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Synthesis and characterization of titania based stationary phases for HPLC

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Synthesis And Characterization of Titania Based Stationary Phases For HPLC

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Jayasri Ramakrishnan

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF TITANIA BASED STATIONARY PHASES FOR HPLC

by Jayasri Ramakrishnan

High Performance Liquid Chromatography (HPLC) is an important analytical technique used for the separation and characterization of a wide variety of chemical compounds. Silica and its bonded derivatives are commonly used as stationary phases in HPLC. However, its use is limited to pH 2 - 8.

In this research, titania is synthesized by a sol-gel method and converted to octadecyl titania (ODT) by a TES-silanization followed by a hydrosilation scheme. Various analytical techniques, such as Fourier transform Infrared spectroscopy in the DRIFT mode, thermogravimetric analysis (TGA), elemental analysis and cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS-NMR) were used to confirm the success of the modification scheme. Finally, ODT was packed into columns and characterized chromatographically. Comparisons were made with a commercially available source of titania subjected to the same modification scheme.

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Chapter 1

Introduction

1.1. BACKGROUND

High Performance Liquid Chromatography (HPLC) is a powerful separation technique used in the field of chemistry. It is well known that the chemical nature of the support used as the stationary phase can strongly affect the efficiency of separation. Therefore, the development of HPLC as an efficient separation technique was always dependent on the synthesis of suitable packing materials.

Historically, silica and its bonded derivatives have been commonly used as the stationary phase in packed column chromatography. They are mechanically stable and can be processed into particles of specific size, surface area and pore size. By controlling these parameters accurately, the base material can be made versatile and reproducible separations can be achieved under controlled experimental conditions.

1.2. STRUCTURE OF SILICA

The study of the crystal structure of silica, SiO_2 , has shown that it forms 'giant molecules' by linking together a number of tetrahedra in which a silicon atom is linked to four oxygen atoms. This structure, though extending three dimensionally, may be represented, for the sake of convenience, by a planar formula, as shown in Fig 1.

Figure 1. Structure of silica

The essential feature of silica in its application as a stationary phase in chromatography is its surface. The surface activity is dominated by the presence of free hydroxyl (-OH) groups. They are frequently referred to as silanol groups. However, the presence of hydroxyl groups is detrimental in its application as a column packing material. Therefore, a reliable method that can replace the hydroxyl group with some other chemical moiety while still retaining the same reactivity should prove useful.

1.3. MODIFICATION SCHEMES

In the late 1960's, bonded phases on a silica gel surface were first modified by using an esterification reaction between an alcohol and silanol groups (1).

This reaction produces Si - O - C linkages. The major disadvantage of this reaction is that it produces a phase that is very much prone to hydrolysis. This susceptibility limits the use of water in the mobile phase and increases the potential for exchange at the surface with alcohols in either the mobile phase or the sample.

In the early 1970's commercial phases utilizing organosilanes became available (2). The reaction of surface silanols with alkylchlorosilanes produce Si - O - Si - C linkages. The reaction scheme can be represented as follows:

where X = halide R = alkyl group

They displayed good hydrolytic stability over a wide pH range. However, they showed limited long term hydrolytic stability when an aggressive mobile phase with a low or high pH aqueous component was used.

In reaction 1, the reaction of silanol sites with dimethylalkylchlorosilane results in a stationary phase where the surface is covered only with a monomolecular layer of the hydrocarbonaceous functions that are anchored via siloxane bridges to the silica surface as shown in Fig 2. Such a stationary phase is referred to as a 'monomeric phase' since only one bond is formed per silane molecule. Di and trifunctional silane reagents may also be used to produce monomeric phases (Eqn 2) if precautions are taken to exclude water. Under carefully controlled reaction conditions, a monomeric bonded phase can be produced by this reaction. However, in the presence of water, a cross linked alkylpolysiloxane layer is produced at the surface and such a stationary phase is 'polymeric' in nature. Fig 3 illustrates the chemical structure of the polymer.

In the late 1970's, bonded phases were produced by first chlorinating the surface followed by a reaction of the chlorinated silica with a Grignard or organolithium reagent. This produces a highly stable Si - C bond at the surface that is hydrolytically more stable than the Si - O - Si - C linkage.

Fig 2. Synthesis of monomeric phase.

Figure 3. Synthesis of polymeric phase

or

However, this method has two disadvantages. One, the reaction is extremely sensitive to moisture in each step. Two, the organometallic reaction produces undesirable side products such as MgClBr or LiCl which often become entrapped in the silica matrix and produce undesirable and non uniform retention characteristics in the final product.

In the 1980's, Pesek and his coworkers (3,4,5) developed a new approach to produce a hydride modified support that serves as an intermediate for the synthesis of chromatographic bonded phases. This procedure, referred to as "TES silianization," involves the controlled deposition of the hydrolysis product of triethoxysilane (TES) to preferentially form a monolayer of Si- H on the surface using dioxane as the solvent and 0.1M HCl as the catalyst. Silanization is followed by " hydrosilation" that involves the catalytic addition of a terminal olefin in the presence of hexachloroplatinic acid as the catalyst to form an Si -C linkage.

In this reaction scheme, TES silanization followed by hydrosilation has several advantages over the other modification schemes. It eliminates the strictly dry conditions required by the chlorination / reduction method. In fact, the presence of water is needed to hydrolyze the ethoxy groups of TES into silanols. The process time is reduced from 3-4 days to about 4 hours. In addition to its greater simplicity, silanization with TES provides superior SiH coverages as compared to the previous methods. Octyl bonded phases produced as a result of the 'hydrosilation' reaction were shown to have good ligand density and also displayed enhanced resistance to phase deterioration (5).

1.4. LIMITATIONS OF SILICA

In spite of the progress made in modifying the surface of silica, there is one inherent disadvantage of silica that limits its use to pH 2 -8. Within this pH range, the amount of soluble silica remains negligible. Below pH 2, the bonded organic phase can undergo hydrolysis and above pH 8, the silica matrix itself begins to dissolve due to the formation of silicate ions and monosilicic acid:

Several approaches have been developed to overcome the problem of this pH limitation. One such approach involves the proper choice of organic moiety that is able to impose steric factors and protect the surface (6). However, by this approach, the vulnerable point of all silica based matrices, the siloxane linkages, Si - O - Si which constitute the backbone of the matrix is not protected. The second approach for producing bonded phases with increased hydrolytic stability involves the use of organic polymer materials (7,8). However, they do not possess the high mechanical strength shown by silica based materials.

