SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS SILICA WITH CYCLODEXTRIN DERIVATIVES AS TEMPLATES.

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ABSTRACT

Certain small molecules such as cyclodextrins can form inclusion compounds with polymers. The guest polymer chains are confined to narrow, cylindrical channels created by the host molecular. The inclusion compound between cyclodextrin and Poly (ethylene glycol)-block –poly (propylene glycol)-block poly (ethylene glycol)have been successfully prepared and studied in this thesis. Several methods including TGA, X-ray diffraction, FTIR and NMR have been developed to characterize and confirm that polymer chains have been successfully included inside the IC narrow channels formed by the cyclodextrins.

Mesoporous silica with additional mesopores has been synthesized by using dimethyloctasilyl-ß-cyclodextrin and triblock polymer (poly (ethylene glycol)-poly (propylene glycol)-poly (ethylene glycol)) P123 as the structure directing agent. X-ray diffraction (XRD) and NMR techniques were used to characterize the calcined sample.

CHAPTER I

INTRODUCTION

1.1 GENERAL CHEMICAL AND PHYSICAL PROPERTIES OF CYCLODEXTRINS:

Cyclodextrins (CDs) have been of continuous interest over the last 50 years. The most frequently, compounds isolated have been α-, β-, γ- and δ-CDs (containing, respectively, 6, 7, 8 and 9 glucopyranose units. CDs have stimulated a large number of investigations. Their peculiar chemical structure, i.e. three different hydroxyl groups in each 1, 4-linked glucopyranose structural unit and a spatial arrangement in a hollow truncated cone shaped molecule, allows the formation of inclusion complexes. The cyclodextrins are cylindrical in shape with an axial cavity as shown in Figure 1. One part of the cavity is hydrophilic due to presence of hydroxyl groups at the smaller and larger lips of the cavity.[1] The primary hydroxyl group can rotate freely and interact with each other via hydrogen bonds. These hydrogen bonding interactions do not occur between the secondary hydroxyl groups. The secondary hydroxyl group is bonded more rigidly. The cyclodextrin molecule takes the form of a toroid due to the formation of hydrogen bonds by the primary hydroxyl groups. The inner portion of the cavity is formed by C-H groups and glycosidic oxygen bridges, and, as a result of this interior of the cavity, is relatively hydrophobic. The inner cavity also shows Lewis base character due to this glycosidic oxygen.

Cyclodextrin molecules are fairly stable in alkaline solution. However, they are quite susceptible to acid catalysis.

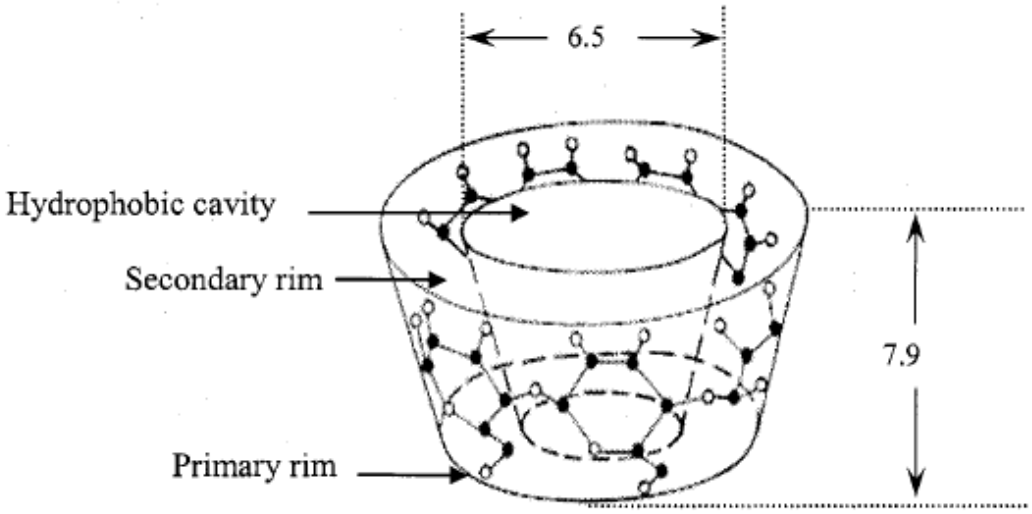

Figure 1. Structural representation of β-cyclodextrin.[1]

Some of their properties are given in Table 1.[2]

Table 1 Physical properties of cyclodextrin.[2]

	α-CD	β-CD	γ-CD
Molecular weight	972	1134	1296
Inner cavity diameter (pm)	500	620	800
Outer diameter (pm)	1460	1540	1750
Volume cavity ($10^6 pm^3$)	174	262	427
Surface Tension(	71	71	71
Number of water molecule in cavity	6	11	17
Crystal water content	10.2	13-15	8-18

1.2 SYNTHESIS:

Cyclodextrins are currently prepared by the action bacterial CGTases (cyclodextrin glycosyl transferases) on gelatized starch which is linear. Since the enzymes do not show length specificity, the resulting cyclodextrins contain 6-12 glucose units per ring. There have been steady developments in the investigations of new enzymes for the production of cyclodextrin.[3] Some European countries and Japan have already approved the use of cyclodextrins in food products. ß-Cyclodextrin is the least-expensive.

1.3 SYNTHESIS OF CYCLODEXTRIN DERIVATIVES:

Cyclodextrin derivatives have much greater scope and a broader range of applications.[4] The relative functionalities in all α-, β-, and γ-cyclodextrins are the primary (position -6) hydroxyls and the secondary (position 2 and 3) hydroxyls. The cyclodextrin derivatives are allowed to react at either all three (2, 3, 6) positions or selectively at any one of them. Some cyclodextrin derivatives that have been prepared are acylated cyclodextrin, [5,6] alkylated cyclodextrins,[7] amino and azido derivatives of cyclodextrins,[8] and halogen derivatives,[9] derivatives with alcohols, aldehydes, and ketones.[10,11] Other derivatives are known and contain silicon, boron, or tin functional groups.[12,13] If cyclodextrins are linked to polyethers, water soluble polymers are produced. Cyclodextrins can also be bound to polymeric resins.

1.4 SYNTHESIS OF INCLUSION COMPLEXES OF CYCLODEXTRINS:

The most amazing property of the cyclodextrins is their ability to form inclusion complexes with different molecules. The guest compounds are located in the cavity of cyclodextrins (host) and involve non-covalent bonding in the process of complexation. Different molecular interactions have been proposed as being responsible for the formation of cyclodextrin inclusion complexes in a aqueous solution[14] such as hydrophobic interaction; hydrogen bonding; the relief of high energy water from the cyclodextrin cavity upon substrate inclusion.

Water plays a crucial role in the inclusion process. It has been reported that the thermodynamic stabilities of some inclusion complexes in aqueous solution decrease markedly with addition of a dimethyl sulfoxide. The complexation mechanism of inclusion compound is shown in Figure 2.

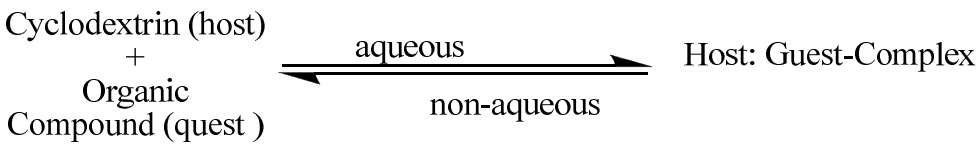

Figure 2. Complexation mechanism of the inclusion compound.

The method to synthesize the cyclodextrin guest-complex depends on the properties of the guest complex. When a guest molecule, of suitable size and preferably hydrophobic character, is added to cyclodextrin solution, water molecules in the cyclodextrin cavity are replaced by the guest molecules. Inclusion of the guest molecules induces structural changes in the cyclodextrin. Complex formation changes the elliptically distorted macrocyclic ring to a round structure with pseudo nine-fold symmetry.[15] When the cyclodextrins form a complex with a guest molecule larger than the cavity space, the guest molecule is only partially included in the host cavity. In such complex molecules, the guest molecules are not only in contact with inner surface of the macrocyclic ring but also with adjacent cyclodextrin molecules and solvent molecules incorporated in the crystals. Hydrogen bonds, Vander Waals interaction, electrostatic interactions, etc., have been mentioned as attractive interactions to stabilize the structure of the cyclodextrin complexes. For example, in the crystal of the a-cyclodextrin complex with 4-nitrophenol, the nitrophenyl group is well fitted to the a-cyclodextrin ring, which is rather elliptical in shape for the accommodation of the planar group.[16]

In the crystals of cyclodextrin complexes, the crystal structure arrangements are generally governed by the arrangements of cyclodextrin molecules because they dominate the intermolecular contact to form a crystal lattice. The arrangement mode is

not unique for a particular cyclodextrin but varies according to the guest molecule. There are three types of arrangement namely cage type, channel type, and layer type. Guest molecules determine the selection of one these packing modes. The cage type packing is frequently observed for relatively small guest molecules which can be enclosed in the host cavity. Cyclodextrin molecules are arranged in a herring-bone fashion, and both ends of the host cavity are closed by the adjacent molecules to create an isolated cage. The channel type structure is formed by linear stacking of cyclodextrin rings. The columnlike structure has an infinite cylindrical channel that can accommodate long molecules such as an alkyl chain or a linear polymer. There are two types of cyclodextrin arrangements called head to head and head to tail. The head to head arrangement is formed by the linear arrangement of head to head cyclodextrin dimers. In the dimer unit, the secondary hydroxyl groups of two molecules are face each another and connect by hydrogen bonds to create a barrel-like cavity. In the head to arrangement, cyclodextrin rings are linearly stacked, and the primary hydroxyl side faces the secondary hydroxyl side of the next molecules exposing hydrogen bonds.

The layer type arrangement structure has been sometimes observed when the guest molecule is so large that a part of molecule cannot be accommodated within cyclodextrin cavity. Guest molecules included in cyclodextrin are non-covalently bound.

1.5 β-CYCLODEXTRIN COMPLEXES:

The mode of inclusion depends not only on the size and shape of the guest molecule but also on its physicochemical properties. Nonionic small molecules tend

to form the cage-type packing structure, such as hydrogen iodide,[17] methanol,[17] ethylene glycol,[18] and glycerol.[18] The β-cyclodextrin cavity is fully occupied by squaric acid,[19] cyclohexane-1,4,-diol,[20] 2-acetooxybenzoic acid,[21] and hexamethylenentetraamine.[21]

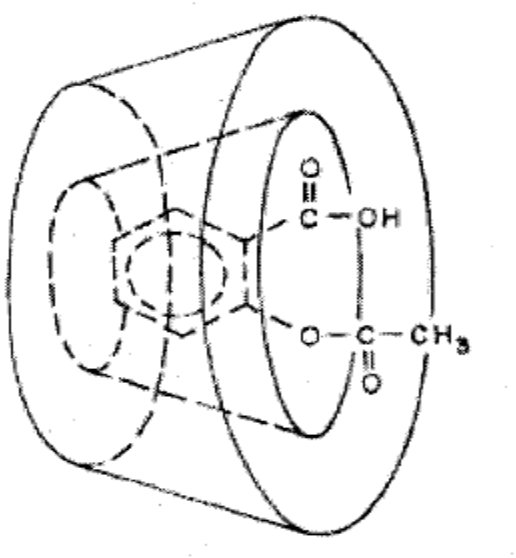

Figure 3. Proposed schematic of the inclusion compound[21]

β-Cyclodextrin complexes with guests that are considerably larger than the host cavity form a head to tail channel type structure. In β-cyclodextrin complexes with piroxicam sodium,[22] and mefenamic acid,[23] the cyclodextrin rings are linearly stacked to form the column like structure. In the channel type structure the dimer units are linearly stacked and helically arranged on the crystallographic two-fold axis

1.6 APPLICATIONS OF CYCLODEXTRIN:

Cyclodextrins have been known for almost a century and their ability to form inclusion

complexes has been recognized for about 40 years. Some of practical applications of

cyclodextrin[24] are include food preservation, chromatographic purification, catalysis, pharmacology (enhancement of drug bioavailability, pharmaceutical industry (drug purification), dye stabilizers,[25] agriculture, polymers and spectroscopy. Large scale applications of native cyclodextrin have been made possible by low cost. Unknowingly the food industry products involve cyclodextrin in everyday life. For instance, drinking grapefruit juice with bitter-tasting naringin removed by complexation with β-cyclodextrin is known and Earl Grey tea in which the flavoring agents are stabilized in the form of cyclodextrin complexes has been developed.

