .................................... 82
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic showing various silanol groups</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic showing silylation reactions</td>
<td>7</td>
</tr>
<tr>
<td>1.3</td>
<td>Optical layout for diffuse reflectance spectroscopy</td>
<td>17</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic showing silylation of silica with two organosilanes</td>
<td>25</td>
</tr>
<tr>
<td>3.1</td>
<td>DRIFTS spectra of unmodified, 200°C- and 600°C-treated Davison-948 silica</td>
<td>31</td>
</tr>
<tr>
<td>3.2</td>
<td>DRIFTS spectra of HMDS-modified silica</td>
<td>36</td>
</tr>
<tr>
<td>3.3</td>
<td>Plots of CH and SiOH percent band area ratios of HMDS-modified silica versus HMDS concentration</td>
<td>39</td>
</tr>
<tr>
<td>3.4</td>
<td>DRIFTS spectra of ODMS-modified silica</td>
<td>40</td>
</tr>
<tr>
<td>3.5</td>
<td>Plots of CH and SiOH percent band area ratios of ODMS-modified silica versus ODMS concentration</td>
<td>41</td>
</tr>
<tr>
<td>3.6</td>
<td>DRIFTS spectra of PDES-modified silica</td>
<td>43</td>
</tr>
<tr>
<td>3.7</td>
<td>Plots of CH and SiOH percent band area ratios of PDES-modified silica versus PDES concentration</td>
<td>44</td>
</tr>
<tr>
<td>3.8</td>
<td>Percent band area ratios of SiOH reacted with various organosilanes</td>
<td>47</td>
</tr>
<tr>
<td>3.9</td>
<td>DRIFTS spectra of HMDS/APDMS-modified silica</td>
<td>49</td>
</tr>
</tbody>
</table>
3.10 DRIFTS spectra of HMDS/CETS-modified silica........50
3.11 Percent band area ratios of SiOH reacted
with HMDS and either APDMS or CETS...............52
3.12 Plot of CH percent band area ratios on
HMDS/APDMS-modified silica versus HMDS
concentration........................................54
3.13 Plot of CN percent band area ratios of silica
modified with HMDS and CETS versus HMDS
concentration........................................55
3.14 DRIFTS spectra of ODMS/APDMS-modified silica........57
3.15 DRIFTS spectra of ODMS/CETS-modified silica........58
3.16 Percent band area ratios of SiOH reacted
with ODMS and either APDMS or CETS.................59
3.17 Plot of CN band area ratios of ODMS/cyano-
modified silica versus ODMS concentration.........60
3.18 DRIFTS spectra of PDES/CETS-modified silica........61
3.19 Plot of CN band area ratios of PDES/CETS-
modified silica versus PDES concentration........62
3.20 Percent band area ratios of SiOH on PDES/CETS-
modified silica reacted with PDES and CETS........63
3.21 DRIFTS spectra of HMDS/PDES-modified silica........66
3.22 DRIFTS spectra of ODMS/PDES-modified silica........67
3.23 Percent band area ratios of SiOH on HMDS/PDES-modified silica reacted with HMDS and PDES........68
3.24 Percent band area ratios of SiOH on ODMS/PDES-modified silica reacted with ODMS and PDES........69
3.25 Normalized band area ratios of SiOH reacted with APDMS and CETS........................................71
3.26 Normalized band area ratios of SiOH reacted with PDES..........................................................72
3.27 DRIFTS spectra of silica surfaces prepared by reacting HMDS-modified silica with an excess of various organosilanes .........................................................75
3.28 DRIFTS spectra of silica surfaces prepared by reacting PDES-modified silica with various organosilanes.............................................................77
3.29 DRIFTS spectra of silica surfaces prepared by reacting 0.1 mmol/g HMDS and 5 mmol/g PDES in one step and in two steps........................81
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Bifunctional silica surfaces prepared</td>
<td>24</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 Introduction

Surface-modified silica gels are an extremely useful and versatile class of materials for numerous and wide-ranging applications such as stationary phases for chromatography, catalysis, inorganic polymer fillers, ion collection, drug-delivery agents, immobilized enzymes, and antimicrobials. References to these applications were cited elsewhere (1,2). The chemical and physical properties of the silica surface are largely responsible for the widespread utility of these surfaces (3).

An organosilane is reacted with silica surface silanols to impart desirable chemical properties to the surface. By variation of the functional group on the organosilane, surface properties can be varied. Potentially useful surface properties can be obtained by reaction of the silica surface with two or more organofunctional silanes. Interesting mixed acid-base properties for heterogeneous catalysts, and chromatographic stationary phases with enhanced selectivity can be envisioned. The relative ratios of the organosilanes on the surface can be varied, thus surface properties can be
In this thesis, the synthesis of silica surfaces modified with two different organofunctional groups is described. The surfaces were quantitatively characterized by diffuse reflectance infrared spectroscopy (DRIFTS).

1.2 Surface-modification reactions

Basic concepts relating to silica-silane reactions are described in the following sections. Detailed descriptions and exhaustive reviews can be found in Iler's book (3). An overview of the subject was presented by Bergna (4).

1.2.1 The nature of silica gel surface

The surface of silica gel consists of silicon atoms bonded to each other through siloxane (Si-O-Si) bonds and to hydroxyl groups forming silanols (Si-O-H)(3-5). The silanol groups dominate the chemistry of the hydroxylated silica surface and provide sites for attachment of silane coupling agents. There are vicinal (hydrogen-bonded or associated), isolated (unassociated), and geminal (silanediols) silanol groups (see Figure 1.1). The silanols, being hydrophillic, are often associated with water molecules by hydrogen bonds.
(6). The reactivity and thermal stability of the silanols differ. Silanediols, which constitute about 15% of the total silanols on a fully hydroxylated silica surface (4,7,8), are more reactive than isolated silanols (9,10), which in turn are more reactive than vicinal silanols (11-13). Silanediols and isolated silanols are thermally more stable than vicinal silanols (3,4).

1.2.2 Silylating agents

Organosilanes of type $R_{4-n}SiX_n$ (n=1, 2 or 3), where $R$ is an alkyl or substituted alkyl group and $X$ is a hydrolyzable group such as a halogen (mostly chlorine) or alkoxy group, are commonly used to modify silica surfaces (3,5). The alkyl group ($R$) imparts various chemical properties to the surface. The selectivity of a chromatographic stationary phase can be varied by changing the organic moiety ($R$) (14). Alkylalkoxysilanes are more stable, less reactive and easier to handle than alkylchlorosilanes. The byproduct of silanization reactions when silylating agents are alkoxy silanes are alcohols, which are less harmful compared to corrosive HCl produced when silylating agents are chlorosilanes.
(a) Hydrogen-bonded silanols

```
  H   H   H
 / \ / \ /
 O   O   O
|   |   |
Si   Si   Si
```

(b) Isolated silanols

```
  H   H   H
 |   |   |
 O   O   O
|   |   |
Si   Si   Si
```

(c) Silanediols

```
  H   H
 \ / \
 O   O
 \ /
 /\  
Si
```

Figure 1.1. Schematic showing various silanol groups.
Disilazanes (R₃Si-NH-SiR₃) are also used to modify silica surfaces. For example, hexamethyldisilazane (HMDS) reacts with silica to give trimethylsilyl groups on the silica surface (9,15-18).