1.5. OTHER SUBSTRATES

Recently, ceramic oxides have attracted a lot of attention. They are used for a variety of purposes; namely, heat resistant materials, sensor elements and mechanical parts due to their ability to withstand heat, mechanical shock and the effects of various chemicals. These characteristics indicate that they have the potential to be used as column packing materials in chromatography. It is known that aluminum oxide, zirconium oxide, titanium oxide and thorium oxide have much better chemical and thermal stability than silica and display greater stability when exposed to high pH.

Most work involving surface modification of other metal oxides for use in HPLC has involved alumina. Increased stability and selectivity comparable to octadecyl silica (ODS) has been demonstrated by coating alumina with polybutadiene (10). The

modification of alumina involving the bonding of organophosphates has produced a bonded phase with a range of selectivity and enhanced hydrolytic stability (11). However, the use of certain mobile phase additives such as phosphate buffers may lead to bonded phase degradation. Octadecyl alumina has been synthesized by using TES silanization followed by hydrosilation in the presence of an acid catalyst (12).

It has been shown that bare zirconia as well as chemically modified zirconia can be used as the stationary phase for the separation of polycyclic aromatic hydrocarbons, nucleotides, and proteins (13-16). Modification of zirconia with organosilanes has been shown to result in stationary phases with a range of polarities similar to that of silica (16). Porous, amorphous zirconia and titania have been synthesized by a sol- gel process using a sol- hydrogel- xerogel conversion and the titania synthesized by this process has been shown to be useful in the separation of a mixture of polyaromatic hydrocarbons (13). Octadecyl Titania (ODT) synthesized for use in reverse phase HPLC has demonstrated durability and resistance to alkaline eluents at pH 12 even after being exposed to the mobile phases for 280 hrs (17). However, the separation of aniline derivatives using an ODT column with methanol / 0.1 M glycine- 0.1 M sodium chloride-sodium hydroxide buffer (pH 12) as the eluent showed peak tailing due to the interaction of the residual titanol groups on the ODT with the protonated species of the amines that exist even at this pH (18).

Since the TES silanization followed by hydrosilation scheme has been shown to be superior to other modification schemes, it is believed that a similar reaction protocol on titania will produce octadecyl titania with a minimum number of residual hydroxide groups. This modification scheme has been carried out on four different oxides namely, alumina, zirconia, titania and thoria successfully (19). However, chromatographic characterization was not possible because of the small size of the particles.

1.6. GOALS OF THE RESEARCH

The purpose of this project is fourfold. A primary goal is to synthesize titania using a sol - gel process (20). The second objective is to convert the synthesized titania to octadecyl titania (ODT). The modification is done in two steps. First, a layer of Si-H is produced on the surface using TES silanization reaction followed by hydrosilation with octadecene in the presence of the catalyst, hexachloroplatinic acid. The chemistry can be described as follows :

On the oxide surface,

$\text{R} = \text{C}_{16}\text{H}_{33}$ - product ODT (octadecyl titania)

The Si -H layer on the surface is expected to produce a maximum of siloxane linkages and minimum number of uncondensed silanols. The third goal of this research is chromatographic characterization of the ODT. Finally, comparisons were made with ODT synthesized on a commercially available source of titania by the same modification scheme.

1.7. ANALYTICAL TECHNIQUES

Prior to modification, bare titania was evaluated by thermogravimetric analysis (TGA). The hydride modified titania and octadecyl titania were evaluated by using various analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), cross- polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS-NMR) and elemental analysis.

1.7.1. TGA Background

In a thermogravimetric analysis experiment, a certain amount of the preweighed sample is heated and the change in its mass is recorded continuously as its temperature is increased linearly from ambient to as high as 1200°C. The number of titanol groups can be calculated from this experimental data.

1.7.2. FT-IR Background

Infrared Spectroscopy is the study of molecular vibrations. It is based on the fact that bonds and groups of bonds vibrate at characteristic frequencies. When a sample is subjected to infrared radiation, it selectively absorbs infrared frequencies that match those of its allowed vibrational modes and therefore, the infrared spectrum of the sample can

reveal the functional groups that are present. Only vibrations that result in an asymmetric change in the dipole moment of the molecule are observed in the infrared. Since there is no change in dipole moment in O₂ and N₂, the FTIR spectra can be collected in air.

1.7.3. FT-NMR Background

Nuclear magnetic resonance (NMR) spectroscopy is basically another form of absorption spectroscopy. It is based on the measurement of absorption of electromagnetic radiation in the radiofrequency region when the sample is in a magnetic field. Absorption is a function of certain nuclei in the sample. A plot of the frequencies of absorption peaks versus peak intensities constitutes an NMR spectrum. In the Fourier transform interferometric method, within a short time, a large number of interferograms can be obtained and thus, by averaging the interferograms, the signal to noise ratio can be improved.

Due to the fixed orientation, the NMR of solids are characterized by very broad, uninterpretable peaks. Magic angle spinning and cross polarization techniques are used to extract the chemical shift information hidden under the broad peaks. By mechanically spinning the sample in an air driven rotor at an angle of 54.7° between the rotation axis and magnetic field direction, the dipolar line broadening effects are eliminated in the MAS technique. In the CP technique, the higher spin density of ¹H is transferred to the signals of nuclei of low natural abundance and small magnetogyric ratio during the contact time. Sensitivity is improved as a result of this transfer.

1.7.4. Elemental Analysis

Each of the synthesized bonded phases were characterized by elemental analysis. Background corrections were made for the bonded phases by subtracting the percent

carbon determinations of the unbonded titania substrates from the bonded phase values.

The value of α_R , surface coverage is calculated using the equation proposed by Berendsen and De Galan (21).

$$\alpha_R (\mu\text{mol} / \text{m}^2) = 10^6 P_C / 10^2 (M_C n_C - P_C M_R) S_{\text{BET}}$$

where

α_R = Concentration of surface bonded groups

P_C = Carbon percentage by weight of bonded material

n_C = Number of carbon atoms in the bonded organic group

S_{BET} = Specific surface area of hydride intermediate as determined by
Brunauer, Emmet and Teller (BET) nitrogen adsorption method

M_R = Molecular weight of olefin

M_C = Atomic weight of carbon

CHAPTER II

EXPERIMENTAL

2.1. MATERIALS

All the materials used for this research are listed in Tables 1 and 2. Most chemicals used were reagent grade. The reagents were used directly without further purification.