Cyclodextrins are also used as flavor components such as in apple, citrus, fruits, and plums and in spices such as cinnamon, garlic, and herbs. For example, in the production of candies and cookies using these flavors, the cyclodextrin complexes are added for processing. A product can be obtained using far smaller amounts for flavor than would be required conventionally. Docosahexaenoic acid (DHA) is one of the .-polysaturated fatty acid derived from fish oil. DHA smells badly and is unstable when exposed to heat, light or oxygen. By powdering it with cyclodextrin, however, the unpleasant smell and taste can be reduced[26] and the stability can be improved.[27] Cyclodextrins are used in the production of linolenic acid in powder form. The powdered linolenic acid is fixed on the fiber of the underwear. The linolenic acid can be directly absorbed by the skin. It is believed that cyclodextrin has many potential applications, some of which are already known while others remain undiscovered.

1.7 MICROPOROUS AND MESOPOROUS MATERIALS:

The synthesis and characterization of novel porous material have been strongly encouraged due to their wide application in the field of adsorption, catalysis and polymers. The micro and mesoporous silica can be traced back to the idea of zeolite synthesis, first introduced by Barrera and Deny. The idea was further studied by the Mobil research laboratories, which led to discovery of many new zeolites. During the early 1990's, Mobil research synthesized new class of mesoporous silicates known's as M41S, which were synthesized by using longer chain alkyl ammonium ions as the templates.[28] Kresge and his colleagues at Mobil coined the term "Liquid crystal templating" to describe the new synthetic method. The new family of material were denoted as M41S was divided into three subgroups distinguished by their mesophase geometry; namely hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50 phases. These materials are reported to have a surface area > 1000m^2/g and high degree of ordering with high sorption capacities for cyclohexane, n-hexane, and benzene. The liquid crystal templating synthetic method consists of mixing metal oxide precursors with a surfactant. The metal oxide precursors were tetramethylammonium silicate and precipitated silica while the ionic surfactant was hexadecyltrimethylammonium ion. At the proper reaction conditions and molar ratios, the surfactant self assembled into a micellular network with polymerized silica formed around the mesostructured template. The proposed mechanism of formation involves strong electrostatic interactions and charge matching between micelles assemblies of quaternary ammonium cations (S+), as the structure directing agents and the anionic silicate oligomer species (I-). The liquid is autoclaved at 150°C for 48 hours. After cooling to room temperature the solid precipitate

was filtered and dried. This precipitate was the silicon oxide network with the organized micelles throughout. Sintering of this material at 545°C removed the volatile organic surfactant leaving behind the mesoporous metal oxide network with interconnected mesopores arranged in the structure of the micelles.

As the field of inorganic oxides expanded, there was a push to create these ordered mesoporous silica network materials with larger pore sizes. Non-ionic block polymers presents an inexpensive, environmentally benign route to achieving a mesoporous oxide with larger pores. There have been growing demands for new types of mesoporous materials after discovering that M41S materials[29] have poor thermal stress properties. A novel material SBA-15 was first synthesized by the research group lead by Stucky.[30] SBA-15 earned much attention in the last decade owing to it excellent thermal stability, variable pore size, and tailored particle morphology. The pore topology consists of a two dimensional mesoporous network of uniform dimensions formed by microporous walls. Compared to zeolites which have pores in the micro range (4. to 14.), SBA-15 material is a new type of mesoporous materials with micropores. Zeolites are crystalline while SBA-15's pore walls are essentially amorphous, however, the mesopores of SBA-15 material are regularly spaced due to the templates liquid crystals micelle arrangements.[31]

SBA-15 is synthesized by the use of amphiphilic triblock copolymer, (poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-PPO-PEO) as the organic structure directing agent. PEO blocks are hydrophilic while PPO blocks are hydrophobic. Hence, direct formation of cylindrical micelles with the PEO blocks on the outside can be achieved in the aqueous solution. The aqueous silica cations locate themselves within the hydrophilic regions of the self assembled system and associate

preferentially with the PEO blocks. Removal of the polymer results in a mesoporous solid due to the hexagonal arrangements of the cylindrical polymers aggregates and also micro porosity generated by PEO segments.[32]

The process to obtain solid powder SBA-15 involves dissolving the template polymer in acidic solution, adding a silica source, which is typically either tetraethyl orthosilicate (TEOS), tetra methyl orthosilicate (TMOS), or sodium silicate. The mixed solution is aged at a temperature slightly above room temperature for 20-24 hours and heated up to 80-100 ºC in a conventional oven or in a microwave oven for an appropriate amount of time. Precipitated solids are centrifuged, washed, and dried. Finally, the organic polymer is removed by calcination's and by extraction using a solvent. Due to its structurally interesting properties and potential applications, there is a growing interest to investigate the structural properties of SBA-15 at optimized synthesis conditions. This motivated studies on the formation mechanism of SBA-15. Results from in-stiu SAXS,[33] time resolved NMR and TEM,[34] and EPR studies gave insight that the hexagonally packed structure is obtained within 2 hours after addition of the silica source. Fulvio and coworker synthesized SBA-15 with TEOS and sodium met silicate with an aging time of 2 hours, which is 10-12-fold reduction of commonly knowing aging time. Aged samples were heated at a higher temperature (100 ºC) for longer periods of time (12-48 hours). Thus, prepared samples exhibited a p6mm space group which is the characteristic feature of hexagonal structure found with X-ray diffraction. Two of the samples exhibited similar surface area. However, SBA-15 prepared with TEOS showed slightly larger pores volume than that formed using sodium met silicate. Sodium metasilicate precursor resulted in SBA-15 with higher microporosity and thicker pore walls. It has also been

found that the samples surface area decreased with increasing time and temperature from the hydrothermal treatment. However, the mesopore size distributions became narrower, and the mesopore widths and volume increased as a function of hydrothermal reaction time and temperature.[35]

There have been a great number of studies on controlling the microporosity of SBA-15 materials. When the SBA-15 was first synthesized by Stucky, there were controversies among research groups over whether SBA-15 is simply an array of uniform mesopores or a network of mesopores and microspores. However, Ryoo and coworkers, for the first time, reported that SBA-15 synthesized with P123 not only consists of ordered mesopores but also of micropores and even smaller mesopores that provide the connectivity between the ordered mesopores. It was later found that micropores exist in the silica walls of the ordered mesopores of SBA-15 as analyzed by gas adsorption, SAXS, and HRTEM. Microporosity of material can be tuned by many different factors: a) the source of silica, b) the polymer chain length of block copolymers used for the template,[36] c) heating method, d) the synthesis temperature and time,[37] e) the pH value, f) the silica source/surfactant ratio,[38] g) addition of co-solvent and salt. It is not easy to understand how each factor influenced the microporosity, since the factors typically are not independent.

As mentioned earlier, the microporosity originates from the PEO block in the tri-block copolymer, which penetrates into the silica wall and leaves micropores upon removal. As the synthesis temperature increased, the micropore volume decreased. This is due to the partial dehydration of the PEO blocks at elevated temperatures. Consequently, the result is a decrease in the interaction between micelles through the

PEO chains so that these become less occluded into the silica wall. This generates a reduction in the microporosity. Due to its distinct structure, it was claimed that SBA-15 would provide an ideal reactor or catalyst support. While mesopores act as channels for the reactant transport with little diffusion limitation, micropores in the wall act as active sites for reactions. Hence, SBA-15 silica has a high potential for applications in various areas of catalysis, separations, sensors and templates for the synthesis of novel mesoporous materials.

CHAPTER II

CHARACTERIZATION AND EXPERIMENTAL TECHNIQUES.

They are many ways to characterize mesoporous materials and inclusion compounds of ß-cyclodextrin. Some of the techniques are discussed below:

2.1 THERMO GRAVIMETRIC ANALYSIS:

In thermo-gravimetric analysis, the mass of a sample in a controlled atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample is increased. A plot of mass or mass percentage as a function of time is called a thermogram or a thermal decomposition curve. A commercial instrument for TGA consist of (1) a sensitive microbalance, (called thermobalance), (2) a furnace,(3) a purge-gas system for providing an inert, or sometimes reactive, atmosphere; and (4) a computer system for instrument control, data acquisition, and data processing.

Thermal analyses were performed using Shimadzu TGA-50 thermo gravimetric analysis (TGA). Samples of 2-5mg were used in tests. The furnace was heated from 30 ºC to 600 ºC at heating rate of 10 ºC/min after calibration with calcium carbonate. The instrument used air as the purge gas.

2.2 FTIR SPECTROSCOPY:

FTIR is an effective analytical tool for identification of unknowns, sample screening and profiling samples. It provides information about the chemical bonding or molecular

structure of materials, whether organic or inorganic. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies are translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in an FTIR library.

Varian 800 FTIR spectrometer was used for recording an absorbance spectra in the region of 400-4000 cm-1 under the following conditions: resolution 4 cm-1, scans 72.

2.3 X-RAY DIFFRACTION:

X-Rays are electromagnetic radiation with typical photon energies in the range of 100 ev-100 keV. For diffraction applications, only short wavelength X-rays (hard X-rays) in the range of a few angstroms to 0.1 angstrom (1 keV-120 keV) are used. Because the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure. X-rays are produced generally by either x-ray tubes or synchrotron radiation. In a X-Ray tube, which is the primary X-ray source used in laboratory x-ray instruments, X-rays are generated when a focused electron beam accelerated across a high voltage field bombards a stationary or rotating solid target. As electrons collide with atoms in the target and slow down, a continuous spectrum of X-rays are emitted, which is termed Bremsstrahlung radiation. The high energy electrons also eject inner shell

electrons in atoms through an ionization process. When a free electron fills the shell, a X-ray photon with energy characteristic of the target material is emitted. Common targets used in X-ray tubes include Cu and Mo, which emit 8 keV and 14 keV, X-rays with corresponding wavelengths of 1.54 Å and 0.8 Å, respectively.

Powder XRD (X-ray Diffraction) is perhaps the most widely used x-ray diffraction technique for characterizing materials. As the name suggests, the sample is usually in a powder form, consisting of fine grains of single crystalline material to be studied. The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore when a 2-D diffraction pattern is recorded, concentric rings of scattering peaks are displayed and correspond to the various d spacings in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. For example, the diffraction lines of graphite are different from diamond even though they both are made of carbon atoms. This phase identification is important because the material properties are highly dependent on structure .