1.2.3 Silylation reactions

Silica gel is subjected to thermal treatment before and after it is reacted with an alkoxyisilane. The degree of hydration and hydroxylation is determined by the temperature during thermal pretreatment (3,4). Hydrogen-bonded water on the silica surface and water that may be adsorbed in micropores is removed by heating silica gel to 180°C. Thermal treatment to 600°C result in vicinal silanols condensing to form siloxane bonds and water, leaving isolated silanols and silanediols on the silica surface. When a chain of vicinal silanols containing an odd number of silanols condense, a siloxane bridge, an isolated silanol and water are formed:

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
/ & / & / & \text{H} \\
\text{O} & \quad \text{O} & \quad \text{O} & \rightarrow \quad \text{O} & \quad \text{O} & + \text{H}_2\text{O} \\
\text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} & \quad \text{Si} \quad \text{Si} & \quad \text{Si}
\end{align*}
\]
Condensation of an odd number of vicinal silanols result in an increase in the number of isolated silanols.

Organoalkoxysilanes, in vapor phase or in a suitable organic solvent, react with surface silanols to form a bonded phase of the siloxane (Si-O-Si) type. Depending on the number of alkoxy groups on each organoalkoxysilane, there are various ways in which the organoalkoxysilane can be bonded to the silica surface (Figure 1.2) (1,3). Reactions shown are for reactions done in dry conditions, and assume that alkoxy groups not bonded to the surface do not hydrolyze. If these groups are hydrolyzed, they provide sites for attachment of other organosilanes, resulting in cross-linked phases or the formation of a polymer. A base is sometimes required to catalyze silanization reactions.

In the presence of water, the organoalkoxysilane is hydrolyzed before it reacts directly with the surface. Hydrolysis of di- and trialkoxysilanes result in the formation of silanediols and silane triols, which may condense slowly to form polymeric organic siloxanols. Siloxanols subsequently react with the silica surface. Monoalkoxysilanes are incapable of polymerization and result in the formation of a monomolecular bonded layer. The composition of a
A. Monoalkoxysilane

\[
\text{Si-O-H + R-Si-O-R''} \rightarrow \text{Si-O-Si-R + R''-OH}
\]

B. Dialkoxysilane
i)

\[
\text{R} \\
\text{H} \quad \text{H} \quad \text{R} \\
\text{O} \quad \text{O} \quad + \text{R''-O-Si-O-R''} \rightarrow \text{R-Si-O-R''} \quad \text{H} \quad + \text{R''-OH}
\]

ii)

\[
\text{R} \\
\text{H} \quad \text{H} \quad \text{R} \\
\text{O} \quad \text{O} \quad + \text{R''-O-Si-O-R''} \rightarrow \text{R''-OH} + 2\text{R''-OH}
\]

C. Trialkoxysilane:

i)

\[
\text{R} \\
\text{H} \quad \text{H} \quad \text{OR''} \\
\text{O} \quad \text{O} \quad + \text{R''O-Si-OR''} \rightarrow \text{R''O-Si-O-R''} \quad \text{H} \quad + \text{R''-OH}
\]

ii)

\[
\text{R} \\
\text{H} \quad \text{H} \quad \text{OR''} \\
\text{O} \quad \text{O} \quad + \text{R''O-Si-OR''} \rightarrow \text{R''-OH} + 2\text{R''-OH}
\]

Figure 1.2. Schematic showing silylation reactions.
monomolecular bonded layer is reproducible.

As mentioned earlier, HMDS can also be used to modify the surface of silica. The net reaction of HMDS with silanols is shown below.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} + (\text{CH}_3)_3\text{SiNHSi(\text{CH}_3)}_3 \rightarrow \text{H}_3\text{C-Si-CH}_3 \quad \text{H}_3\text{C-Si-CH}_3 \\
\text{Si} & \quad \text{Si}
\end{align*}
\]

Ammonia evolved during the reaction catalyzes this reaction.

Post-reaction thermal treatment (curing) stabilizes the coating. Post-reaction curing ensures that silanes which are physically adsorbed on the surface are either chemically bonded to the surface or desorbed (19-22).

1.2.4 Amine catalysis

Amines are catalysts for the reaction of organoalkoxysilanes with silica surfaces (1,23). Solution (24) and vapor (25) phase reactions of a variety of organofunctional alkoxysilanes with silica are accelerated by several orders of magnitude in the presence of an amine. Organosilanes with an amine functional group (e.g. (3-
aminopropyl)triethoxysilane, \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_2\text{CH}_3)_3 \) or which release an amine upon initial reaction (e.g. HMDS) catalyze their reactions with silica. The amine attaches to the surface silanols by hydrogen bonds. Hydrogen-bonding renders the Si-O group of the silanol more nucleophilic and consequently more reactive towards electrophilic species such as organoalkoxyxilanes. The more acidic isolated silanols preferentially bond to the amine. High temperature post-reaction curing is not necessary for amine-catalyzed reactions of organoalkoxyxilanes with silica.

1.2.5 Steric hindrance

The extent of surface modification depends on the critical dimensions of the organic substituents in organofunctional silanes (5). Due to steric reasons, silanes in which critical dimensions of the substituents are greater than the distance between surface silanol groups do not react with all surface silanols.

1.3 Potential utility of mixed functional silica surfaces

Chemically modified surfaces of mixed functionality are
potentially useful in a variety of applications. One possibility is as a unique support for dual site catalysts. Multifunctional surfaces can also be used as stationary phases in chromatography.

The first step in analyzing complex chemical mixtures involves a molecular separation to resolve the mixture into individual types of molecules. Chromatography is one of the most powerful tools to separate molecules in complex mixtures. In a chromatographic experiment, a gas or liquid phase mixture is passed through a column packed with an insoluble, usually rigid, matrix or stationary phase. In liquid chromatography, retention (effecting molecular separations) is governed by specific interactions between the solute molecules with the stationary and mobile phases (26,27). In gas chromatography, interactions between the solute and stationary phase effect the separation. Because molecules have different chemical and physical properties, they interact to differing degrees with the stationary phase. It is these varying interactions which provide the separation. A molecule that interacts strongly with the stationary phase takes longer to get to the end of the column than a molecule that interacts weakly with the stationary phase.
Chromatographic stationary phases often consist of organosilane-modified silica gel surfaces (28). The silica surface plays a direct role in analyte retention through interactions between solutes and surface-active sites. The silica surface is usually modified so that different molecules or classes of molecules interact to differing degrees with the surface. Monofunctional stationary phases with various chemical properties, and therefore various retention mechanisms, are prepared by reacting surface silanols with various organofunctional silanes (21). Monofunctional stationary phases are generally effective in separating simple solute mixtures. For a complex mixture, however, more than one retention mechanism may be required to obtain sufficient resolution. Two possibilities of doing chromatographic separations employing two or more retention mechanisms are: (i) multidimensional chromatography, and (ii) the synthesis of multifunctional stationary phases.

In multidimensional chromatography, components of a sample are separated by using series-connected columns of different capacity or selectivity (27). The separation mechanism in each column is different. Samples may be separated by classes in the primary column, and the individual
components of a class are separated in the secondary column(s). An orthogonal multidimensional separation is one in which retention in the constituent dimensions is determined by \( n \) different and independent mechanisms (where \( n \) is the number of dimensions) and so provides \( n \) independent measures of molecular properties (29). The peak capacity of an orthogonal multidimensional separation is equal to the product of peak capacities in each dimension (30). Improved peak capacities are therefore obtained.