2.2. INSTRUMENTAL PROCEDURES

TGA experiments were done at Lockheed Martin Missiles & Space, Material and Process Control Laboratories, Sunnyvale, CA- 94089. Specific surface area (m^2/g) determinations were done at Chevron Research Center, Richmond, CA using the Brunauer, Emmet and Teller (BET) nitrogen adsorption method. Scanning electron microscopy was done at Department of Material Science, San Jose State University. Elemental analysis was done at Desert Analytics, Tucson, AZ.

2.2.1. Diffuse Reflectance Infrared Spectroscopy

DRIFT spectra were taken using a Perkin- Elmer (P-E) Model 1800 Infrared spectrometer (Norwalk, Connecticut) equipped with a deuterated triglycine sulfate (DTGS) detector and controlled by a Perkin- Elmer Model 7500 computer with CDS-3

Table 1. List of chemicals used in synthesis & characterization

Name	Manufacturer
Glycerol	J.T. Baker Chemical Co., Phillipsburg, NJ
Titanium isopropylate	Strem Chemicals, Newburyport, MA
2 - Propanol	Fisher Scientific, Fairlawn, NJ
Triethoxysilane (TES)	Aldrich Chemical Co., St. Louis, MO
1 - Octadecene	Sigma Chemical Co., St. Louis, MO
Tetrahydrofuran(THF) anhydrous (99 %)	Fisher Scientific, Fairlawn NJ
Diethylether	Fisher Scientific, Fairlawn, NJ
Toulene	Aldrich Chemical Co., Milwaukee, WI
Methylene Chloride	Fisher Scientific, Fairlawn, NJ
Titanium dioxide	YMC - Gel, Germany
p- Dioxane	J.T. Baker Chemical Co., Phillipsburg, NJ
Potassium Bromide (KBr) IR grade	J.T. Baker Chemical Co., Phillipsburg, NJ
Chloroplatinic Acid Hexahydrate (38-40 % Pt)	Strem Chemicals, Newburyport, MA
12 M HCl	Fisher Scientific, Fairlawn, NJ

Table 2. List of chemicals used in HPLC work

Name	Manufacturer
Benzene	J.T. Baker Chemical Co., Phillipsburg, N.J
Naphthalene	Allied chemical, New York, NY
Biphenyl	Aldrich Chemical Co., Phillipsburg, N.J
Phenanthrene	J.T. Baker Chemical Co., Phillipsburg, N.J
Anthracene	J.T. Baker Chemical Co., Phillipsburg, N.J
Pyrene	Aldrich Chemical Co., Phillipsburg, N.J
N-Methylaniline	Eastman Kodak Co., Rochester, NY
N- Ethylaniline	Eastman Kodak Co., Rochester, NY
N,N- Dimethylaniline	Alfa Products, Danvers, MA
Benzylamine	Scientific Products, Irvine, CA
2-Phenylethylamine	Eastman Kodak Co., Rochester, NY
Methanol (HPLC grade)	Fisher Chemical Co., Fairlawn, N.J,

software. A diffuse reflectance accessory (Spectra Tech., Stamford, CT) with a 2 mm-deep sampling cup was used. The samples were prepared by diluting the titania samples with finely ground KBr powder (1:1 wt/wt). A smooth sample surface was formed by gently pressing a microscope slide on the sample cup. In order to get a maximum signal throughput, the height of the sample cup was adjusted by applying an alignment routine in the P-E standard software. The instrument was purged (~ 20 minutes) with nitrogen gas from a liquid nitrogen tank to provide a moisture-free sample atmosphere. Spectra were collected at 2 cm^{-1} resolution in the region of $4000 - 450\text{ cm}^{-1}$ and averaged over 100 scans. All sample scans were referenced to KBr.

2.2.2. Nuclear Magnetic Resonance Spectroscopy

A Bruker MSL 300 NMR spectrometer, an Aspect 3000 computer system which was equipped with a Hewlett - Packard 7550A graphics plotter and an MAS-DB pneumatic unit were used for the ^{13}C and ^{29}Si CP-MAS- NMR. Solid samples were placed in ZrO_2 , double bearing motor spun at 4700 - 5200 Hz. External glycine and polyhydridosiloxane samples served as references for the ^{13}C and ^{29}Si analyses, respectively. A pulse width of 6.5 and 5.0 μs were used for the ^{13}C and ^{29}Si spectra, respectively. A 5s contact time and a 5s repetition rate were used for both analyses. The probe temperature was $20 \pm 2^\circ\text{C}$.

2.2.3. High Performance Liquid Chromatography

The liquid chromatograph used in this work was a EM -Science, Hitachi system equipped with a L-6200 intelligent pump, L-4000 variable wavelength UV detector and a Spectra Physics Analytical 4400, Chromjet integrator station. The organic solvents and

water were degassed using high purity grade helium gas for approximately 10 minutes prior to use. The back pressure was maintained below 1600 psi.

Bonded material was packed into 1/4 in O.D., 4.6 mm I.D × 150 -mm stainless steel tubes (Altech Co., Deerfield, IL) using a Haskel (Burbank, CA) pneumatic pump. Modified titania was mixed with chloroform / methanol (90:10) in a 50 mL beaker followed by 10 minutes sonication. This slurry was added slowly to the reservoir and the remaining volume of the reservoir was filled with filtered methanol. Methanol was filtered through a 4.0 µm nylon membrane. The mixture in the reservoir was packed into the column in the presence of nitrogen under approximately 6000 psi. After completion, the column remained attached to the packing apparatus for about 30 minutes before removal.

The separations were performed under reverse phase conditions. After separations were finished, the column was flushed with methanol. The mobile phases composition was altered in increments of 10% by volume.

2.3. SYNTHETIC PROCEDURES

2.3.1. Synthesis of Titania

Three hundred grams of glycerol were placed in a 1L beaker and then 500 grams of 2-Propanol and 5 mL of Milli-Q water were added. It was stirred with a glass rod in a glove box under an atmosphere of nitrogen. Twenty mL of titanium isopropylate was added and the mixture was stirred. The solution was allowed to stand at room temperature for 3 days. At the end of this period, the supernatant liquid was separated from the precipitate and transferred to another beaker. It was allowed to stand for another seven days at room temperature. At the end of seven days, the precipitate was

washed with Milli-Q water, stirred for 10 minutes using a 1.5 cm magnetic stirrer bar and centrifuged for 10 minutes at 1500rpm using an IEC HN-S centrifuge machine. This procedure was repeated until the supernatant liquid became clear and the precipitate was air dried until all the water evaporated. Then it was dried in a vacuum oven (VWR Scientific, model 1410) at 110°C and -50 KPa overnight.