SAXS measurements typically are concerned with scattering angles < 10. As dictated by Bragg's Law, the diffraction information about structures with large d-spacing lies in the region. Therefore the SAXS technique is commonly used for probing large length scale structures such as high molecular weight polymers, biological macromolecules (proteins, nucleic acids, etc.), and self-assembled superstructures. Small angle X-ray diffraction measurements were recorded at ambient conditions.

2.4 NMR SPECTROSCOPY:

NMR gives information about the number of magnetically distinct atoms of the type being studied. Many atomic nuclei have a property called spin. In fact any atomic nucleus that possess either an odd mass, an odd atomic number, or both has a quantized spin angular moment and magnetic moment.

Spin states are not of equivalent energy in an applied magnetic because the nucleus is a charged particle, and any moving charge generates a magnetic field of its own. Thus, the nucleus has a magnetic moment, μ, generated by its charge and spin. It is given by following equation:

$$\mu = \gamma * \square$$

Where γ is a magnetogyric ratio. It is apparent from the formula that γ is simply a proportionality constant between the magnetic moment and spin. The γ is specific to each nucleus. Both the negative and positive values of γ exist, with the difference being that positive values result in parallel spin and magnetic moment of the nucleus, while the negative value results in anti-parallel spins and magnetic moments. In a magnetic field, the spin begins to precess about the field. The frequency of precession (ω) in radians per second is given by :

$$\omega = -\gamma B_0$$

B_0 is the magnetic field. Changes in the angle of the precession cone are brought about by the magnetic fields of the other nuclei and electrons and the rapid movements of molecules. These microscopic fields interact with the spin, and change the angle gradually over time. Eventually, this allows for spins to find an energy minimum and

develop an equilibrium spin polarization. The energy of a spin in a magnetic field is given by equation below:

$$E = \hat{\mu} \bullet B_0 = -\gamma * \hat{I}_z \bullet B_O$$

$$\hat{I}_z = \eta * m_I$$

$\hbar$ is Planck's constant divided by 2p, and m1 is the quantum number corresponding to state of the spin. The z subscript of IZ indicates that this term corresponds to the z-axis component of this operator. In the case of a proton, Iz = h/2, leading to m1 = +1/2 or -1/2. By plugging in m1 values for proton, it is clear that the +1/2 state is lower in energy than the -1/2. It is possible to calculate the energy of transition between these two quantum states by subtracting their energies to obtain:

$$\Delta E = - \gamma * \hbar * B_0 * \Delta m_1$$

Selection rules limit the value of Δm_1 to +1 or -1 for I_z greater than ½ leaving the equation as:

$$\Delta E = \gamma * \hbar * B_0$$

For adsorption of energy between states, the equation is:

$$\Delta E = - \gamma * \hbar * B_0$$

The proton, which possesses one of the highest magnetogyric ratios of all nuclei, has $\omega = (-9.8*10^8*2\pi)$ rads/sec in some of the strongest magnetic fields presently used in NMR. This frequency gives energy of transition $(5.96*10^{-25}J)$. When this is plugged into the Boltzmann equation, one obtains:

$$\frac{N_\beta}{N_\alpha} = e^{-\frac{\Delta E}{k*T}} = 0.999855$$

2.4.1 PULSED FOURIER TRANSFORM SPECTROSCOPY:

The CW type of NMR spectrometer operates by exciting the nuclei of the isotope under observation by one nucleus at a time. When the pulse is discontinued, the excited nuclease begins to lose excitation energy and return to a original spin state. As each excited nucleus relaxes, it emits electromagnetic radiation. Since the molecule contains many different nuclei, many different frequencies of electromagnetic radiation are emitted simultaneously. The emission is called free induction decay (FID) signal. The signal decays exponentially with time as the nuclei relax and their signals diminishes. Since the horizontal axis on this is time. The FID is sometime called a time domain signal. The observed FID is actually an interference signal between the radiofrequency source and the frequency emitted by the excited nucleus. The interference signal represents the difference in the two frequencies. Since the frequency of the pulse is known, one can readily determine the exact frequency. The Fourier transform (FT) is a mathematical technique for converting time domain data to frequency domain data, and vice versa. The NMR characterization was performed on 300 MHz Bruker DSX solid state

spectrometer.

CHAPTER III

FORMATION AND CHARACTERIZATION OF POLY(ETHYLENE GLYCOL)-BLOCK-POLY(PROPYLENE GLYCOL)-BLOCK-POLY(ETHYLENE GLYCOL) CHAINS IN THE INCLUSION COMPOUNDS WITH CYCLODEXTRIN.

3.1 INTRODUCTION:

Cyclodextrin are cyclic molecules consisting of six to eight glucose units joined by a-1-, 4,-glycosidic linkages. According to Stoddart “Cyclodextrins are all purpose molecularcontainers for organic, inorganic, orgnometallic, and metalloorganic compounds that may be neutral, cationic, anionic or radical.” Cyclodextrin can form large number of inclusion compound. The significance of cyclodextrin both in research and applications lies in their ability to selectively form inclusion complexes with other molecules, ions, or even radicals. Complex formation changes the properties of the both host and guest, allowing one to monitor the process by several experimental techniques. Usually smaller molecules can enter the cavity forming inclusion complexes. Harda first observed that cyclodextrin formed crystalline inclusion complexes with polymers. The inclusion compounds formed between cyclodextrin and low molecular weight guests can have either channel or cage structures.

3.2 EXPERIMENTAL:

Poly(ethylene glycol)-block –poly (propylene glycol)-block poly (ethylene glycol), also known as P123 with average molecular weight of 5800g/mol, was obtained from Aldrich Chemical Company. ß-cyclodextrin was obtained from Cyclodextrin Technologies Development Inc. and was used after drying in a vacuum at 60 °C for 24 hours. Then 0.3 grams of P123 was dissolved in 50 ml of water and added drop wise to 50 ml of an aqueous solution saturated with ß-cyclodextrin while continuously warming at 60 °C for 3 hours. The solution was then cooled to room temperature, and a white precipitate obtained overnight was filtered and dried. The yield of the reaction is 87% of the inclusion complex.

3.3 CHARACTERIZATION of P123- β-CD-IC.

3.3.1 NMR SPECTROSCOPY:

The ^{13}C NMR spectra of β-cyclodextrin and the inclusion compound of β-cyclodextrin and P123 are presented in Figures 5 and 6. The ^{13}C NMR spectra of β-cyclodextrin consistent with the spectrum of pure-cage-structure β-CD molecules in the less symmetric and rigid conformation adopted when they are not entrapping guest molecules within their cavities. The ^{13}C NMR spectra of β-cyclodextrin shows multiple peaks for each carbon type. Whereas the spectra with the inclusion compound shows a single peak for each carbon type. The carbon resonances are observed for the methyl carbon of P123. The methyl intensity is quite reduced in the ^{13}C NMR spectra of inclusion compound comparison with those in ^{13}C NMR spectra of P123. The peaks at 16 ppm confirm that P123 is formed an inclusion compound, since the signal is from P123. The calculation of peak intensities and a literature analysis showed that the inclusion

compound of P123 and β-cyclodextrin have channel structure. In figure 5 the chemical shifts at 62.5 ppm corresponds to primary hydroxyl groups, the chemical shift at 74.4 ppm and 74.1 ppm corresponds to secondary hydroxyl group and the chemical shift at 110.1ppm corresponds to ether linkage. Similarly ^{13}C NMR spectrum of P123 was ran and the ^{13}C NMR chemical shifts were observed at17.6, 61.3, 63.9, 74.1 , 77.8, and 78.2.

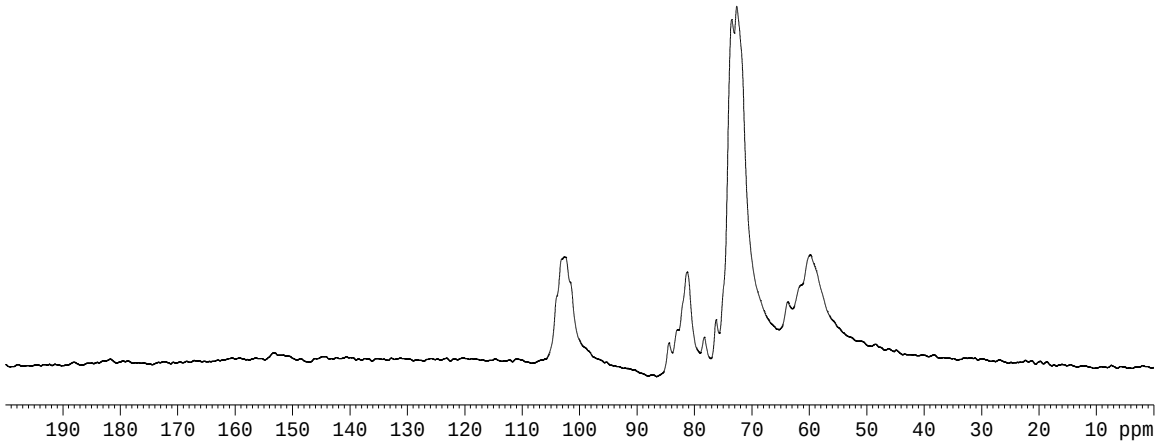

Figure 4. ^{13}C NMR spectra of β-cyclodextrin

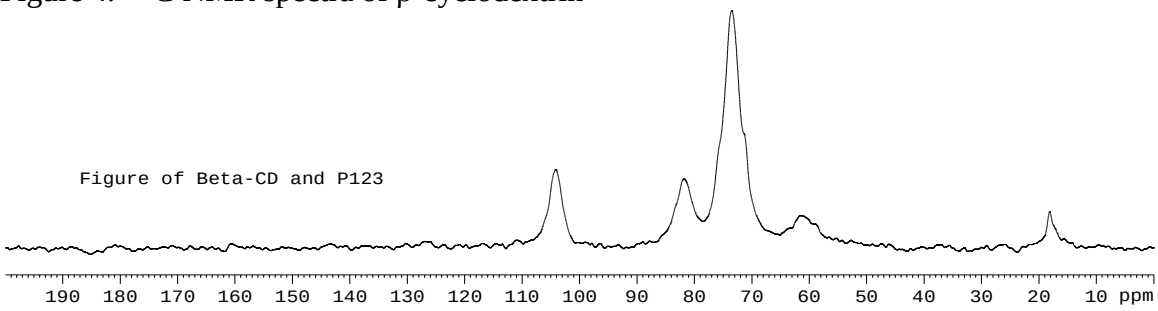

Figure 5. ^{13}C NMR spectra of inclusion compound of P123 and β-cyclodextrin.

3.3.2 X-Ray DIFFRACTION:

The X-ray diffractogram of the inclusion compound of ß-cyclodextrin and P123 shown in Figure 7. The X- ray diffractogram shows that it is not mixture of ß-cyclodextrin and P123 but crystalline complex has been formed between two. Major

peaks are observed for ß-cyclodextrin at 6.1, 10.2, 12.8 and 13.5. A major peak was observed at 7.5º for the inclusion compound. The X-ray pattern is similar to that of an inclusion compound between different valeric acid and cyclodextrin.