Venkatramani et. al. (29) described a 2-dimensional gas chromatographic system using a nonpolar stationary phase (dimethylpolysiloxane) in the primary column and a moderately polar stationary phase (50\% cyanopropylphenylmethyl-polysiloxane) in the secondary column. Two independent separation mechanisms were involved in the primary and secondary columns. Dispersive interactions with the nonpolar stationary phase and nondispersive interactions with the polar stationary phase were the basis of separation in the primary and secondary columns, respectively. A 2-dimensional liquid chromatography system combining anion exchange and reversed phase separation techniques has also been reported (31). The first and second dimensions consisted of microcolumns packed
with a bonded quartenary amine and octadecylsilyl particles, respectively. Separation mechanisms in the first and second column were respectively based on charge and hydrophobic interactions. Multidimensional chromatography requires two or more columns to be connected. As the number of columns increases, the instrumentation becomes more complex.

The synthesis of multifunctional stationary phases offers another possibility of improving chromatographic selectivity. The separation technique in which multifunctional stationary phases are used is called mixed-mode chromatography. Using a multifunctional bonded phase, it is possible to separate analyte mixtures with completely different retention mechanisms on the same column. The application of multifunctional stationary phases for enhanced selectivity has not received much attention, perhaps because it is not easy to carry out multidimensional surface modifications and to characterize the surfaces. In a review article, McLaughlin described multifunctional stationary phases applied in the separation of nucleic acids (32). Ionic interactions between phosphodiester groups and a cationic stationary phase (e.g. a protonated amine) and hydrophobic interactions between nucleobases and an alkyl stationary phase were the two
independent retention mechanisms (32).

One study described the synthesis of a mixed octyl and nitrile bonded phase by literally mixing the monofunctional silicas together and packing the resulting material for chromatography (33). Although this approach has the disadvantage of not having mixed functionality at the molecular level, this bonded phase was found useful to optimize the chromatographic analysis of phenylthiohydantoin amino acids. The synthesis of mixed bonded phase consisting of an alkyl- and cyanoalkyldimethylaminosilane has also been reported (34). Mixed bonded phases of varying composition were obtained by varying the relative concentrations of the organosilanes in solution during the reaction (34). This must presumably be done on a trial and error basis since different organosilanes have varying reactivities with silica surfaces. Another disadvantage is that dialkylamino groups are always present using this method.

A different synthetic scheme involved reacting the silica surface with a mixture of chlorosilanes (35). The monochlorosilane reacts to form an alkyl group on the surface. Organosilanes with >1 chloro group were bonded and subsequently modified with other reagents to give the desired
functionality. These multifunctional stationary phases provided mixed retention mechanisms and unique selectivities for the separation of nucleosides, nucleotides, and catecholamines. A multi-step synthesis is involved however, and it is difficult to ascertain or predict bonded phase structures. Others have also described the synthesis of mixed bonded phases with similar shortcomings (36). The ratio of the constituent silanes would influence the selectivity of the stationary phase. It is therefore necessary to be able to characterize the individual organic groups on the silica surface. The synthesis and characterization of bifunctional stationary phases, under controlled conditions, is described in this thesis.

1.4 Characterization of silica surfaces

Infrared (IR) spectroscopy, on its own or in combination with chemical, thermal, elemental and/or other spectroscopic techniques, has been used extensively to study modified silica surfaces. A review of the subject was presented by Unger (37). IR spectroscopy is capable of distinguishing between isolated and vicinal silanols. IR absorption bands characteristic of the alkyl group(s) and/or other functional
group(s) constituting an organofunctional silane often do not overlap with silica bands. Therefore, the extent of surface reactions can be followed by observing changes in band intensities of silanols and bonded species.

A Fourier Transform Infrared (FTIR) spectrometer is used to record IR spectra. In addition to acquiring spectra in the direct transmission mode, an FTIR spectrometer can be coupled with other sampling techniques such as diffuse reflectance, internal reflectance, external reflectance and photoacoustic spectroscopy (38).

Diffuse reflectance infrared spectroscopy (DRIFTS) is a highly sensitive, rapid sampling technique suitable for the analysis of samples in powder form (38). A diffuse reflectance accessory is fitted in the sample compartment of an FTIR spectrometer. The theory of diffuse reflectance can be found in books by Griffiths (39) and Ferraro (40) as well as in an article by Leyden (38).

A schematic of the optical phenomenon responsible for generating the diffuse reflectance spectrum of a powdered sample is shown in Figure 1.3. If the particle size of the sample is comparable to the wavelength of radiation, then a large portion of the incident radiation is absorbed,
Figure 1.3. Optical layout for diffuse reflectance spectroscopy.
refracted, and diffracted by the particles. The angular distribution of the emerging radiation is independent of the angle of incidence. Such diffusely reflected radiation contains spectral information about the sample. A typical DR spectrum is acquired as follows (38,40):

1. The background spectrum of a finely ground, nonabsorbing matrix (such as KCl or KBr) is recorded.

2. The spectrum of the sample, dispersed in the same nonabsorbing matrix, is acquired.

3. The ratio of the sample spectrum to the background spectrum gives the reflectance spectrum.

4. The reflectance spectrum is converted to Kubelka-Munk units using the relation

\[ f(R) = \frac{(1 - R')}{2R'} = \frac{2.303eC}{s} \]

where \( R' \) = relative reflectance,

\( e \) = extinction coefficient,

\( C \) = molar concentration of the analyte, and

\( s \) = scattering coefficient of the non-absorber matrix.

The scattering coefficient depends on particle shape, size, and packing density of the nonabsorbing matrix (38,40). These
factors should be kept constant for the Kubelka-Munk function to relate linearly with concentration. Leyden et. al. (41) showed that for silica samples of particle size < 5µm and an optimum concentration of about 15%, quantitative measurements of the concentration of (3-aminopropyl)triethoxysilane loaded on the surface of silica can be obtained.

Several reports also describe the use of DRIFTS in quantitative surface characterization (24,25,42-44).

1.5 Purpose of this study

As mentioned earlier, the selectivity of a stationary phase varies with the composition of the stationary phase. Depending on the polarity of the bonded phase, various solute/stationary phase interactions are possible. For example, nonpolar stationary phases, which are obtained by reacting stationary phases with alkylsilanes, employ nonspecific hydrophobic interactions to effect separation. In these phases, retention increases with increasing number of carbons in the stationary phase (45). Highly polar stationary phases, such as those with an aminoalkyl group, may hydrogen bond to the solute or function as either a Bronsted acid or base (45). A medium polarity stationary phase may be obtained
by using a cyanoalkyl substituent (45). Aromatic interactions are the basis of separation when using a stationary phase with a phenyl group (45).

In this study, stationary phases with greater than one retention mechanism were synthesized. Organofunctional silanes with polar and nonpolar organic moieties were reacted with the same silica to form a bifunctional phase. Surfaces were characterized before and after bonding the second organosilane.
2.1 Introduction

Surface modification reactions with two different organosilanes were done in two steps. The silica surface was characterized using DRIFTS before and after the surface was reacted with a second organosilane. This enabled the determination of relative ratios of each organosilane from normalized band areas of the silanol peak. This would not have been possible if the samples were prepared using a mixture of organosilanes.