2.3.2. Acid Treatment of bare Titania

Titania synthesized by the above method contained considerable organic material either trapped in the matrix or attached to the surface. So, in order to free the hydroxide groups on the surface and further modify them, it was treated with 0.1 M HCl. The procedure used is as follows: Two grams of titania was mixed with 10 mL of 0.1M HCl in a beaker and stirred using a 1.5 inch magnetic stirrer bar for 24 hours. At the end of this period, the titania was washed with Milli-Q water, stirred for 10 minutes and centrifuged at 1500 rpm for another 10 minutes. This procedure was repeated until the supernatant liquid became clear. The beaker was partially covered with a watch glass and placed in the hood until all the water evaporated. The solid was dried in the vacuum oven at 110°C at -50 KPa for 24 hours.

2.3.3. TES Silanization Experiments

In the first step of the modification, acid treated titania was reacted with TES in the presence of water, an acid catalyst, and dioxane to form a monolayer of trisiloxane type linkages on the surface. The OH :TES ratio was kept at 1:1 since it was determined to be the best molar ratio in a previous study (19). In order to obtain the optimum conditions for the formation of the hydride intermediate, the experiment was performed

at different acid concentrations and at different reaction times. The amounts of titania, dioxane, TES, and acid used in the reactions are given in Table 3.

2.3.3.1. Small Scale Silanization Experiments

In a N₂ filled glove box, triethoxysilane (TES) was placed in a pressure - equalizing additional funnel. *p*-Dioxane was then added to the TES. Titania was transferred to a 100 mL, 3- necked, round bottomed flask equipped with a West condenser, thermometer and a magnetic stir bar. A specified amount of *p*-dioxane was added followed by a 2.4M HCl solution. The joints were greased with lubriseal (Thomas Scientific). The reaction mixture was heated to reflux at 93°C and the TES solution was added dropwise to the flask from the addition funnel. After complete addition of the TES solution, the reaction mixture was refluxed for a specified amount of time. At the end of the reaction time, the contents of the flask were allowed to cool. The joints were degreased with xylene, and the *p*-dioxane was poured off from the flask without losing the titania. The contents of the flask were transferred evenly into centrifuge tubes equipped with a stir bar. Using an IEC HN-S centrifuge, the tubes were centrifuged for 10 minutes at 1500 rpm. The washing steps consisted of adding about 20 - 80 mL of each of the following solvents to the centrifuge tube.

Solvent	Number of washing steps
THF:H ₂ O	2 times
THF	2 times
Diethyl ether	2 times

After the washing procedure was complete, the contents of the centrifuge tube were covered with a watch glass and placed overnight in the hood to evaporate the solvents.

Table 3. Chemicals and amounts used in small batch TES silanization reactions

Name	Amount (gm)	Dioxane (mL)	TES solution (mL)	2.4M HCl (mL)	Reaction time(hr)
Lab - TiO ₂	0.25	43.00	7.90	1.67	2
Lab TiO ₂	0.25	43.00	7.90	1.67	5
Lab -TiO ₂	0.25	42.00	7.90	2.37	5
YMC- TiO ₂	0.50	10.10	0.50	0.50	3

The next day, the solid was placed in the drying oven at 110°C and a pressure of -50 KPa overnight.

2.3.3.2. Large Scale TES Silanization Experiment

The amounts of the reactants used in the large scale experiment are given in Table 4. The same procedure was followed as in the small scale experiment but using larger volume glassware.

2.3.4. Hydrosilation Experiments

2.3.4.1. Small Scale Hydrosilation Experiment

A measured amount of 1-octadecene was added to a 150 mL, 3-necked, round-bottomed flask equipped with a West condenser, thermometer, stopper, and magnetic stir bar. A specified amount of 50 mM hexachloroplatinic acid was then added as needed. The mixture was heated to 70°C and maintained at this temperature. Next, the hydride titania was slowly added through a funnel using an electric engraver (Model V-74) for vibration. When the addition was complete, the temperature was raised to $90 \pm 2^\circ\text{C}$ and refluxed for 96 hours. After 96 hours reaction time, the final products were transferred to centrifuge tubes. The washing steps consisted of adding about 20 - 80 mL of each of the following solvents to the centrifuge tube.

Solvent	Number of washing steps
Toulene	4 times
Dichloromethane	2 times
Diethylether	2 times

Table 4. Chemicals and amounts used in big batch TES silanization reactions

Name	Amount (gm)	Dioxane (mL)	TES solution (mL)	2.4 M HCl (mL)	Reaction Time (hr)
Lab -TiO ₂	4.7285	781.3	145.00	41.5	5
YMC- TiO ₂	5.00	101.00	5.00	4.75	3

The mixture was stirred using a 1.5 cm magnetic bar for about 5 minutes and then centrifuged for 5 minutes in order to separate the product. After the washing procedure was complete, the centrifuge tubes were covered with a watch glass and placed overnight in the hood to evaporate the solvent. The next day, the solid was placed in the drying oven at 110°C and a pressure of -50 KPa overnight. The amounts of hydride titania, 1-octadecene, and the hexachloroplatinic acid catalyst are given in Table 5.

2.3.4.2. *Large Scale Hydrosilation Experiment*

The same procedure as in the small scale experiment was followed but using larger volume glassware. The amounts of hydride titania, 1-octadecene, and the hexachloroplatinic acid catalyst are given in Table 5.