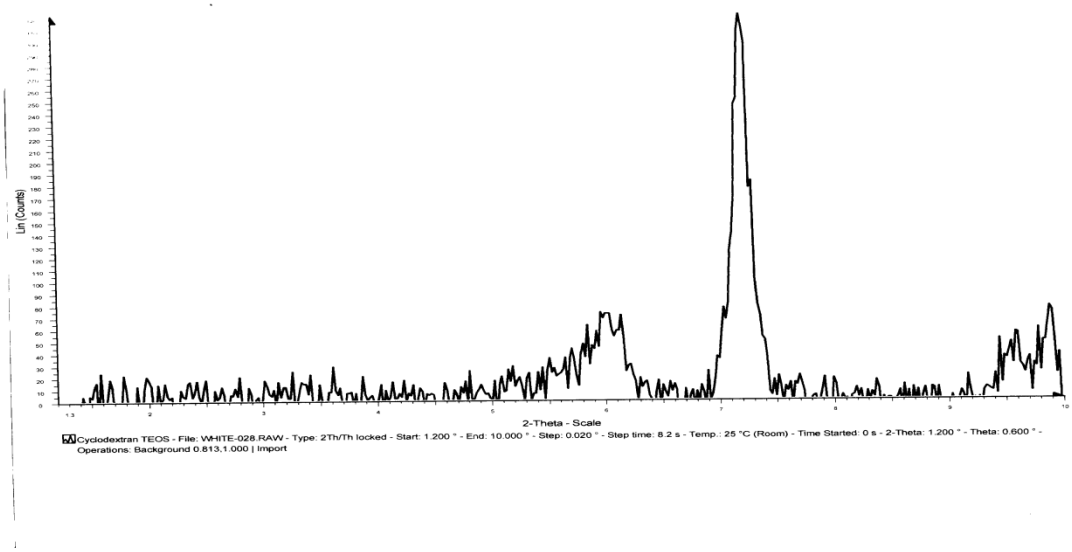

Figure 6. X-Ray diffractogram of the inclusion compound of β-cyclodextrin and P123.

3.3.3 THERMAL PROPERTY ANALYSIS:

The formation of the inclusion compound was confirmed from the melting behavior. The samples were evaluated by heating at rate of 10 ºC/min till 600 ºC. The Figure 8 shows TGA Thermograms of pure ß-cyclodextrin and P123-ßCD-IC. The pure ß-cyclodextrin starts to decompose at 300 ºC, and the weight remaining 87.2% at this temperature. It is observed for P123-ßCD-IC complex is that the decomposition temperature is 100 ºC lower than that of pure β-cyclodextrin. The greater weight loss at decomposition temperature may also be attributed to the dehydration of the complex.

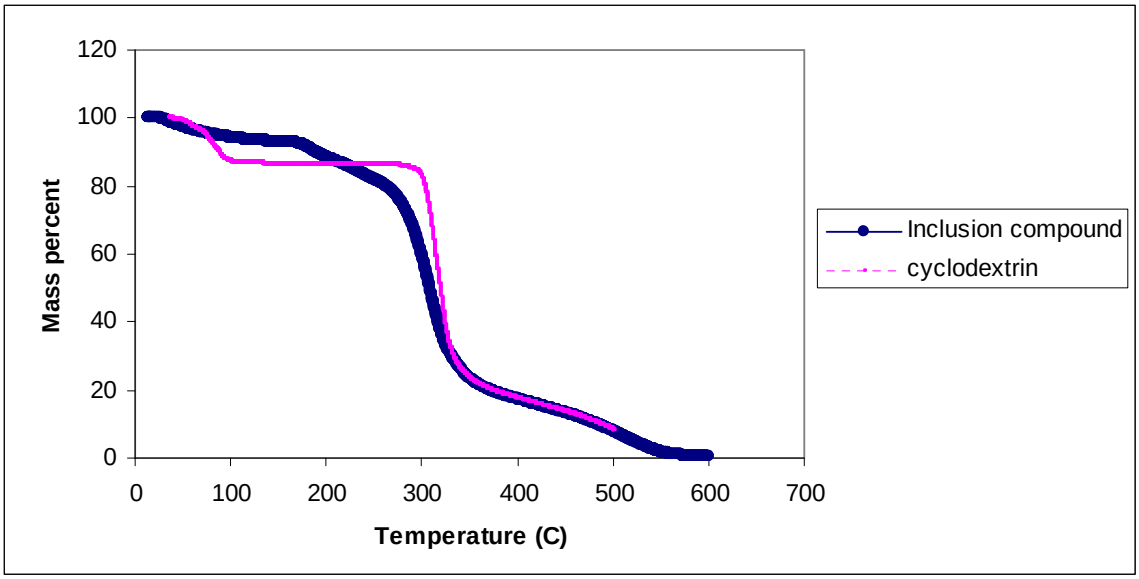

Figure 7. Thermal property analysis of β-cyclodextrin and the inclusion compound

3.3.4 FTIR SPECTROSCOPY:

The FTIR spectra of ß-cyclodextrin, P123, and the P123-ß CD-IC complex in the region from 200 cm^{-1} to 4200 cm^{-1} are presented in the Figure 9, 10 and 11. The peak from 3000 to 4000 cm-1 is normally assigned to symmetric and antisymmetric O-H modes. The position this band for pure ß-cyclodextrin is 3304 cm^{-1}. It is shifted to a higher frequency 3390 cm^{-1} when it forms the inclusion compound with the triblock polymer. The FTIR spectrum of the inclusion compound has a new band at 2950 cm^{-1} .

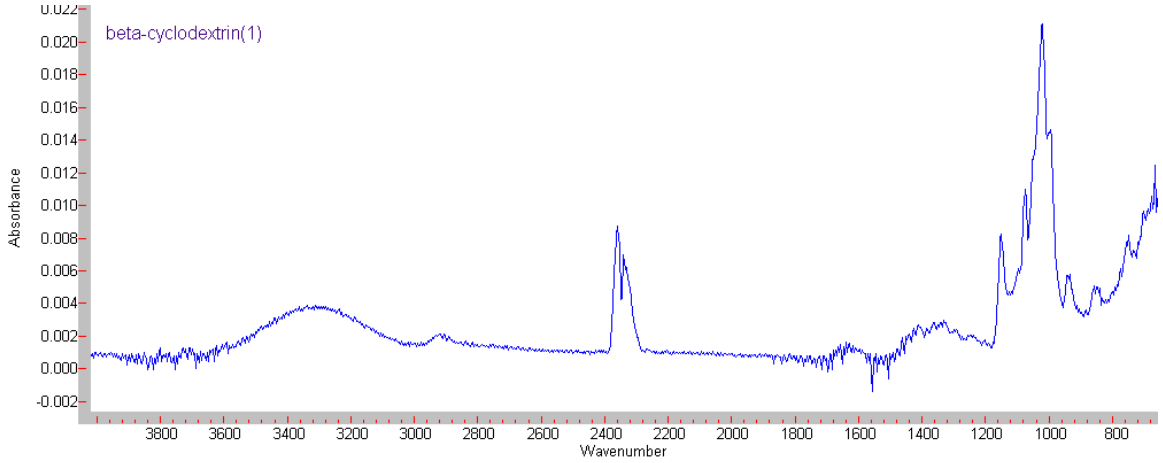

Figure 8. FTIR spectrum of β-cyclodextrin

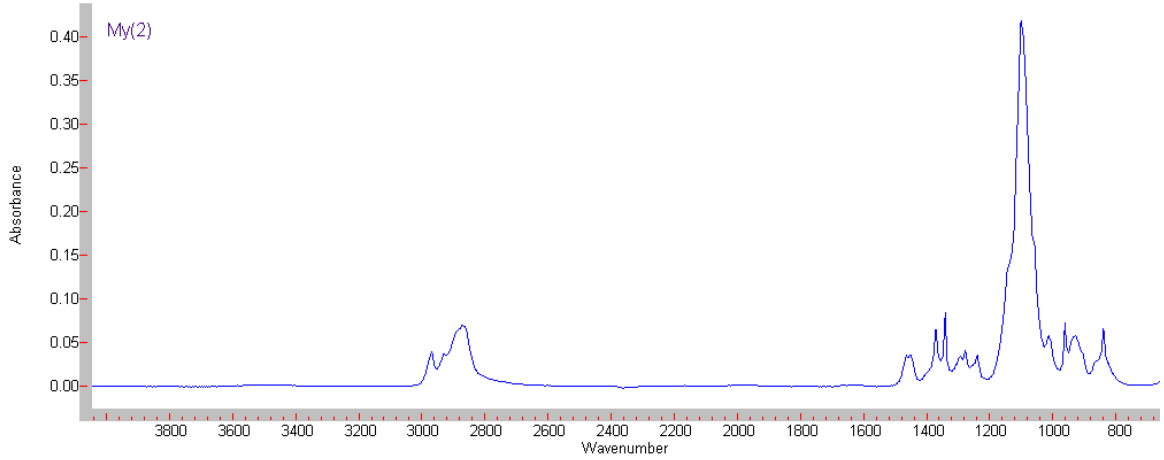

Figure 9. FTIR spectrum of poly(ethylene glycol)-block –poly(propylene glycol)-block poly(ethylene glycol).

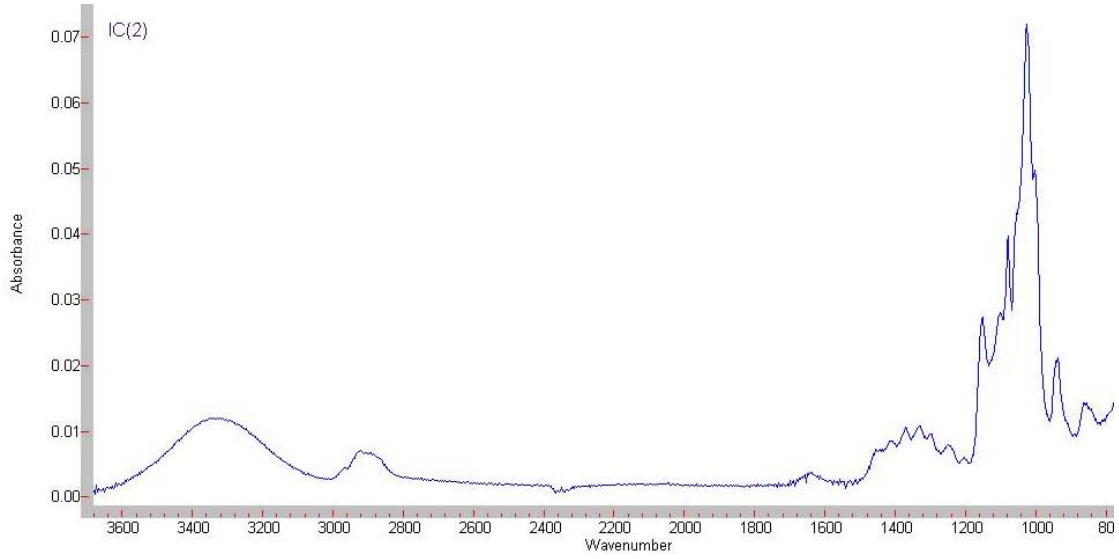

Figure 10. FTIR spectrum of inclusion compound of β-cyclodextrin and P123.

3.4 CONCLUSIONS:

We have confirmed the formation of an inclusion compound between β-cyclodextrin and P123. It was identified using different techniques such as ^{13}C NMR, XRD, FTIR and TGA analyses. The thermal stability of the inclusion compound is less than that of pure β-cyclodextrin.

CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS SILICA USING DIMETHYLOCTYLSILYL-β-CYCLODEXTRIN.

4.1 INTRODUCTION:

ß-Cyclodextrin is a cyclic oligosaccharide consisting of seven linked D-gluco-pyranose units. Cyclodextrin are known to form inclusion complexes[39] with a variety of commercially available block copolymers.[40] The mesoporous materials are of great interest in catalysis[41] and nanoparticles synthesis due their high surface areas and the presence of certain organic groups. Most recently, pore size and pore organization have been controlled through the choice of a surfactant, introduction of a co-solvent, rigorous control of processing conditions such as temperature and evaporation rate during synthesis, or a combination of the above.[42,43,44, 45] Only a few mesoporous materials containing a covalently bound organic host, such as cyclam,[46] have been prepared.