2.2 Materials

Silica gel (Davison 948) was pretreated by heating in an oven at 600°C for 6 h. (3-Aminopropyl)dimethylmethoxysilane (APDMS), phenyldimethylethoxysilane (PDES), octyldimethylmethoxysilane (ODMS) (all obtained from Silar Laboratories), hexamethyldisilazane (HMDS) (obtained from Huls America Inc.), trimethylmethoxysilane (TMMS), (2-cyanoethyl)triethoxysilane (CETS) (all obtained from PCR Incorporated) and reagent grade toluene (Fisher) were used without further purification. Potassium chloride (EM Science)
was finely ground to < 5 µm in a Wig-L-Bug (Crescent Dental Manufacturing Co.) capsule with a steel ball (41) and dried in an oven at 110°C for at least 12 h before being used as a dispersing medium for the silica gel samples.

2.3 Instrumentation

DRIFTS spectra were obtained with a Nicolet 7000 series FTIR spectrometer (Nicolet Analytical Instruments) purged with dry air and equipped with a liquid-nitrogen-cooled wide band mercury-cadmium telluride detector and a Harrick Scientific Corp. diffuse reflectance accessory (DRA-2CN). Spectra were acquired at a nominal resolution of 4 cm⁻¹ after signal averaging 128 scans. 10% (w/w) dispersions of silica in KCl were mixed in a Wig-L-Bug capsule without a steel ball for 30 s. The samples were filled in the sample cup with gentle tapping and levelled with minimal pressure with a flat object. The sample height was adjusted to obtain the maximum peak intensity of the interferogram. Band areas of the spectra, in Kubelka-Munk units, were integrated by using standard Nicolet software.

2.4 General considerations
2.4.1 Synthesis

Table 2.1 shows which bifunctional silica surfaces were prepared and characterized. For each pair of functional groups, six samples consisting of different concentrations of the first organosilane (and consequently the second organosilane) were prepared. This allows for variation in the polarity for stationary phases containing the same pairs of organosilanes. In addition to the bifunctional silica surfaces, monofunctional silica surfaces modified by reacting silica with an excess amount of each of the organosilanes listed in Table 2.1 were prepared.

Figure 2.1 is a reaction scheme depicting how silica can be modified with two organosilanes. A general description of the steps undertaken in synthesizing bifunctional silica surfaces follows.

(i). For organosilanes which do not have an amine functionality (ODMS and PDES), an amine (n-butylamine) was adsorbed on the surface of pretreated (600°C) silica to catalyze the reaction. This step was found not to be necessary when using HMDS because it releases an amine which catalyzes the reaction.

(ii). A stoichiometric amount of the first organosilane
Table 2.1. Bifunctional Silica Surfaces Prepared

<table>
<thead>
<tr>
<th>Bifunctional phase*</th>
<th>Organosilanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈ /amino</td>
<td>HMDS/APDMS</td>
</tr>
<tr>
<td>C₈ /cyano</td>
<td>HMDS/CETS</td>
</tr>
<tr>
<td>C₈ /phenyl</td>
<td>HMDS/PDES or TMMS/PDES</td>
</tr>
<tr>
<td>C₈ /amino</td>
<td>ODMS/APDMS</td>
</tr>
<tr>
<td>C₈ /cyano</td>
<td>ODMS/CETS</td>
</tr>
<tr>
<td>C₈ /phenyl</td>
<td>ODMS/PDES</td>
</tr>
<tr>
<td>phenyl/cyano</td>
<td>ODMS/CETS</td>
</tr>
</tbody>
</table>

*Abbreviations:

C₈ = trimethyldimethylsilyl
C₈ = octyldimethylsilyl
phenyl = phenyldimethylsilyl
amino = (3-aminopropyl)dimethylsilyl
cyano = (2-cyanoethyl)diethoxysilyl or (2-cyanoethyl)ethoxysilyl (assuming that one or two hydrolyzable group is attached to the surface and that no polymerization occurs)
Figure 2.1. Schematic showing amine-catalyzed silylation of silica with two organosilanes.
was then reacted with silica. The extent of the first silylation reaction was controlled by variation of the concentration of the organosilane. The concentrations of the first organosilane were such that there would be residual silanols on all but one sample in a series.

(iii). Reaction by-products, solvent and amine catalyst were removed during post-reaction thermal treatment. Organosilanes which are physically adsorbed on the surface are also desorbed.

(iv). An amine was adsorbed on residual silanols on the surface of monofunctional silica. This step was found not to be necessary when the second organosilane is APDMS.

(v). An excess amount of the second organosilane was reacted with residual silanols on the surface of monofunctional silica. All accessible silanols should be reacted during this step.

(vi). Step (iii) was repeated.

2.4.2 Characterization

To ensure that the Kubelka-Munk function is linear with concentration, samples were analyzed as follows. To obtain optimum particle size, the KCl was ground to <5 \( \mu \text{m} \) using a
Wig-L-Bug. 10% (w/w) dispersions of silica in KCl were used. The same batch of ground KCl was used to analyze samples that were to be compared. When possible, the same background spectrum was used. All samples were packed in the sample cup by tapping and using a flat object to level the samples. To improve signal to noise ratio, 128 scans were averaged. The band area of the peak at 1860 cm\(^{-1}\) was used as an internal reference (41). For each sample of silica, at least three spectra of independently packed samples were acquired and average band areas were calculated.

2.5 Procedures

2.5.1 Synthesis of monofunctional silica surfaces

Silica surfaces with different amounts of either trimethyloxysilyl, octyldimethyloxysilyl, or phenyldimethyloxysilyl group were prepared by respectively adding different concentrations of either HMDS, ODMS or PDES into a reaction flask containing 4 g samples of the 600°C-treated silica gel and 30 mL toluene. In reactions involving either ODMS or PDES, which require a base catalyst, n-butylamine (0.1 mL) was added into the silica slurry before introducing the organosilane. The concentrations of each organosilane used
were 5.00, 2.00, 1.00, 0.50, 0.25 and 0.10 mmol per gram of silica. The flask was stoppered and the reaction was allowed to proceed for 2 h. The silica samples were then filtered using a Buchner funnel and washed with 30 mL toluene. Samples were dried under vacuum for 2 h at 100°C. The temperature of the sandbath, used to heat sample flasks when drying, was controlled with a rheostat.

Silica surfaces modified with either (3-aminopropyl)dimethylsilyl, (2-cyanoethyl)diethoxysilyl or trimethylsilyl groups were prepared by reacting 5 mmol/g of either APDMS, CETS or TMMS with 0.5 g of the 600°C-treated silica. The reaction of APDMS was done without n-butylamine whereas CETS and TMMS reactions were done both with and without n-butylamine.

2.5.2 Synthesis of bifunctional silica surfaces

To obtain bifunctional silica surfaces, 0.5 g of each of the silica surfaces modified with either HMDS or ODMS was reacted with an excess amount (5 mmol/g) of either APDMS, CETS or PDES. PDES-modified silica samples were also reacted with CETS (5 mmol/g). Reactions of silica (0.5 g) modified with 0.1 mmol/g PDES with an excess amount of either HMDS, TMMS,
ODMS or PDES were also done. Silica (0.5 g) modified with 0.1 mmol/g of HMDS was also reacted with 5 mmol/g of either HMDS or ODMS. With the exception of reactions involving APDMS or HMDS, all reactions were catalyzed with n-butylamine (0.1 mL). The samples were filtered and dried as described above.