Table 5. Chemicals and amounts used in hydrosilation reactions

Name	Amount (gm)	1- Octadecene (mL)	Catalyst (mL)
Lab Ti - O- Si -H	0.10	7.00	0.05
Lab Ti - O- Si -H	4.00	75.00	0.50
YMC Ti -O-Si -H	0.10	7.00	0.05
YMC- Ti- O- Si- H	4.00	75.00	0.50

CHAPTER 3

RESULTS AND DISCUSSION

The first goal of this project was to synthesize titania using a sol - gel process. The sol - gel process is the synthesis of an inorganic, initially amorphous network, by a low temperature polymerization reaction. The best starting materials for the sol - gel preparations are the class of materials known as metal alkoxides. In alcohol / water solutions, the metal alkoxides are rapidly hydrolyzed to corresponding hydroxides by addition of catalysts. Since titanium isopropylate is very reactive to water, the reaction was run in the absence of the hydrolysis catalyst. Subsequent condensation reactions involving the hydroxyl groups yield two or three dimensional networks composed of inorganic oxide linkages. The reactions can be represented as follows:

Hydrolysis

Condensation (Polymerization)

where $\text{M} = \text{Ti}$ and $\text{R} = -\text{OCH}(\text{CH}_3)_2$

The physical properties of synthesized titania and commercial source are given in Table 6. The size of the titania particles collected at the end of three days and seven days were evaluated by optical microscopy and scanning electron microscopy. The

Table 6. Physical characteristics of titania

Type of oxide	BET m^2g^{-1}	vp mLg^{-1}	pd (nm)
Lab -TiO ₂	134	0.3	8.7
YMC - TiO ₂	51	0.16	12.3

BET - specific surface area

vp - specific pore volume

pd - particle diameter

synthesized titania was subjected to treatment with 0.1M HCl for 24 hours before converting it to the hydride intermediate. The hydride modified supports and the olefin bonded products were evaluated and characterized by FTIR and CP-MAS-NMR. Preliminary chromatography studies were conducted. The results are given and discussed in this chapter.

3.1. OPTICAL MICROSCOPY

Titania obtained at the end of three days and seven days were evaluated using an Olympus photomicroscopic system. Comparison between the 3 day and seven day products revealed differences in the size of the particles. Three day titania particles were very small while the seven day titania particles were bigger in comparison and spherical in shape. The results are shown in Figures 4 and 5.

3.2. SCANNING ELECTRON MICROSCOPY

SEM pictures of the three day and seven day titania particles confirm the results of optical microscopy. The results are shown in Figures 6 and 7.

3.3. TGA DATA

The purpose of doing the TGA experiments was to obtain quantitative information from this thermal analytical method to detect by gradual weight loss, the number of -OH groups on the surface of the oxide. The data from the TGA work are presented as the gradual weight loss of the oxide in the temperature range from 110°C to 900°C. The

Figure 4. Optical microscope picture of 3 day titania

Figure 5. Optical microscope picture of 7 day titania

Figure 6. SEM picture of 3 day titania

Figure 7. SEM picture of 7 day titania

weight loss occurs because of condensation of two adjacent titanols on the surface of the oxide support. The chemical process can be shown as follows:

Figures 8 and 9 present the TGA thermograms of titania after acid treatment and a commercial source, YMC gel TiO_2 , respectively for the temperature range of 110°C to 900°C. From the TGA data, one can calculate the number of -OH groups (mmol/g) on the surface of the oxides. The equation used to calculate this is,

$$\text{OH (mmol /g)} = \frac{\% \text{ Weight loss}}{100} \times \frac{10^3}{18.0} \times \frac{2}{1}$$

To calculate the amount of TES required (in mL) for the experiments, the following equation was used.

$$\text{TES (mL)} = \alpha \text{ OH} \times \frac{(\text{OH:TES}) \text{ ratio}}{1 \text{ mmol OH}} \times \frac{1 \text{ mL TES}}{5.326 \text{ mmol/mL}}$$

A OH:TES ratio of 1:1 was used. Results of the TGA data and hydroxyl content calculated are listed in Table 7.

Figure 8. TGA thermogram of laboratory synthesized titania

Figure 9. TGA thermogram of YMC gel titania

Table 7. TGA results and hydroxyl content calculations

Name	% Weight loss	Hydroxyl content OH (mmol / gm)
Lab - TiO ₂	15.00%	16.68
YMC -TiO ₂	1.00%	1.11

3.4. FTIR (DRIFT) DATA

DRIFT spectroscopy provides a qualitative means for identifying functional groups on the surface and monitoring the chemical changes.

3.4.1. DRIFT Data of Titania synthesized in the laboratory

The DRIFT spectra of 3 day titania (curve A) and 7 day titania (curve B) are shown in Figure 10. The band at 3750 cm^{-1} is due to the isolated Ti - OH groups (i.e., not hydrogen bonded). The broad band centered between $3500 - 3200\text{ cm}^{-1}$ region is attributed to hydrogen bonded - OH groups and / or adsorbed water. Also, the band near 1630 cm^{-1} is assigned to water (6). The band centered between $3000 - 2750\text{ cm}^{-1}$ is believed to be due to alcohol or glycerol either trapped inside the matrix or attached to the surface. The intensity of the stretching is greater in the case of 3 day titania than in the 7 day titania. Organic material trapped in the crystal lattice could lead to irreproducible behavior in chromatographic separations. Attempts to convert 7 day titania to the hydride modified intermediate were unsuccessful. In order to remove the organic groups and expose the surface -OH groups, the 7 day titania was subjected to treatment with 0.1M HCl and then reacted with TES in the presence of an acid catalyst and dioxane as the solvent.

Figure 11 compares the TES silanization reaction carried out on 7 day titania for 2 hours (curve A) and 5 hours (curve B). For the hydride intermediate, (curve B, Figure 11) the strong band in the range of $2300 - 2100\text{ cm}^{-1}$ represents the Si - H stretching. A strong Si -H stretching band at 2255 cm^{-1} was detected by FTIR after TES silanization. This indicates that the silicon - hydride species was successfully bonded to the titania

Figure 10. DRIFT spectra of 3 day titania (curve A) and 7 day titania (curve B)

Figure 11. DRIFT spectra of hydride intermediate resulting after reaction time of 2 hours (curve A) and 5 hours (curve B)

surface. The intensity of -Si-H stretching is greater when the reaction is run for 5 hours. It can be concluded that more of the available -OH groups are converted to hydride when the reaction is run for a longer period of time. Figure 12 compares the TES silanization reaction carried out on 7 day titania with two different acid concentrations of the acid catalyst, 0.075M (curve A) and 0.103 M (curve B). The stretching band centered between $3000 - 2750 \text{ cm}^{-1}$ disappeared with higher acid concentration. Since organic material trapped in the crystal lattice could lead to irreproducible behavior, it is desirable to remove as much of the material trapped as possible. Therefore, big batch conversions were carried out using the higher concentration of the acid catalyst.