In this chapter we report the synthesis of micro and mesoporous silica using non-ionic block polymer P123 and dimethyloctasliyl-β-cyclodextrin as a structure directing agent.

4.2 EXPERIMENTAL.

β-Cyclodextrin was obtained from Cyclodextrin Development Research Inc. It was purified by recrystallization from water and dried in vacuum oven at 80 °C for 24 hr. The DMF employed in synthesis was dried over calcium hydride.

1-Chlorodimethyloctylsilane obtained from Aldrich Chemical Company and was used without further purification. Tetraethoxysilane (TEOS) and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) were also purchased from Aldrich Chemical Company and were used without further purification.

4.2.1 SYNTHESIS OF DIMETHYLOCTASILYL-β-CYCLODEXTRIN:

To a stirred solution of purified β-cyclodextrin (0.88 mmol) in 40 ml of dried DMF was added 1 gram of 1-chlorodimethyloctylsilane. The solution was stirred at 40 ºC for 24 hours under nitrogen. Water was added, and the precipitate was collected and washed with water. The precipitate was dried in vacuum oven at 80 ºC for 24 hours. The product monomer was obtained as a white solid. The ^{13}C NMR chemical shifts were observed at 3.0, 14.1, 20.3, 20.7, 22.4, 22.7, 29.9, 31.9, 34.7, 62.4, 62.5, 63.3, 69.9, 72.5, 74.1, 75.2, 83.1 and 110. 1. The yield is 68%.

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4.2.2 PREPARATION OF SYNTHESIZED ORGANOSILCIA MATERIAL:

The P123 was dissolved in DMF and let it stir for about 4 hours at room temperature. The monomer was added to a solution of DMF and P123. The solution was heated at 60ºC for 3 hours. Sodium hydroxide solution prepared by dissolving 0.25g of NaOH and deionized water (58.5 g) was added slowly to solution of monomer and P123. TEOS was added to this homogeneous solution under vigorous stirring. The mixture was

stirred at 60 ºC for 6 hours. Subsequently, the resulting mixture was transferred into a Teflon-lined autoclave and heated at 80 ºC for an additional 24 hours under static conditions. The solid product was collected by filtration, washed thoroughly with water, and air-dried at room temperature. The surfactant template was removed from the synthesized organosilica material through calcinations at 550 ºC for 14 hours.

4.3. CHARACTERIZATION:

4.3.1 NMR CHARACTERIZATION:

The chemical structure of the mesoporous dimethyloctasiliyl-β-cyclodextrin material was studied with solid-state NMR. The carbon signals in the β-cyclodextrin unit are found in the region 60-110ppm indicating that the covalently bound β-cyclodextrin units are intact during the template directed solgel process. The carbon spectrum of mesoporous dimethyloctasiliyl-β-cyclodextrin material lacks all carbon resonance a from P123, indicating the formation of inclusion complex as shown in the Figure 12. The peak at 110 ppm corresponds to ether linkage in the cyclodextrin molecule, whereas the peak at 3.0 ppm corresponds to Si-O-C linkage. The peak at 14.1 ppm corresponds to methyl group and the peak from 20.7 ppm to 32ppm corresponds to CH_2-group.

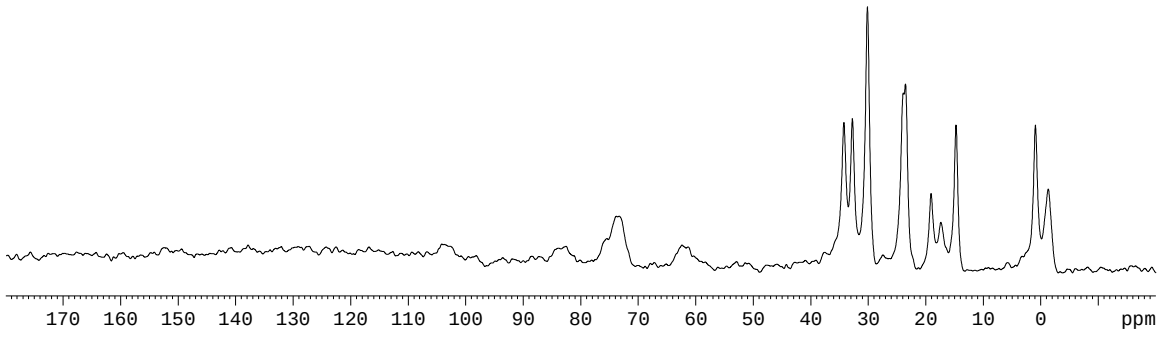

Figure 11. The ^{13}C NMR spectrum of dimethyloctasilyl-β-cyclodextrin organosilica

4.3.2 THERMAL PROPERTY ANALYSIS:

The presence of dimethyloctasilyl-ß-cyclodextrin in the mesoporous was confirmed from the melting behavior. The samples were evaluated by heating at rate of 10 ºC/min up to 600ºC. The Figure13 shows TGA thermograms of pure β-cyclodextrin, SBA-15 and mesoporous material synthesized using dimethyloctasilyl-β-cyclodextrin. The thermograms shows that β-cyclodextrin starts to decompose at 300 ºC, where SBA-15 remains stable and mesoporous material synthesized using dimethyloctasilyl-β-cyclodextrin as a template start to decompose temperature about 200 ºC due to presence of organic template (dimethyloctasilyl-β-cyclodextrin).

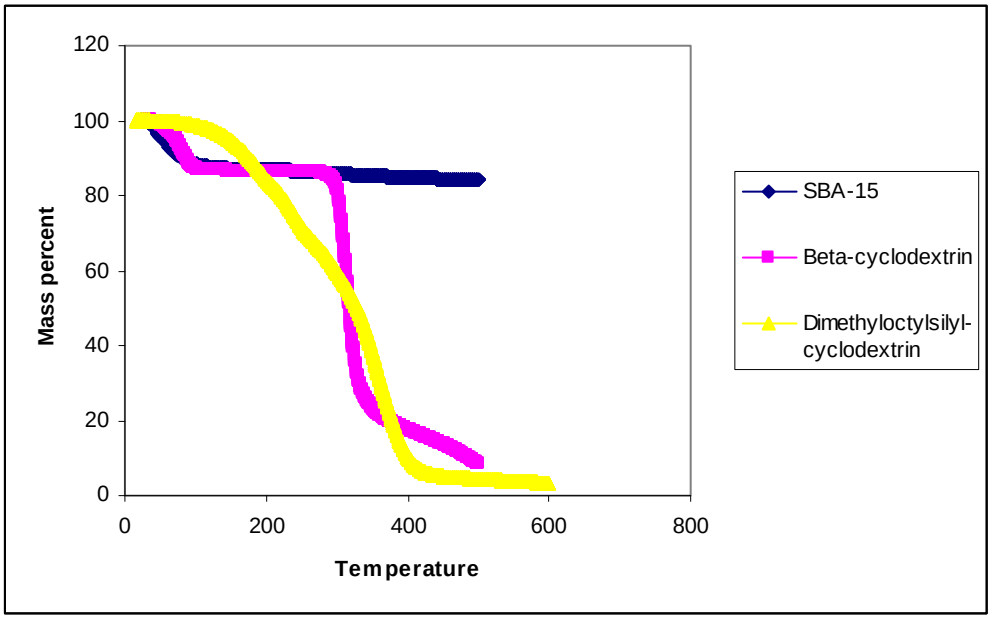

Figure 12. Thermal property analysis of SBA-15, β-cyclodextrin and dimethyloctasilyl-β-cyclodextrin.

4.3.3 X-Ray DIFFRACTION:

The Figure 14 shows the XRD pattern of the SBA-15. The XRD pattern of SBA-15 pure silica material shows a single strong and sharp low angle diffraction at 2θ= 1.02º, corresponding to the presence of a highly ordered mesoporous structure with d-spacing of 86. The XRD pattern of silica material synthesized using molar ratio 0.15: 1 of dimethyloctasilyl-ß-cyclodextrin and P123 is shown in Figure 15, show strong angle diffraction at 2θ = 0.34º with d-spacing of 261 and also reveal broad single at 2θ = 1.02º with d-spacing of 86, which indicates that material does not possess a highly ordered mesoporous structure. As the molar ratio of dimethyloctasilyl-ß-cyclodextrin was increased to 1 and then 2, no pronounced diffraction peak appeared in its small angle XRD pattern, indicating that material synthesized using molar ratio 1:1 and 1:2 of P123 and dimethyloctasilyl-cyclodextrin lacked any ordered porous material as shown in Figure 17.

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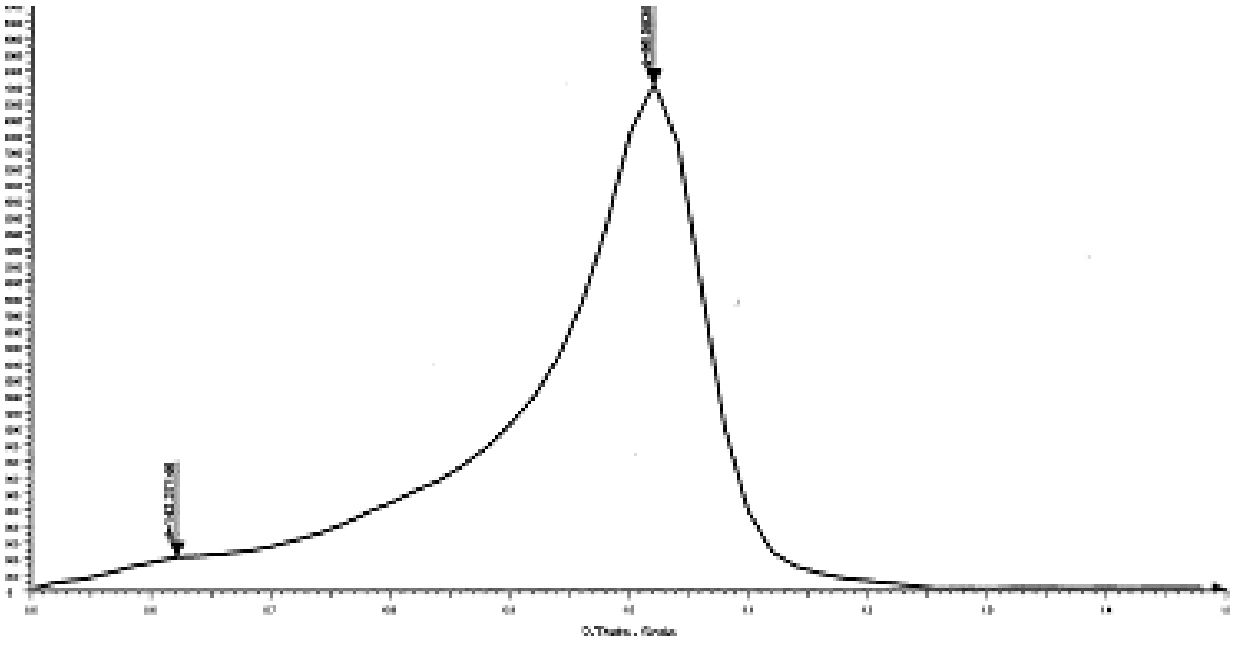


Figure 13. The XRD pattern of SBA-15.