2.5.3. Reaction of HMDS and PDES with silica in one step.

**Method A:**

600°C-treated silica (0.5 g) was immersed in 30 mL toluene. HMDS (0.1 mmol/g) was added into the slurry and allowed to react for 2 h. n-Butylamine (0.1 mL) and 5 mmol/g PDES were then introduced into the reaction mixture. The reaction was allowed to run for 2 h longer. The sample was filtered and dried as described above.

**Method B:**

600°C-treated silica (0.5 g) was immersed in 10 mL toluene containing 0.1 mL n-butylamine. A mixture of 0.1 mmol/g HMDS and 5 mmol/g PDES in 20 mL toluene was added into the slurry and allowed to react for 2 h. The sample was filtered and dried as described above.
3.1 Monofunctional silica

Figure 3.1 shows DRIFTS spectra of Davison-948 silica gel thermally treated at 200 and 600°C. The spectra were recorded at room temperature. The region below 1400 cm\(^{-1}\) is of little interest because of intense absorptions due to the Si-O-Si group. The spectrum of silica preheated at 200 °C contains a peak at 3660 cm\(^{-1}\). This peak is assigned to vicinal (hydrogen-bonded) silanols (3,37). 200°C-treated silica is hydrophillic and reabsorbs moisture rapidly. The broad band at 3400 cm\(^{-1}\) is due to physically adsorbed water. The loss of physisorbed water and vicinal silanols upon thermal treatment of silica at 600°C is indicated by the absence of their characteristic peaks. Several peaks appear in both spectra. The IR absorption band at 3745 cm\(^{-1}\) is due to the vibration of isolated silanol groups on the silica surface (3,37). The intensity of the isolated silanol peak on 600°C-treated silica is higher than that on 200°C-treated silica. This increase can be attributed to a condensation process whereby a chain of vicinal silanols containing an odd number of silanols condense to liberate water, thereby creating a siloxane bridge site and
Figure 3.1. DRIFTS spectra of unmodified, 200°C- and 600°C-treated Davison-948 silica.
an isolated silanol. A combination mode of the Si-O-Si group gives rise to the peak centered at 1860 cm \(^{-1}\) (38). An overtone of the Si-O-Si band occurs at 1620 cm \(^{-1}\). This peak overlaps with the IR absorption band due to the bending vibration of surface adsorbed water (46).

In this study, 600°C-treated silica was chosen based on the following reasons. The number of isolated silanols is higher on 600°C-treated silica than on 200°C-treated silica. The isolated silanol peak on 600°C-treated silica does not overlap with any other peaks. Since this study involves integration of the isolated silanol peak, the integration limits can be set such that the band area obtained would be from isolated silanols only. Isolated silanols are generally more reactive than vicinal silanols (12, 13). For samples which are only partially modified, isolated silanols would be expected to react, leaving vicinal silanols unreacted. Because 200°C-treated silica is hydrophillic, it would be necessary to work in a dry box in order to avoid water from being physically adsorbed. A special diffuse reflectance sample cell would also be needed if samples are not to be exposed to the atmosphere when taking spectra. 600°C-treated silica gel is hydrophobic and does not absorb moisture.
It is worth mentioning that a peak due to asymmetrical stretching of carbon dioxide (CO$_2$) may appear at 2350 cm$^{-1}$ in some spectra. The occurrence of this peak is caused by differences in the content of CO$_2$ inside the spectrometer when recording reference and sample spectra.

Previous studies by Leyden et. al. (38) have shown that for silica samples of particle size < 5µm and an optimum concentration of about 15%, the ratio of the CH band area of 3-aminopropyltrimethoxysilane to the band area of the Si-O-Si combination mode at 1860 cm$^{-1}$ can be used to obtain quantitative measurements of the concentration of the organosilane on the silica surface. The relative amount of isolated surface silanols was obtained by integrating the peak area of the band at 3745 cm$^{-1}$ and obtaining its ratio against the peak area of the Si-O-Si band at 1860 cm$^{-1}$. The silanol peak was integrated from 3785 cm$^{-1}$ to 3710 cm$^{-1}$ and the siloxane peak was integrated from 1940 cm$^{-1}$ to 1790 cm$^{-1}$.

The absence of IR absorptions in the C-H (2800-3100 cm$^{-1}$) and C=C (1400-1500 cm$^{-1}$) stretching regions (47) in the spectrum of heat-treated silica allows for the identification of alkyl and alkenyl groups on surfaces of silica modified with these groups. Characteristic stretching frequencies of
many functional groups also occur in regions where there are no silica peaks. For example, stretching modes of aliphatic nitriles and aliphatic amines result in IR bands in the regions 2300-2220 cm⁻¹ and 3400-3250 cm⁻¹, respectively (47).

Monofunctional silica gels modified with trimethylsilyl, octyldimethylsilyl and phenyldimethylsilyl groups were prepared by reacting 600°C-treated silica with HMDS, ODMS and PDES respectively. Synthetic methods are described in Section 2.5.1. By reacting silica with different concentrations of an organosilane, the amount of the organosilane loaded on the surface of silica can be varied. Six samples of silica modified with varying amounts of a particular organosilane were prepared. The concentrations of the organosilane were such that there would be residual silanols on the silica surface on all but one sample in each series of monofunctional silica surfaces.

Since the organosilane reacts with isolated silanols, it is expected that the intensity of the silanol band will decrease, and the intensity of the peaks characteristic of the organosilane will increase, as the amount (mmoles) of the organosilane reacted with silica increases. Comparison of the intensities of the IR peaks provides a semiquantitative
measure of the extent of the reaction. Quantitative data can be obtained by normalizing band areas of peaks due to the organosilane to the band area of the siloxane peak at 1860 cm\(^{-1}\). Plots of band area ratios as a function of the concentration of organosilane can be used to show these trends. Alternatively, a plot of the silanol band area ratios against the band area ratios of the peaks due to the organosilane should be linear because the respective band area ratios should be inversely proportional to each other.

DRIFTS spectra of silica modified with HMDS are presented in Figure 3.2. To enable comparison of peak intensities by observation, the spectra are normalized so that the Si-O-Si combination band at 1860 cm\(^{-1}\) is constant. The amounts of HMDS added to the reaction mixture when preparing various surfaces are also shown. It has to be noted that the mmoles added are not necessarily the mmoles reacted with silica. Since the exact mmoles reacted were not determined in this project, mmoles added are used. Bands in the regions 3000-2925 cm\(^{-1}\) and 2920-2860 cm\(^{-1}\) are respectively due to asymmetric and symmetric C-H stretching vibrations of the methyl groups. Inspection of the isolated silanol peak at 3745 cm\(^{-1}\) and the C-H bands reveal that the intensity of the silanol peak decreases and the
Figure 3.2. DRIFTS spectra of HMDS-modified silica.
intensity of the C-H peaks increases as the mmoles of HMDS added to silica increases.