After small scale hydrosilation reaction, the -Si -H peak is reduced in intensity and additional -C-H stretching bands are seen in the range of $2800-3000 \text{ cm}^{-1}$. This result indicates that the olefin has successfully bonded to the hydride intermediate (Figure 13). Figure 14 shows the FTIR spectra of hydride modified titania (curve A) and C-18 bonded product, ODT (curve B) in the large scale experiment. The same behaviour is observed in the big batch experiments.

3.4.2. DRIFT Data of YMC-Gel TiO_2

The DRIFT spectra of YMC gel bare titania is shown in Figure 15. The results of the small scale experiments of TES silanization (curve A) and hydrosilation (curve B) are shown in Figure 16. The results of the big batch experiments are shown in Figure 17. The spectra of bare titania show bands at 3750 cm^{-1} which are attributed to the isolated Ti-OH groups. The broad band centered between $3500-3200 \text{ cm}^{-1}$ region is due to the hydrogen bonded - OH groups and / or adsorbed water. The band at 1630 cm^{-1} is also

Figure 12. DRIFT spectra of hydride intermediate obtained at an acid concentration of 0.075 M (curve A) and 0.103 M (curve B)

Figure 13. DRIFT spectra of Lab - ODT

Figure 14. DRIFT spectra of big batch hydride intermediate (curve A)
and Lab - ODT (curve B)

Figure 15. DRIFT spectra of bare YMC- gel titania

Figure 16. DRIFT spectra of small batch YMC - hydride intermediate (curve A) and YMC - ODT (curve B)

Figure 17. DRIFT spectra of big batch YMC - hydride intermediate (curve A) and YMC - ODT (curve B)

due to water. The band centered between 3000-2750 cm^{-1} may be due to organic matter trapped inside the matrix rather than attached to the surface because subsequent TES silanization reaction to convert to the hydride intermediate was successful without prior acid treatment. For the hydride intermediate, (curve A , Figure 16) the strong band in the range of 2300 -2100 cm^{-1} represents the Si - H stretching. A strong Si -H stretching band at 2255 cm^{-1} was detected by FTIR after TES silanization. This indicates that the silicon - hydride species was successfully bonded to the titania surface. After hydrosilation, the -Si -H peak is reduced in intensity and additional -C-H stretching bands are seen in the range of 2800-3000 cm^{-1} . This result indicates that the olefin has successfully bonded to the hydride intermediate (Figure 16, curve B). The same trend is observed in the big batch experiments confirming the success of the modification reactions.

3.5. CP-MAS -NMR DATA

CP-MAS-NMR spectroscopic analyses were used to obtain qualitative environmental information about the ^{29}Si and ^{13}C nuclei for the hydride modified and C-18 bonded products (ODT) and to confirm FTIR results. ^{29}Si CP-MAS-NMR gives a better indication of the nature of the hydride modified material than FTIR.

3.5.1. CP-MAS-NMR Data of Synthesized Titania

The ^{29}Si CP-MAS-NMR spectrum of the hydride modified titania is shown in Figure 18. It shows peaks at -85 ppm, -100 ppm. The peak at -85 ppm is due to the silicon atom with a hydride and three oxygen linkages, $\text{HSi}^*(\text{OSi})_3$. The peak observed

Figure 18. ^{29}Si CP-MAS-NMR spectra of big batch laboratory hydride intermediate

at -100 ppm is due to the presence of a silicon atom with four siloxane linkages. Such a result is not expected if a true monolayer exists with crosslinking and bonding to the surface oxide. This indicates that either polymerization of the TES has occurred or some decomposition of the TES has occurred in the presence of the oxide which led to the formation of a mixed layer including some areas of pure silica character. Figure 19 represents the ^{29}Si CP-MAS-NMR spectra of the hydrosilation product, Lab- ODT. It can be seen that the intensity of the peak, -Si -H at -85 ppm has decreased in intensity with respect to the peak at - 100 ppm . This confirms the success of the hydrosilation reaction. The ^{13}C CP-MAS-NMR spectrum of Lab -ODT is shown in Figure 20. ^{13}C CP-MAS-NMR spectra done on the olefin modified bonded phase of the following structure

will show peaks at 12 ppm, 23 ppm, 30 ppm and 32 ppm. The peak at 12 ppm is due to C1 and C18. The peak at 23 ppm is due to C2 and C17. The peak at 30 ppm is assigned to C4 through C15 while the peak at 32 ppm is due to C3 and C16. The appearance of peaks at 12 ppm, 23ppm and 30 ppm confirms that an alkyl ligand has chemically bonded on the hydride modified site of the C18 bonded products. This data supports the FTIR spectra (peaks in the range of $2800 - 3000 \text{ cm}^{-1}$) which show formation of additional surface species when the hydride intermediate is reacted with an olefin. The peaks appearing between 60 to 90 ppm are due to the isopropyl groups attached to the surface of titania.

Figure 19. ^{29}Si CP-MAS-NMR spectra of big batch Lab-ODT

Figure 20. ^{13}C CP-MAS-NMR spectra big batch of Lab-ODT

3.5.2. CP-MAS-NMR Data of YMC Gel Titania

The ^{29}Si CP-MAS-NMR spectrum of the hydride modified product is shown in Figure 21. It shows peaks at -85 ppm, -100 ppm. The peak at -85 ppm is due to the silicon atom with a hydride and three oxygen linkages, $\text{HSi}^*(\text{OSi})_3$. The peak observed at -100 ppm is due to the presence of a silicon atom with four siloxane linkages. Such a result is not expected. This indicates that either polymerization of the TES has occurred or some decomposition of the TES has occurred in the presence of the oxide which led to the formation of a mixed layer including some areas of pure silica character.

Figure 22 shows the ^{29}Si CP-MAS-NMR spectrum of the YMC-ODT. It can be seen that the peak at -85 ppm has decreased in intensity with respect to the peak at -100 ppm. The decrease in intensity is even more in the YMC hydride intermediate indicating that the degree of conversion of the available hydride groups is more in this case than in the synthesized titania. The appearance of peaks at 12 ppm, 23 ppm and 30 ppm in the ^{13}C CP-MAS-NMR (Figure 23) further confirm the success of the hydrosilation reaction. No peaks are observed between 60 to 90 ppm which is what was expected.