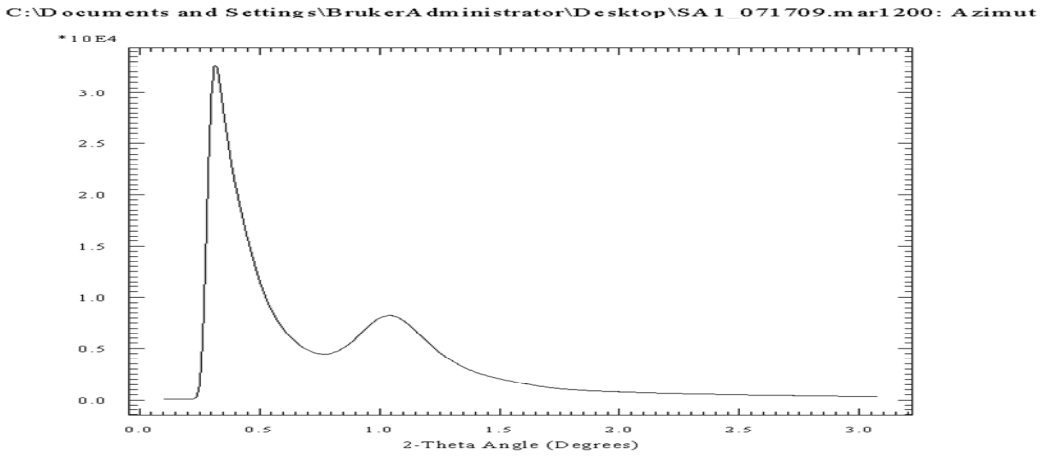


Figure 14a.The XRD pattern of silica material synthesized using a molar ratio of dimethyloctasilyl-ß-cyclodextrin and P123 of 0.15:1.

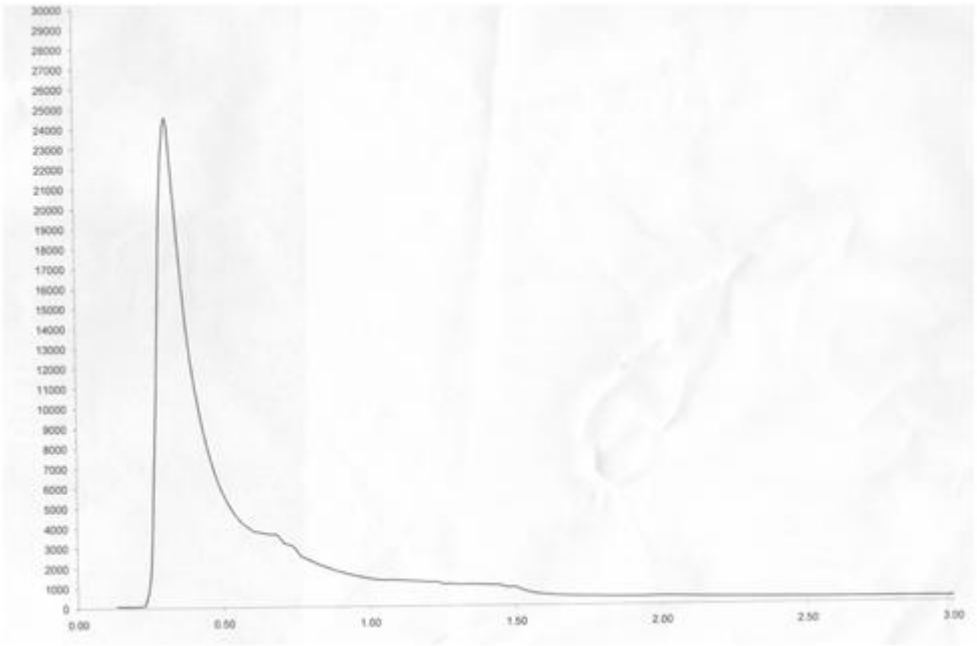
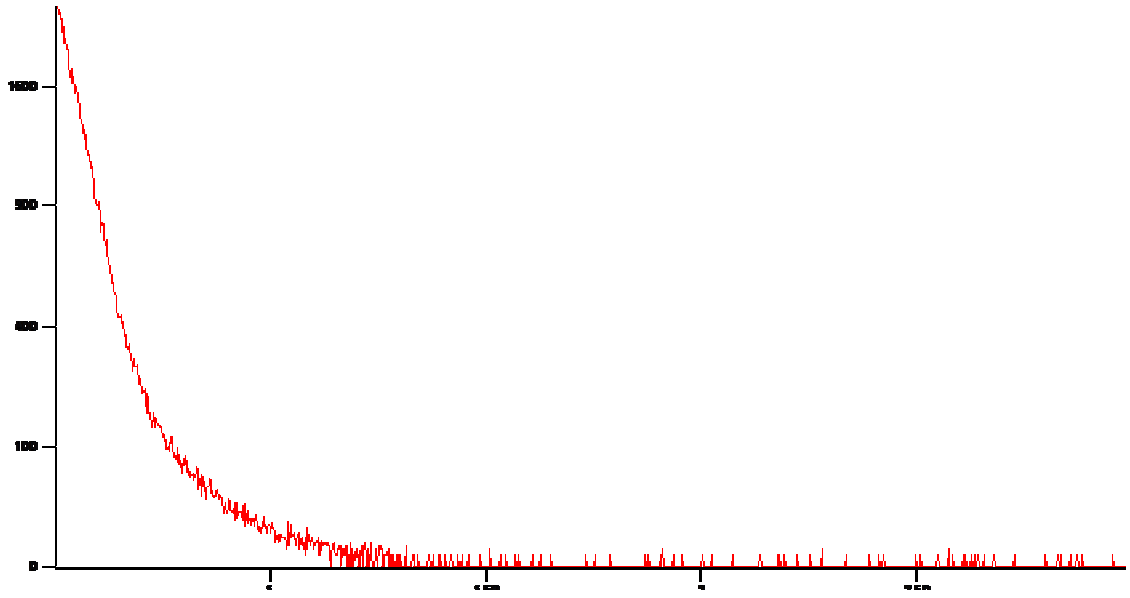


Figure 15b**.** The XRD pattern of silica material synthesized using a molar ratio of dimethyloctasilyl-ß-cyclodextrin and P123 of 0.30:1.



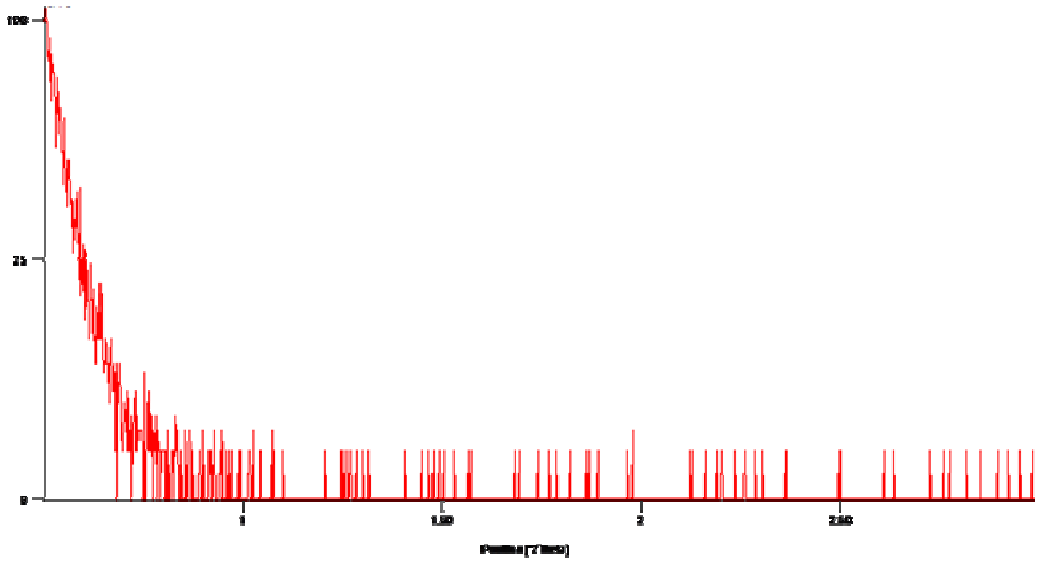


Figure 16. Mesoporous materials synthesized using molar ratios of 1:1 and 1:2 of P123 and dimethyloctasilyl-β-cyclodextrin.

4.3.4 BET SURFACE AREA:

Table 2 gives the BET surface areas measured by varying different molar ratio between P123 and dimethyloctasilyl-β-cyclodextrin. The BET surface area decreased with an increase in the molar ratio of dimethyloctasilyl-β-cyclodextrin. The area decreased sharply from 457 m^2/g to 72 m^2/g as an increase in number of moles of dimethyloctasilyl-β-cyclodextrin went from 0.15 to 1.

Table 2. BET surface area of organosilica material.

Sample Number	Moles of P123	Moles of dimethyloctasilyl-β-cyclodextrin	BET Surface area (m^2/g)
1	1	0	690
2	1	0.15	457
3	1	0.3	311
4	1	1	72
5	1	2	21

4.4 DISCUSSION:

The mesoporous silica material has been prepared using many different templating agents such as P123, amphiphilic carbohydrates or ionic surfactants. In this work the focus was to synthesize mesoporous material using P123 and dimethyloctasilyl-ß-cyclodextrin as a structure directing agents.

By variation of the cyclodextrin concentration by mol percent in the starting mixture, the influence on the structure of the resulting silica product was clearly shown in the above results. The surface decreased with an increase in concentration of dimethyloctasilyl-ß-cyclodextrin. One possible explanation might be that the dimethyloctasilyl-ß-cyclodextrin disturbed the formation of micropores.

4.5 CONCLUSIONS:

A new method for the preparation of ordered porous silica with dimethyloctasilylcyclodextrin has been developed. Hexagonally arranged mesoporous materials with surface areas ranging from 457-311 m2/g have been prepared. Mesoporous material containing dimethyloctasilyl-ß-cyclodextrin was synthesized and possessed a low surface area compared to SBA-15. The new material is potentially useful for wide variety of applications in environmental remediation and catalysis.

CHAPTER V

SYNTHESIS OF TRIMETHYLSILYL-β-CYCLODEXTRIN AND OCTA-DECYLDIMETHYLSILYL-β-CYCLODEXTRIN.

5.1 INTRODUCTION:

The selective modification of CDs was performed by a direct procedure, involving a specific activation process with bulky triphenylphosphonium salts or via protection of primary hydroxyl functions by t-butyl-silylation and by an indirect method, based on the protection of all alcohol groups as benzoates, followed by selective de-protection of primary hydroxyl groups (Takeo et. al 1989). Since the substitution of hydroxyl groups with less polar organic radicals affects the internal-hydrophobic/external-hydrophilic ratio of CD molecules and their conformation, with a strong influence upon the complexation properties, permethylated CDs were also prepared and their inclusion ability has been demonstrated. The general idea in the preparation of CD inclusion complexes was the modification of physical (volatility and solubility) or chemical (reactivity) properties of organic compounds or the synthesis of new materials with special characteristics. Derivatized CDs and different inclusion complexes were evaluated as catalysts in organic chemistry. Polyrotaxanes based on CD molecules threaded on various polymers such as poly(ethylene oxide) ,poly(propylene oxide), poly(methylvinyl ether), polyamides, polyesters, cationic polymers, polyisobutene,

polyazomethines or polydimethylsiloxanes were also prepared. To date, the silylation of hydroxyl groups in carbohydrate compounds and polymers has been used only as a protecting method. Different types of very efficient silylating agents were required. Moreover, the halogenosilanes with bulky organic radicals (t-butyltrimehylsilylchlorosilane), in the presence of imidazole as acid acceptor were proved to substitute the primary hydroxyl groups of a-, ß- and γ-CDs with a selectivity of 70%.