The relative amount of residual (unreacted) silanols, which is inversely proportional to organosilane loading on the silica surface, was quantitatively obtained by integrating the band area of the peak at 3745 cm\(^{-1}\) and calculating its ratio against the band area of the peak at 1860 cm\(^{-1}\). The percentage of residual silanols was determined by using the equation:

\[
\% \text{ SiOH BA ratio} = \frac{\text{SiOH BA ratio on modified silica}}{\text{SiOH BA ratio on unmodified silica}} \times 100
\]

where BA = band area.

To obtain the relative amount of HMDS loading on the surface of silica, the ratio of the band area of asymmetric C-H stretching peaks to the band area of the Si-O-Si band at 1860 cm\(^{-1}\) was calculated. The respective upper and lower integration limits of the C-H stretching bands were 2995 and 2925 cm\(^{-1}\). The band area ratio of the surface modified with an excess amount of HMDS (5 mmol/g) was assumed to be the maximum (i.e. 100 \%) organosilane loading. Other band area ratios were expressed as percentages relative to the maximum band area ratio.
\[
\% \text{ C-H band area ratio} = \frac{C-H \text{ band area ratio}}{\text{Maximum C-H band area ratio}} \times 100
\]

The percentage band area ratios of the silanol band at 3745 cm\(^{-1}\) and the asymmetric C-H stretch bands at 2965 cm\(^{-1}\) are plotted as a function of the mmoles HMDS added per gram of silica (Figure 3.3). Error bars represent standard deviations after averaging band area ratios of five independently recorded spectra. The expected decrease in percentage band area of the SiOH peak, and increase in percentage band area of CH peaks as the mmoles of HMDS increase are observed.

Figure 3.4 shows normalized DRIFTS spectra of silica modified with varying amounts of ODMS. In addition to asymmetric and symmetric C-H stretching vibrations from methyl groups (2995-2920 cm\(^{-1}\)), two other absorption bands appear in the C-H stretching region. These peaks are assigned to asymmetric and symmetric C-H stretching of the methylene (CH\(_2\)) group. Because these peaks overlap, the whole C-H stretching region (2995 - 2820 cm\(^{-1}\)) was integrated. The band areas were normalized against the band area of the 1860 cm\(^{-1}\) peak and converted to percentages relative to the band area of the silica surface modified with 5 mmol/g ODMS. As expected, the
Figure 3.3. Plots of CH (A) and SiOH (B) % band area ratios of HMDS-modified silica versus HMDS concentration.
Figure 3.4. DRIFTS spectra of ODMS-modified silica.
Figure 3.5. Plots of CH (A) and SiOH (B) % band area ratios of ODMS-modified silica versus ODMS concentration.
intensity of the silanol peak decreases as the intensities of C-H stretching bands increase. Plots of the silanol and C-H percentage band area ratios against mmoles of ODMS per gram of silica (Figure 3.5) quantitatively confirm the observed inverse relationship between silanol and C-H band areas.

The spectra of silica modified with phenyldimethylsilyl functional group are given in Figure 3.6. Aromatic C-H stretching bands occur between $3000$ and $3100$ cm$^{-1}$ (47). Peaks between $2800$ and $3000$ cm$^{-1}$ are due to symmetric and asymmetric C-H stretching of the methyl groups. The sharp peak in the region $1415-1440$ cm$^{-1}$ result from C=C ring stretching (47). It is evident from Figure 3.6 that the SiOH peak at $3745$ cm$^{-1}$ diminishes while the peaks in the regions $3100-3000$ cm$^{-1}$, $3000-2800$ cm$^{-1}$ and $1440-1415$ cm$^{-1}$ increase with increasing concentration of PDES added to silica. Plots of percent band area ratios of isolated silanols and methyl CH stretching vibrations against concentration of PDES (Figure 3.7) confirm the observed trend.

From plots of percent band area ratios as a function of organosilane concentration (Figures 3.3, 3.5 and 3.7), it appears as if the amount of silanols lost exceed the amount of organosilane loaded. For example, the CH and SiOH percent
Figure 3.6. DRIFTS spectra of PDES-modified silica.
Figure 3.7. Plots of CH (A) and SiOH (B) band area ratios of PDES-modified silica versus PDES concentration.
band area ratios obtained for silica modified with 0.1 mmol/g HMDS are 18 and 50% respectively. Interactions between the residual isolated silanols and organofunctional groups are responsible for a larger than expected decrease in the percent band area of the silanol peak. Silanols interacting with an organosilane absorb at a lower wavenumber than isolated silanols. As a consequence of these interactions, the intensity of the isolated silanol (and the band area ratio) would be lower. The appearance of a band in the region were hydrogen-bonded silanols absorb (3660 cm\(^{-1}\)) is evidence that interactions between silanols and organosilanes occur. The intensities of the 3660 cm\(^{-1}\) bands are larger on PDES-modified silica than on silica modified with either HMDS or ODMS because surface silanols interact more strongly with the \(\pi\) electron density of the aromatic ring than with either methyl or octyl groups (48).

Comparison of band areas of silica surfaces modified with 2, 1, 0.5 and 0.25 mmol/g reveals that more silanols react with HMDS than with ODMS (Figure 3.8). In silica surfaces modified with either 2 or 1 mmol/g, silanols reacted with HMDS exceed those reacted with ODMS by about 5%. Silanols on samples modified with 0.5 and 0.25 mmol/g differ by 16 and 20%
Figure 3.8. Percentage band area ratios of SiOH reacted with various organosilanes.
respectively.

The percentage band area ratios of silanol peaks on HMDS-modified silica are larger than the corresponding percentage band area ratios on silica modified with either ODMS or PDES because each molecule of HMDS reacts with two silanols whereas each molecule of ODMS or PDES reacts with one silanol.
3.2 Bifunctional silica

To obtain silica surfaces modified with two functional groups, monofunctional silica surfaces possessing trimethylsilyl, octyldimethylsilyl and phenyldimethylsilyl functional groups were reacted with an excess amount of an organosilane containing either an amino, phenyl or cyano functional group. Organoalkoxysilanes with one alkoxy group (APDMS and PDES), and three alkoxy groups (CETS) were used as silanization agents possessing an amino, phenyl or cyano functional group respectively. Bifunctional silica surfaces prepared and the silanes used for functionalization are listed in Table 2.1.

Figure 3.9 depicts the spectra of silica modified with both HMDS and APDMS. The spectrum of silica modified with APDMS is given on the same figure. The mmoles of HMDS added when preparing monofunctional silica surfaces are also shown. Two peaks due to asymmetric and symmetric N-H stretching vibrations are observed between 3400 and 3250 cm⁻¹. C-H stretching vibrations occur between 3000 and 2800 cm⁻¹.

The spectra of silica modified with HMDS and CETS are shown in Figure 3.10. The spectrum of CETS-modified silica is also included. Infrared spectra of nitriles are characterized
Figure 3.9. DRIFTS spectra of HMDS/APDMS-modified silica.
Figure 3.10. DRIFTS spectra of HMDS/CETS-modified silica.
by the CN triple bond stretching band at 2250 cm\(^{-1}\).

When each of the HMDS-modified silica samples were reacted with either APDMS or CETS (in the presence of n-butylamine for the latter organosilane), the IR absorption peak at 3745 cm\(^{-1}\) disappeared, showing that all the isolated silanols reacted with the organosilane (Figures 3.9 and 3.10). In both cases, silanols reacted with APDMS or CETS equal the residual silanols on HMDS-modified silica.