3.6. ELEMENTAL ANALYSIS

The results of elemental analyses are tabulated in Table 8. The surface coverage was calculated using the elemental analysis data and using the formula proposed by Berendsen and De Galan (21). The surface coverage for the YMC -ODT is greater compared to Lab -ODT.

Figure 21. ^{29}Si CP-MAS-NMR spectra of big batch YMC - hydride intermediate

Figure 22. ^{29}Si CP-MAS-NMR spectra of big batch YMC -ODT

Figure 23. ^{13}C CP-MAS-NMR spectra big batch of YMC -ODT

Table 8. Elemental analysis results and surface coverage calculations

Sample	% Carbon	Surface coverage (μ mol /m ²)
Lab Ti -O -Si - H	2.37	
Lab - ODT	5.39	1.06
YMC - Ti -O -Si -H	0.11	
YMC - ODT	3.3	3.3

3.7. CHROMATOGRAPHIC STUDIES

3.7.1. Chromatographic studies using YMC - ODT

3.7.1.1. *Separation of a mixture of polyaromatic hydrocarbons*

Figure 24 shows the elution profiles of a mixture of polycyclic aromatic hydrocarbons obtained with the YMC gel ODT column using methanol- water (80:20) as the eluent. The analysis was carried out under isocratic conditions with a flow rate of 0.8 mL/ min. The elution order of the aromatic hydrocarbons was, in order, benzene, naphthalene, biphenyl, phenanthrene, anthracene and pyrene indicating a typical reverse phase separation. The capacity factor of the various polycyclic aromatic hydrocarbons was calculated using the formula,

$$k' = \frac{t_R - t_0}{t_0}$$

where t_R is the time it takes for the hydrocarbon to elute from of the column and t_0 is the time taken by the solvent to come out of the column. The capacity factors of the various aromatic hydrocarbons are tabulated in Table 9. Figure 25 shows the elution profile of the aromatic hydrocarbons using methanol : water (70:30) as eluent at a flow rate of 0.8 mL / min.

3.7.1.2. *Separation of Perkin Elmer LC Universal mixture*

The elution profile of a Perkin -Elmer LC universal mixture is shown in Figure 26. The separation was carried out using methanol : water (65:35) as the mobile phase and a

Figure 24. Reverse phase separation of polycyclic aromatic hydrocarbons on YMC ODT-column using MeOH: H₂O (80:20) as eluent, flow rate 0.8 mL/min and 254 nm. Peak identity : 1 = Benzene, 2 = Naphthalene, 3 = Biphenyl, 4 = Phenanthrene, 5 = Anthracene, 6 = Pyrene.

Figure 25. Reverse phase separation of polycyclic aromatic hydrocarbons on YMC-ODT column using MeOH: H₂O (70:30) as eluent, flow rate 0.8 mL/min and 254 nm. Peak identity : 1 = Benzene, 2 = Naphthalene, 3 = Biphenyl, 4 = Phenanthrene, 5 = Anthracene, 6 = Pyrene.

Figure 26. Reverse phase separation of P-E mixture on YMC-ODT column using MeOH:H₂O (65:35) as eluent, flow rate 0.7 mL / min, 254 nm. Peak identity 1 = Sodium chloride, 2 = Benzene, 3 = Toulene, 4 = Ethyl benzene, 5 = Isopropyl benzene, 6 = Tert.butyl benzene, 7 = Anthracene.

Table 9. Capacity factors of polycyclic aromatic hydrocarbons on YMC- ODT

Name	Capacity factor ¹	Capacity factor ²
Benzene	0.94	1.34
Naphthalene	1.48	2.67
Biphenyl	1.84	3.81
Phenanthrene	2.81	6.41
Anthracene	3.02	7.15
Pyrene	4.61	11.71

¹Capacity factor at MeOH :H₂O (80:20)

²Capacity factor at MeOH :H₂O (70:30)

flow rate of 0.7 mL/min. The Perkin - Elmer mixture consisted of a mixture of aromatic hydrocarbons and the elution profile observed is typical of reverse phase separation.

3.7.1.3. Separation of NIST-SRM Test Mixture

The separation of a NIST-SRM test mixture consisting of three polycyclic aromatic hydrocarbons namely benzo[a] pyrene (BaP), tetrabenzo naphthalene (TBN), and phenanthro[3,4-c]phenanthrene (PhPh) was carried out on the YMC-ODT column using acetonitrile:water (85:15) as eluent. A flow rate of 0.8 ml/ min was used. The structures of the three polycyclic aromatic hydrocarbons is shown in Figure 27. The separation of this test mixture is intended primarily for the characterization of C-18 columns. The elution order of the three compounds changes with C-18 phase type (22). Monomerically bound C-18 phases have been shown to give the elution order, BaP $\leq$ PhPH < TBN. Phases prepared using polymeric surface modification procedures have the elution order, PhPh < TBN $\leq$ BaP. Phases with intermediate properties show the elution order, PhPh < BaP < TBN. The elution order obtained using the YMC-ODT column is shown in Figure 28. Comparison to the elution profiles in literature indicates that the YMC-ODT column has properties intermediate between a monomeric phase and polymeric phase.

3.7.1.4. Separation of a Mixture of Anilines

The separation of a mixture of N-methylaniline, N-ethylaniline and N,N-dimethylaniline were carried out on the YMC-ODT column using acetonitrile: water (25:75) as the eluent and a flow rate of 0.8 mL/ min. The chromatogram is shown in Figure 29. The compounds eluted in the order, N-methylaniline, N-ethylaniline and N,N-dimethylaniline. The capacity factors of the three anilines are tabulated in Table 10. The

BENZO[a]PYRENE

TETRABENZONAPHTHALENE

PHENANTHRO[3,4-c]PHENANTHRENE

Figure 27. Structure of NIST-SRM mixture components

Figure 28. Reverse phase separation of NIST-SRM mixture on YMC-ODT column using $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (85:15) as eluent, flow rate 0.8 mL/min, 254 nm. Peak identity 1 = PhPh 2 = BaP 3 = TBN

Figure 29. Reverse phase separation of a mixture of anilines on YMC-ODT column using $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (25:75) as eluent, flow rate 0.8 mL/min, 254 nm. Peak identity : 1 = N-Methyl aniline, 2 = N-Ethyl aniline and 3 = N,N -Dimethyl aniline.