5.2 EXPERIMENTAL:

ß-Cyclodextrin was dried in vacuum oven at 80 ºC for 48 hours. The solvent was over CaH_2 and then distilled.

5.2.1 HEPTAKIS (6-O-TRIMETHYLSILYL) CYCLODEXTRIN.

To a stirred solution of dry ß-cyclodextrin (0.500 g) in dry pyridine(30 ml) at 0 ºC was added dropwise a solution of trimethylchlorosilane (0.9 g) in dry pyridine (10 ml). The mixture was kept at 0 ºC for 3 hours and then was stirred at room temperature overnight. Water was added, and the precipitate was collected and washed with water. The solvent and hexamethyldisiloxane formed by hydrolysis of excess hexamethyldisiloxane were removed by the hydrolysis by vacuum evaporation (60ºC, 24 hour). The yield is 84%.

5.2.2 HEPTAKIS (2, 6-DI-O-TRIMETHYLSILYL) CYCLODEXTRIN.

To a stirring mixture of ß-cyclodextrin (0.500 g) and imidazole (0.9 g) in dry N,N-dimethylformamide (30 ml) was added trimethylchlorosilane (1.0 g) and the mixture was kept at room temperature under argon for 24 hours. Water was added, and the precipitate was collected and washed with water. The solvent and hexamethyldisiloxane formed by hydrolysis of excess hexamethyldisiloxane were removed by the hydrolysis by vacuum

evaporation (60 ºC, 24 hour). The yield is 82%.

5.2.3 HEPTAKIS (6-O-OCTADECYLDIMETHYL SILYL) CYCLODEXTRIN.

The octadecyldimethylsilyl-ß-cyclodextrin was synthesized by stirring a solution of 0.1 mmol of ß-cyclodextrin in dry DMF (30 ml) at 0ºC For 2 hours. To the stirred solution of ß-cyclodextrin at 0 ºC was added a calculated amount of excess of dimethyloctadecylchlorosilane. The mixture was stirred at room temperature for 24 hour. It was then heated to at 80 ºC for another 24 hours. Water was added and the precipitate was collected and washed with water. The solvent and tetramethyldioctadecyldisiloxane, formed by hydrolysis, and excess dimethyloctadecylchlorosilane were removed by vacuum evaporation (60 ºC, 24 hours). The yield is 76% Silylated cyclodextrin obtained in this manner was highly soluble in petroleum ether, toluene, and chloroform. NMR characterization was performed on a Bruker DSX 300 spectrometer.

5.3 NMR CHARACTERIZATION:

The ^{13}C NMR spectrum of trimethylsilyl-ß-cyclodextrin are presented in Figure 16. The peak at 3.6 ppm corresponds to Si-O-C linkage and peak at 110 ppm corresponds to ether linkage. A preliminary investigation by NMR analysis showed that substitution increased with the use of imidazole. This result is clearly supported by ^{29}Si NMR inFigure 17. The chemical shifts at 16 ppm and 28 ppm in the ^{29}Si NMR corresponds to that of Si-O-C and Si-O-Si linkage.

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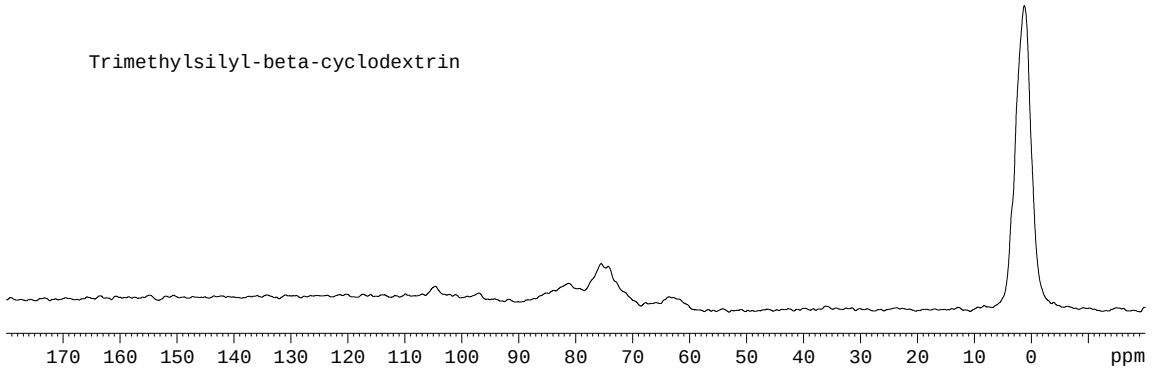

Figure 18. ^{13}C NMR of Trimethylsilylated cyclodextrin

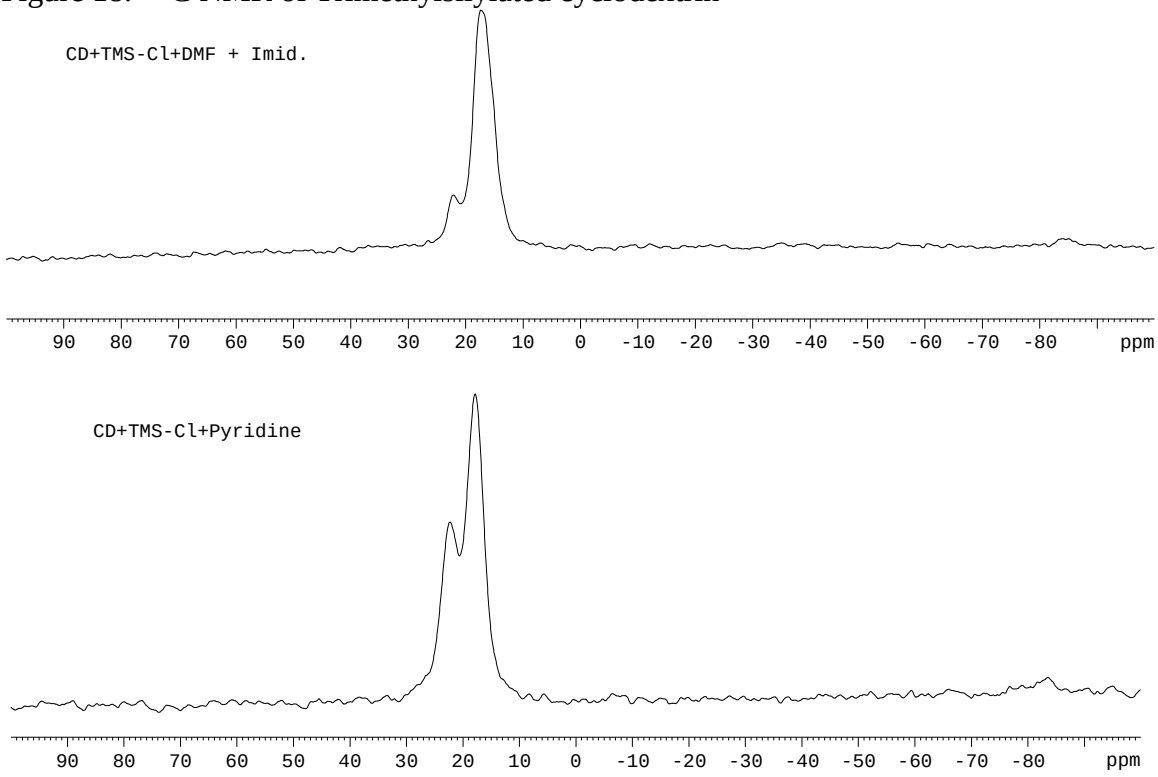

Figure 179. a.) ^{29}Si NMR spectra of trimethylsilyl-β-cyclodextrin using DMF (top) and Imidazole and b) trimethylsilyl-β-cyclodextrin using pyridine (bottom).

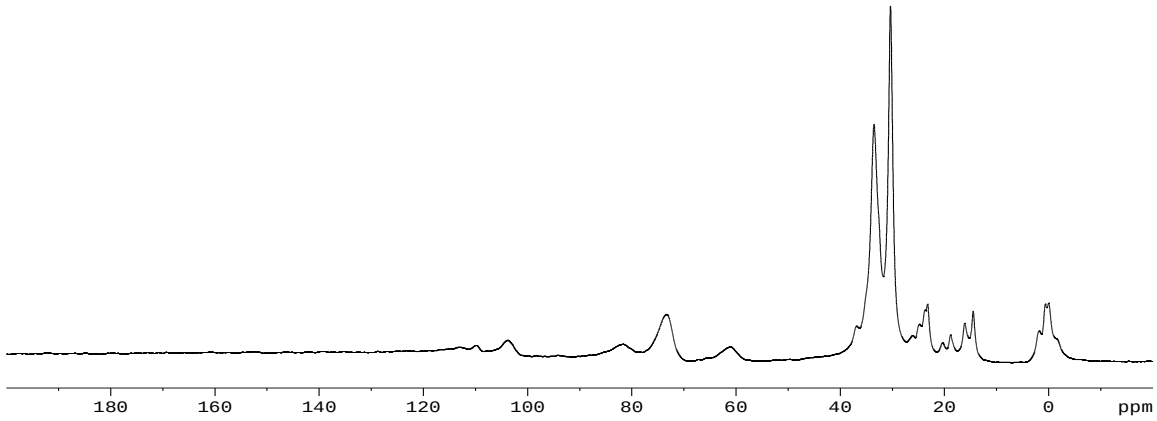

Figure 18. ^{13}C spectrum of dimethyloctadecylsilyl-β-cyclodextrin.

5.4 CONCLUSIONS:

The silylation of ß-cyclodextrin molecules was performed using different silylating agents and bases. Poor silylation was observed with a mixture of trimethylchlorosilane and pyridine. Only partially and unselectively silylated ß-cyclodextrin was obtained with a large excess of trimethylchlorosilane/imidazole system within 48 hours. The hydrophilicity of cyclodextrin molecules decreased as the degree of silylation increased and solubility in DMF was then reduced.

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APPENDIX

CONVERSION OF ISOBUTANE OVER H-BETA CATALYST IN GC/MICROREACTOR PULSED.

6.1 INTRODUCTION:

The microreactor is an indispensable unit for heterogeneous catalysis. Catalysis research often requires bench top reactors running simultaneously, which we believe dictates standard, low-cost designs. In this contribution, we describe in complete detail the components used to construct a pulsed, fixed-bed catalytic microreactor that is suitable for experiments at temperature up to 800 ºC. The catalytic conversion of isobutane over H-ZSM-5 and H-Beta is used as model system to briefly demonstrate the capabilities of the reactor design.