The relative amounts of each organosilane bonded to a surface can be compared by comparing the percent band area ratios of silanols reacted with the first and second organosilane. For surfaces modified with HMDS and either APDMS or CETS, the relative amounts are given in Figure 3.11. It is apparent from the figure that as the amount of the first organosilane loaded on the surface increases, the amount of the second organosilane decreases and vice versa. The sum of the percentage band areas corresponding to SiOH reacted with organosilanes on one surface is 100.

The band area of another band was also used to determine the relative amount of the second organosilane. The IR bands assigned to CH stretching vibrations of the methylene group (CH\(_2\)) were integrated from 2946 to 2920 cm\(^{-1}\), normalized
Figure 3.11. Percent band area ratios of SiOH reacted with HMDS and either APDMS or CETS.
against the band area of the 1860 cm\(^{-1}\) peak, and used to
determine the relative amount of APDMS on the silica surface.
The band area ratio of the surface modified with an excess
amount of APDMS was assumed to be the maximum APDMS loading.
The band area ratios of the methylene peaks on silica modified
with both HMDS and APDMS were expressed as percentages. A
plot of percent band area ratio of the methylene peaks against
the concentration of HMDS used in preparing the monofunctional
surfaces is shown in Figure 3.12. The percentage band area
ratio of methylene peaks decreases as the concentration of
HMDS added when preparing monofunctional silica surfaces
increases. This is expected because there are fewer silanols
on monofunctional silica gels with higher HMDS loaded than in
those with lower HMDS loaded. Supporting information can also
be obtained by inspection of the spectra of silica modified
with both HMDS and APDMS. From Figure 3.9, the intensities of
the NH and the methylene CH stretching peaks increase as the
concentration of HMDS decreases.

The relative amount of CETS reacted with the surface was
obtained from the integrated band area of the CN peak. The
band area of the CN peak was integrated from 2290 to 2220 cm\(^{-1}\)
and ratioed against the band area of the reference peak. The
Figure 3.12. Plot of percentage band area ratios of methylene CH bands on HMDS/APDMS-modified silica versus HMDS concentration.
Figure 3.13. Plot of percentage band area ratios of CN band on HMDS/CETS-modified silica versus HMDS concentration.
band area ratios were converted to percentage relative to the band area of silica modified with 5 mmol/g CETS. The percent band area ratio of this peak is plotted as a function of the concentration of HMDS (Figure 3.13). As expected, the band area ratio of the CN peak decreases as the concentration of HMDS increases. This confirms the decrease in CN band intensities as the amount of HMDS increases observed in Figure 3.10.

Figures 3.14 and 3.15 are DRIFTS spectra of bifunctional silica surfaces obtained by reacting ODMS-modified silica with either APDMS or CETS respectively. As in the case of silica modified with HMDS and either APDMS or CETS, there are no residual silanols as inferred from the absence of the silanol peak at 3745 cm⁻¹. The relative amount of surface silanols reacted with either APDMS or CETS equals the residual silanols on ODMS-modified silica. Bar graphs showing the amount of ODMS and either APDMS or CETS reacted with the surface are given in Figure 3.16. Figure 3.17 is a plot analogous to Figure 3.13. Interpretations used for spectra of silica modified with HMDS and either APDMS or CETS also apply to spectra of silica modified with ODMS and either APDMS or CETS.

Presented in Figure 3.18 are DRIFTS spectra of silica
Figure 3.14. DRIFTS spectra of ODMS/APDMS-modified silica.
Figure 3.15. DRIFTS spectra of ODMS/CETS-modified silica.
Figure 3.16. Percent band area ratios of SiOH reacted with ODMS and APDMS or CETS.
Figure 3.17. Plot of percent band area ratios of CN band on ODMS/CETS-modified silica versus ODMS concentration.
Figure 3.18. DRIFTS spectra of PDES/CETS-modified silica.
Figure 3.19. Plot of percentage band area ratios of CN peak on PDES/CETS-modified silica versus ODMS concentration.
Figure 3.20. Percent band area ratios of SiOH on PDES/CETS-modified silica reacted with PDES and CETS.
modified with PDES and CETS. A plot of percentage band area ratios of the CN peak versus PDES concentration is shown in Figure 3.19. The percentage band area ratios corresponding to silanols reacted with CETS are equal to percentage band area ratios of residual silanols on PDES-modified silica. The percentage band area ratios of the silanols reacted with PDES and CETS are plotted in Figure 3.20.

DRIFTS spectra of silica modified with trimethylsilyl/phenyltrimethylsilyl and octyldimethylsilyl/phenyldimethylsilyl pairs of functional groups are depicted in Figures 3.21 and 3.22. The spectrum of PDES-modified silica is also included on both figures. Absorption bands of interest have been assigned when discussing the spectra of PDES-modified silica. Observation of the intensity of peaks characteristic of PDES in either Figure 3.18 or 3.19 show that the intensity decreases as the concentration of the organosilane used in preparing monofunctionalized silica (either HMDS or ODMS) increases.

As described earlier, there are no residual silanols on bifunctional silica derivatized with the following pairs of organosilanes: HMDS/APDMS, HMDS/CETS, ODMS/APDMS and ODMS/CETS (Figures 3.9, 3.10, 3.13 and 3.14). In contrast, residual
silanols are observed on bifunctional silica modified with either HMDS/PDES or ODMS/PDES pairs of organosilanes. (Figures 3.21 and 3.22), showing that an excess amount of PDES (5 mmol/g) does not react with all the surface silanols on silica derivatized with HMDS or ODMS. This was not anticipated because no silanols remain on the surface of silica reacted with the same concentration of PDES. The percentages of the ratios of the band areas of the peak at 3745 cm⁻¹ were calculated for both monofunctionalized (derivatized with either HMDS or ODMS) and bifunctionalized (modified with PDES and either HMDS or ODMS) silica surfaces. Calculations show that between 0 and 11% of silanols (in terms of band area ratios) remain on the surface of silica modified with HMDS and PDES as compared to between 0 and 14.5% on the surface modified with ODMS and PDES.

The percentage band area ratios corresponding to PDES reacted with the surface silanols is equal to the difference between percentage band area ratios of residual silanols on monofunctional silica and on bifunctional silica. This information is given in Figures 3.23 and 3.24.

Normalized ratios of each organosilane bonded on a surface can be obtained by dividing the percentage silanols
Figure 3.21. DRIFTS spectra of silica modified with HMDS and PDES.
Figure 3.22. DRIFTS spectra of silica modified with ODMS and PDES.
Figure 3.23. Percent band area ratios of SiOH on HMDS/PDES-modified silica reacted with HMDS and PDES.
Figure 3.24: Percent band area ratios of SiOH on ODMS/PDES-modified silica reacted with ODMS and PDES.
reacted with the second organosilane (either APDMS, CETS or PDES) by the percentage of silanols reacted with the first organosilane (either HMDS, ODMS or PDES). When results are expressed in this way, the relative amount of the first organosilane remains constant (unity) and the relative amounts of the second organosilane are fractions of the constant value. For equal fractions of the first and second silane, the ratio of the fraction is 1. Values >1 are obtained when the amount of the second organosilane is more than the amount of the first organosilane. A value <1 reflect that the amount of the second organosilane is less than that of the first organosilane. Normalized values calculated for silica surfaces in which the second organosilane is either APDMS or CETS are given in Figure 3.25. Values for surfaces in which the second organosilane is PDES are plotted in Figure 3.26.
Figure 3.25. Normalized fractions of SiOH reacted with CETS or APDMS
Figure 3.26. Normalized fractions of SiOH reacted with PDES.
3.3 Investigation of the lack of a complete reaction.