Table 10. Capacity factors of anilines on YMC- ODT

Name	Capacity factor	b / a ratio
N-Methylaniline	6.64	1.00
N-Ethylaniline	11.31	1.00
N,N-Dimethylaniline	14.23	1.00

Table 11. Capacity factors of phenylalkylamines on YMC- ODT

Name	Capacity factor	b / a ratio
Benzylamine	1.88	1.07
2-Phenylethylamine	3.29	1.06

peak symmetry was evaluated by calculating the b/a ratio at 10% of the peak height. The results are given in Table 10. A value of 1.00 is obtained in the case of the three anilines showing a symmetrical peak.

3.7.1.5. Separation of a Mixture of Phenylalkylamines

The separation of a mixture of benzylamine and 2-phenylethylamine were carried out using acetonitrile:water (35:65) as eluent and a flow rate of 0.8 mL/ min. The chromatogram is shown in Figure 30. Benzylamine eluted first followed by 2-phenylethylamine. The capacity factors were calculated and the peak symmetry was evaluated by determining the b/a ratio. The results are given in Table 11. A value greater than 1.00 indicates a tailing peak.

3.7.2. Chromatographic Studies on LAB-ODT

The lab-ODT was packed into 1/4 in O.D., 4.6 -mm I.D $\times$ 150 -mm stainless steel tube. When a separation of a mixture of polyaromatic hydrocarbons was attempted, a pressure drop of more than 1600 psi was observed. This is common when one uses smaller sized particles to pack the column. As a result, the particles were packed into a shorter column with the following dimension, 1/4 in O.D., 4.6 mm I.D $\times$ 55 -mm. The elution order of the various polycyclic aromatic hydrocarbons was in the order, benzene, naphthalene, biphenyl, anthracene, phenanthrene, and finally, pyrene indicating typical reverse phase separation. Methanol : water (70:30) was used as the mobile phase at a flow rate of 0.2 mL/ min. However, their retention times were very close together making their separation impossible. The capacity factors of the various polycyclic aromatic hydrocarbons used in the study are given in Table 12. Various mobile phase compositions were tried as well as different flow rates. A complete separation was not

Figure 30. Reverse phase separation of phenylalkylamines on YMC-ODT column using $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (35:65) as eluent, flow rate 0.8 mL/min, 254 nm. Peak identity : 1 = Benzylamine, and 2 = 2- Phenylethylamine.

Table 12. Capacity factors of various analytes on Lab- ODT

Name	Capacity factor
Benzene	0.004
Naphthalene	0.0388
Biphenyl	0.0485
Anthracene	0.141
Phenanthrene	0.126
Pyrene	0.204

achieved in all of the trials. Theoretical considerations show that when one has two different analytes to be separated, their peak maxima is separated by a distance 'd'. On a longer column, their retention times will be increased and so will the distance of separation; that is, the separation distance is directly proportional to the column length. It can be shown that resolution is proportional to the square root of the column length. In conclusion, as long as two analytes have some difference in their partition coefficients, it must be possible to make a column long enough to separate them. It is believed that a complete separation can be achieved in 1/4 in O.D., 4.6 -mm I.D $\times$ 150 -mm column if one can optimize the conditions of the synthesis of titania. The particles synthesized have to be big enough to keep the pressure drop within reasonable limits. Sophisticated separation methods are needed to separate the bigger particles from the smaller ones.

The elution of N-methylaniline and N,N- dimethylaniline on lab -ODT using acetonitrile : water (25:75) as the mobile phase at a flow rate of 0.300 mL/min showed peaks with tailings. Calculation of peak symmetries gave a b/a ratio of 2.11 for N-Methylaniline and 2.09 for N,N -Dimethylaniline. It can be concluded that in addition to reverse phase partition, the retention on ODT is governed by electrostatic interaction of the solutes with titania as well, due to the existence of titanol ($\equiv$ Ti -OH) groups on its surface (23). It has been shown that the surface coverage on lab-ODT is inferior to that of YMC-ODT. The ^{29}Si CP-MAS-NMR spectrum of lab -ODT shows the presence of organic groups attached to its surface. These groups may be expected to start hydrolysing and converted to more titanol groups on the surface during the course of the chromatographic run making the problem of peak tailing even worse. Also, the ^{29}Si CP-MAS-NMR spectrum of lab - ODT indicates the formation of a mixed layer. The silanol groups present in these areas also can interact with the basic solutes leading to peak tailing.

CHAPTER 4

CONCLUSIONS

From the data presented in this study, it can be concluded that

- 1) Titania synthesized by the sol- gel method has physical characteristics that are comparable with the commercial source. FT -IR spectrum of the synthesized titania showed that it has a considerable amount of organic material attached to its surface. The organic material had to be removed by acid treatment before subjecting it to further modifications.
- 2) Modified titania bearing a silicon hydride species on the surface was successfully produced on both the laboratory synthesized titania and the commercial source, YMC- gel by the method of surface silanization with TES. From the results of the FTIR analysis, it can be concluded that the reaction time, as well as the concentration of HCl used in the surface silanization with TES could affect the amount of silicon hydride bonded to the oxide surface.
- 3) An additional modification of the hydride intermediate titania was successfully done on both the sources (laboratory synthesized as well as commercial) by a hydrosilation reaction with a terminal olefin, $C_{18}H_{36}$. This conclusion is supported by the results of FTIR and ^{13}C CP-MAS-NMR.
- 4) Results of elemental analysis show that the surface coverage, α_R ($\mu\text{mol} / \text{m}^2$) of LAB- ODT is less than that of YMC-ODT.
- 5) Chromatography studies done on YMC-ODT show that they behave in a way typical of reverse phase columns. Characterization of the column with NIST-SRM mixture

showed that the column displayed intermediate phase properties. Separation of basic compounds including anilines and phenylalkylamines was achieved using the YMC-ODT column.

There are several additional suggested investigations that could be done in the future. First, the conditions of the synthesis can be optimized to produce bigger particles. Efficient separation methods and tools are needed to separate the bigger particles from the smaller ones. Second, the modification process can be optimized to improve the surface coverage. Optimum surface coverage can be obtained by changing one experimental parameter at a time while keeping the other constant. The variables such as time, catalyst/olefin ratio, different catalysts, temperature and the solvent can be changed one at a time and surface coverage monitored. And finally, a thorough investigation can be done chromatographically to explore its potential as a column packing material.

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