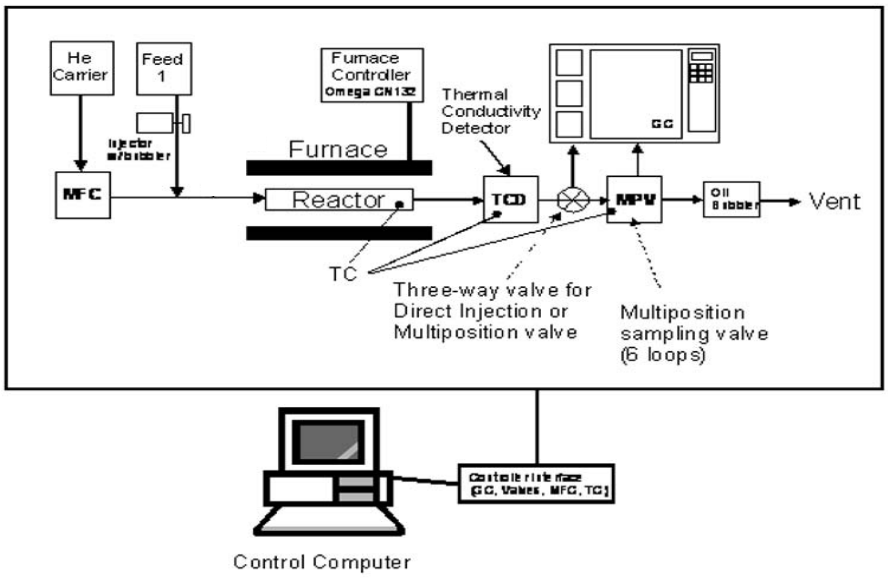

Figure 19. The schematic of microreactor

6.2 EXPERIMENTAL:

The conversion of alkanes was done microreactor that was built in the laboratory as shown in the Figure 19. The gas chromatography microreactor contained a mass flow controller, one six-port two position value for loading and injecting the test gas, thermal conductivity detector, a stainless steel reactor which was heated in a furnace, and a second sixport Valco valve used simultaneously with a Valco multi position collection valve with 250 microliter collection loops. The second sixport valve was used to collect up to 5 samples of the reactor effluent and analyze them offline. The effluent could be sent from the reactor directly to the GC by using a bypass valve which was connected just before the sixport two position valve. The amount of gas used depended on the amount of catalyst used. The basic relationship between the gas and catalyst is based on the number of gas molecules per acidic sites in the catalyst

The Beta catalyst was calcined in stainless steel reactor for 12 hours at 450 ºC at a flow rate of 30 SCCM. The experiment was performed by maintaining the gas at a certain temperature and passing the calculated amount of gas through it. The Beta catalyst bed allowed equilibration at the experimental temperature for about one hour before the injection of the sample. The GC was a model of HP 5890 GC FID fitted with a Restek 50 meters, 0.53 mm ID ,RT-alumina column. The heating setting on the GC maintained the temperature at 40 ºC for 5 minutes after the run start. Then a ramp up to 3 ºC per minute to 180 ºC was maintained at 180 ºC for 12 minutes.

The Thermal conductivity detector was built using Glow-Mac Instrument Company, 4 filament TCD unit and 1.2 V amplifiers, an 18 volt power supply, 2 potentiometers, an ammeter, and an instrumental amplifier. Peak Simple 3.29 software and a model 203

single channel data system from SRI Instrument was used to collect GC/FID data via a HP5980. The entire system, with exception of reactor, was kept at 150 ºC using a heating tape. The TCD detector was maintained at constant temperature (250 ºC) using a tape and a percentage controller. All microreactor functions were controlled with a PC using 2 National Instruments data I/O cards and Lab VIEW® 7 Express Student Edition Software.

In experiment a using a multi-position sample valve samples were collected by the triggering TCD. Only five samples could be collected because the system vented the sixth loop. The collection timing for the experiment was 5 second, 8 seconds, 11 seconds, 14 seconds, and 17 seconds, and the injection amount (250 µl) was same. Sample analyses were done immediately using GC. The helium carrier backpressure was fixed at 8 psi. Using three standard gas mixtures, the retention times were calibrated. The three different standard mixtures were of C1-C6 alkanes, C2-C6 alkenes, and mixtures of branched alkanes. In the direct injection experiment that without the bypass collection loops, 25 mg of calcined catalyst was placed in the microreactor. The microreactor was heated to the desired temperature, and a 250 micro liter loop was pressurized with isobutane. The gas was injected into the microreactor via the reactor control software interface and at the same time, the start button was manually pressed on the GC/FID to initiate analysis.

6.3 RESULTS AND DISSCUSSION:

The main purpose of the reactor was to systematically study conversion and selectivity of isobutane over H-Beta catalyst. Reaction experiments were carried out in 100 ºC with increments from 100 ºC to 550 ºC pulsing 1 equivalent of isobutane per acid

site of H-Beta. The chromatograph at 300 ºC is shown in Figure 20. Systematic analysis of the data showed that the product distribution contained a mixture of alkanes, branched alkanes, olefins, and aromatics. Figure 21 shows that the total conversion of isobutane varied with temperature.

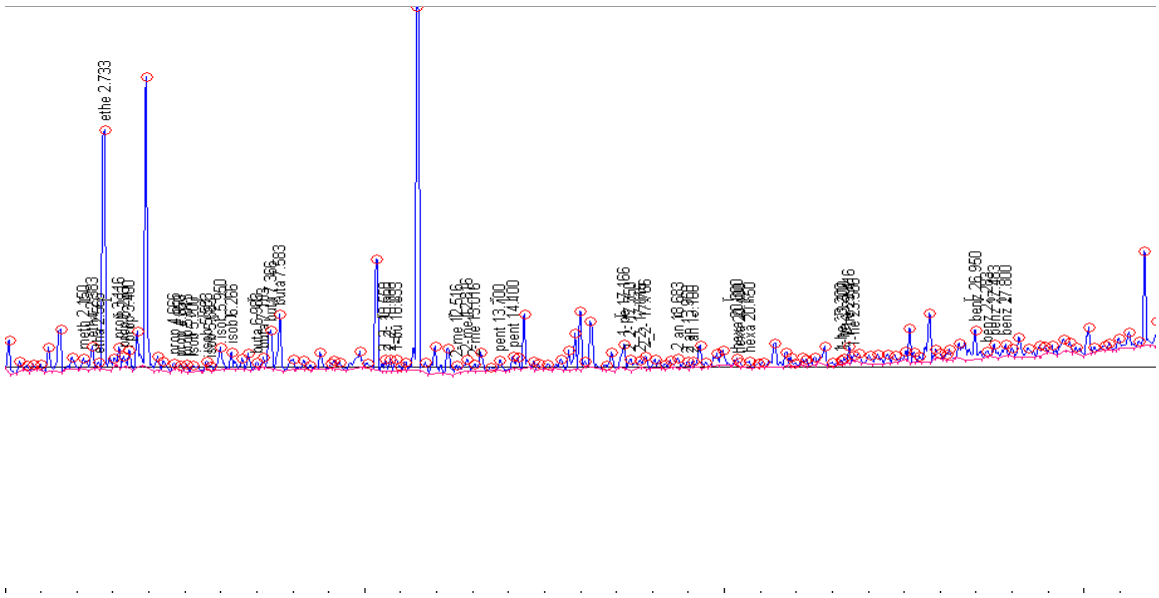

Figure 22. The chromatograph at 300 ºC of isobutane over H-Beta.

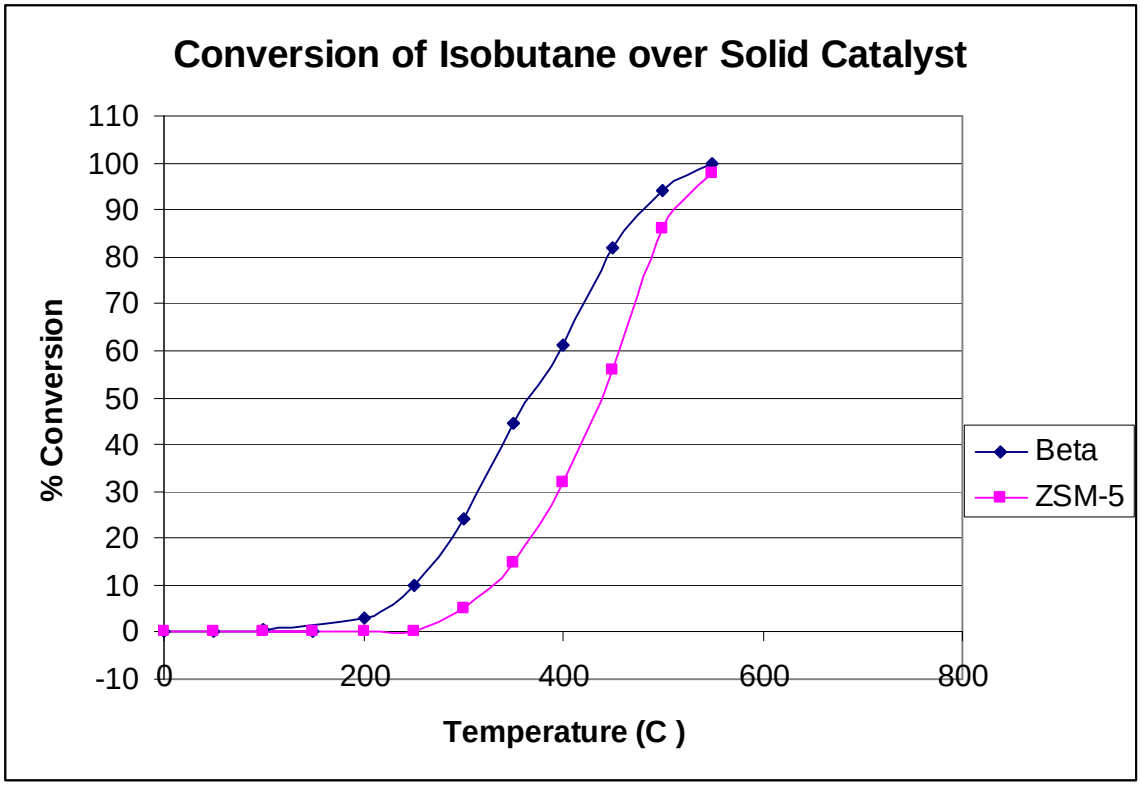

Figure 23. Conversion of isobutane over H-Beta and H-ZSM-5.

The goal was to understand the mechanism by which an alkane reaction is initiate via heterogeneous catalysis. Even in the case where isobutane was free from unsaturated impurities, it is known from control experiments that without a zeolite catalyst in the reactor, olefins and other products are readily formed(depending on temperature) via thermal or a radical mechanism catalyzed in a stainless steel reactor. Around 500 ºC varieties of products were formed including aromatic species. The percent conversion at 500 ºC is 90% which is high. The majority of products formed from hydrocracking rather than from alkylation.

6.4 CONCLUSIONS:

The conversion of isobutane over H-Beta and H-ZSM-5 catalyst was monitored via GC analysis coupled with a pulsed microreactor system. The data clearly indicated that total the isobutane conversion and selectivity was higher over with H-Beta than H-ZSM-5. At lower temperatures, a range of alkylation products were observed, in addition to some cracking products. At higher temperatures where total conversion was larger, cracking products were favored and conversions to benzene and toluene were observed.

VITA

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Findings and Conclusions:

Certain small molecules such as cyclodextrins can form inclusion compounds with polymers. The guest polymer chains are confined to narrow, cylindrical channels created by the host molecular

. The inclusion compound between cyclodextrin and Poly (ethylene glycol)-block –poly (propylene glycol)-block poly (ethylene glycol)have been successfully prepared and studied in this thesis. Several methods including TGA, X-ray diffraction, FTIR and NMR have been developed to characterize and confirm that polymer chains have been successfully included inside the IC narrow channels formed by `the cyclodextrins.

Mesoporous silica with additional mesopores has been synthesized by using dimethyloctasilyl-ß-cyclodextrin and triblock polymer (poly (ethylene glycol)-poly (propylene glycol)-poly (ethylene glycol)) P123 as the structure directing agent. X-ray diffraction (XRD) and NMR techniques were used to characterize the calcined sample.

ADVISER'S APPROVAL: Type Adviser's Name Here