Observation of residual silanols on silica modified with HMDS/PDES and ODMS/PDES pairs of organosilanes prompted an investigation of possible causes of incomplete reactions. The observation that no residual silanols were observed on silica surfaces modified with HMDS/APDMS and HMDS/CETS pairs of organosilanes coupled with the fact that APDMS and CETS are relatively small molecules compared to PDES seemed to suggest that the size of the organosilane may be contributing to observed differences in surface coverage. If either HMDS or ODMS is bonded to the surface in such a way that there are residual silanols between adjacent organic groups on the silica surface, access to these silanols would be limited by the size of the incoming organosilane. For monofunctional silica surfaces modified with a relatively small amount of an organosilane (e.g. 0.1 mmol/g), access to silanols by the second organosilane may be limited by size if the first organosilane reacts in clusters, other than being uniformly distributed on the surface. If this is the case, silanols would be more accessible to sterically less demanding groups than to relatively bulky groups. PDES, being a larger molecule than either APDS or CETS, would then be more
hindered than the less bulky groups. Silanols which are inaccessible to PDES may be the ones giving rise to the absorption band at 3745 cm⁻¹.

Further experiments were done by reacting silica modified with 0.1 mmol/g HMDS with excess amounts of either HMDS or ODMS. DRIFTS spectra are shown in Figure 3.27. HMDS was chosen because the methyl group is the smallest in size compared to 3-aminopropyl, 2-cyanoethyl and phenyl groups on APDMS, CETS and PEDS respectively. On the other hand, the octyl group is larger than the groups just mentioned. It is clear from Figure 3.27 that there are residual silanols on silica modified with HMDS and ODMS whereas HMDS reacted fully with surface silanols on HMDS modified silica. Integration of the band area of the isolated silanol peak from 3785 to 3710 cm⁻¹ yielded the following results: 0.7 %, 11 % and 14% residual silanols are on silica surfaces in which the second organosilane is HMDS, PDES and ODMS respectively. There is an increase in the relative amount of residual silanols as the size of the longest side chain of the organosilane increases.

If organosilanes react in clusters, the spacing between nearest neighbors would be expected to increase with increasing
Figure 3.27: DRIFTS spectra of bifunctional silica surfaces prepared by reacting silica modified with HMDS (0.1 mmol/g) with an excess of various organosilanes. (A) PDES, (B) ODMS, and (C) HMDS.
size of the first organosilane. Silanols between large adjacent organic groups would be more accessible to an organosilane than those between relatively small groups. With this in mind, further silylation reactions were performed on silica partially modified with PDES. Silica modified with 0.1 mmol/g PDES was reacted with either HMDS, TMMS, ODMS and PDES. The spectra are shown in Figure 3.28. Both HMDS and TMMS are sources of relatively less bulky trimethylsilyl groups. Small silanes are often used to endcap silica surfaces of bulky groups. The spacing between two relatively bulky groups (such as phenyldimethylsilyl) on the surface of silica is expected to be larger than when smaller groups are on the surface. Residual silanols on monofunctional silica modified with a relatively large group should therefore be more accessible to a particular organosilane compared to silanols on monofunctional surfaces modified with smaller groups. It is apparent from the spectra of silica modified with PDES and either HMDS or TMMS (Figure 3.28) that HMDS and TMMS react with all silanols. Residual silanols are however observed on the surface of silica in which the second organosilane is either PDES or ODMS. Integration gives 0%, 2% and 7% as the percentage band area ratios of the silanol peak.
Figure 3.28: DRIFTS spectra of bifunctional silica surfaces prepared by reacting silica modified with 0.1 mmol/g PDES with an excess amount of various organosilanes. (a) HMDS, (b) TMMS, (c) PDES, and (d) ODMS.
on surfaces modified with PDES and either HMDS, TMMS and ODMS respectively. The percentage band area of residual silanols on surfaces in which silica partially modified with PDES (0.1 mmol/g) was reacted with ODMS is smaller than that in which silica partially derivatized with HMDS (0.1 mmol/g) was reacted with PDES. Similar results were obtained for surfaces containing HMDS and PDES.

These results are in agreement with the hypothesis that when silica is partially modified with an organosilane, the organosilane reacts in clusters.
3.4 Comparison of one-step and two-step reactions

Bifunctional silica surfaces described thus far were prepared in two steps. Monofunctional silica gels were dried and characterized before derivatization with the second organosilane. However, it may not always be necessary to characterize monofunctional silica, in which case the drying step would be unnecessary. Preparation time would be reduced if bifunctional surfaces can be prepared in one step. Once the loading pattern of the first silane and its relationship with the band area of the second organosilane have been established, the relative amount of the first organosilane can be determined from the band area of the second organosilane. Band areas of bifunctional silica obtained in one and two steps are compared.

One step reactions were done in two different ways. In the first method, HMDS (0.1 mmol/g) was allowed to react for 2 hours, and then an excess amount of PDES and an amine catalyst were added into the reaction mixture. In the second method, a mixture of HMDS (0.1 mmol/g) and PDES (5 mmol/g PDES) in toluene was added into a flask containing silica, toluene and n-butylamine. The spectra, including that of silica prepared in two steps, are shown in Figure 3.29. There
are no residual silanols on the surface modified by mixing the organosilanes (Spectrum C on Figure 3.29). Residual silanols are present on silica prepared in one step by letting HMDS react for 2 h (Spectrum B on Figure 3.29), although the silanol peak intensity is smaller than that in silica modified in two steps (Spectrum A on Figure 3.29). The incomplete reaction of silica after HMDS was allowed to react for 2 h was expected because the reaction procedure is closely related to the reaction in which HMDS-modified silica is silylated with PDES.

It can be concluded from the above observations that reactions done in one step, using a mixture of organosilanes, provide more extensive coverage than in a surface prepared by bonding HMDS first. Reaction times can therefore be reduced by preparing the samples in one step.
Figure 3.29. DRIFTS spectra of bifunctional silica surfaces prepared by reacting 0.1 mmol/g HMDS and 5 mmol/g PDES in one and two steps. (A) Dried HMDS-modified silica reacted with PDES. (B) HMDS allowed to react for 2h before adding PDES, and (C) Mixture of organosilanes.
CONCLUSIONS

Chemically modified silica surfaces of mixed functionality were prepared and characterized using DRIFTS. The relative amounts of organosilanes loaded on a silica surface were obtained from band area ratios of IR bands. Ratios of organosilanes bonded to the same silica surface were calculated from normalized band areas of the isolated silanol peak. The band area ratio of the silanol peak was also used to determine the relative amount of inaccessible silanols in reactions in which surface coverage was incomplete. Comparisons of organosilane loading when reactions were done in one and two steps were also made. It was found that for reactions which are incomplete when the second organosilane is a relatively bulky group, better surface coverage is obtained when silylation reactions are done using a mixture of organosilanes.
REFERENCES


44. Murthy, R.S.S.; Blitz, J.P.; and Leyden, D.E.; *Anal.*
Chem. 1986, 58, 3167.


