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Supramolecular Assembly of Mesoporous Silicas With Neutral Amine Surfactant Structure Directors; Synthesis and Characterization

presented by

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has been accepted towards fulfillment of the requirements for

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SUPRAMOLECULAR ASSEMBLY OF MESOPOROUS SILICAS WITH NEUTRAL AMINE SURFACTANT STRUCTURE DIRECTORS; SYNTHESIS AND CHARACTERIZATION

By

Thomas Ralph Pauly

A DISSERTATION

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DOCTOR OF PHILOSOPHY

Department of Chemistry

ABSTRACT

SUPRAMOLECULAR ASSEMBLY OF MESOPOROUS SILICAS WITH NEUTRAL AMINE SURFACTANT STRUCTURE DIRECTORS; SYNTHESIS AND CHARACTERIZATION

By

Thomas Ralph Pauly

In 1992, Mobil researchers reported the first successful synthesis of mesoporous oxides with uniform pores ranging from 2.0 to 10 nm in diameter. These researchers used micelles formed from amphiphilic surfactants to assemble, through Coulombic interactions, charged silicate species into inorganic 'liquid crystalline' molecular sieves designated as M41S silicas. Removal of the surfactant by calcination results in an accessible open framework pore structure with high surface areas (800-1200 m²/g), high pore volumes (~1.0 mL/g) and uniform pore diameters that are attractive for numerous applications.

Tanev and Pinnavaia adapted this method of mesostructure assembly to include the use of hydrogen bonding interactions between electrically neutral amine surfactant micelles (S^o) and molecular silica species (I^o) as the structure directing driving force for the S^oI^o assembly process. The resulting HMS molecular sieves have been shown to possess many characteristics similar to

M41S silicas. There are, however, significant differences between these materials, specifically in their assembly mechanism, framework structure, framework pore order, and particle texture. Presented here is a comprehensive study of the neutral assembly (S°I°) of mesoporous silica molecular sieves using amine surfactants as the structure directors.

H-bonding between silicic acid derivatives of TEOS and amine surfactants impart curvature to the lamellar micelle assemblies resulting in stable wormhole pore structures. These essential H-bonding interactions are extremely sensitive to both the inorganic precursor (I^o) to organic surfactant (S^o) ratio and the synthesis temperature. Therefore, H-bonding assembly can be indirectly influenced through the manipulation of these factors resulting, in significant changes in pore structure and silica connectivity.

The fundamental grain size and associated textural (intra-particle) porosity of the disordered sponge-like HMS structures were correlated with the solubility of the surfactant in the water - alcohol solvents used for the S^ol^o assembly process. High textural porous HMS silicas were shown to be much more efficient catalysts than monolithic forms due to improved framework accessibility.

Cost effective mesoporous molecular sieve silicas similar to HMS silicas were synthesized from neutral alkylamine surfactants and water soluble silicate sources. Formation of these silicas occurs through H-bonding between neutralized silicate species and long alkyl chain primary or polyamine surfactants. To my wife and children, for all of their love and support!

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I am grateful to my family and friends for the support they have given me even though they may have no idea what it is I do. My parents, Don and Helen Pauly, and my in-laws, Orval and Marilyn Marrs, have continually offered encouragement and support and for that I am extremely thankful!

Most importantly, I would like to express my deepest gratitude to my wife, Denise, for all of the support she has given me over the years. I would not have been able to accomplish this dream of mine with out her. She probably didn't know exactly what she was getting into when she agreed to this, but I hope she doesn't have any regrets

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LIST OF ABBREVIATIONS

2,4-DTBP	-2,4-di - <i>tert</i> - butylphenol.
BET	Brunauer-Emmett-Teller.
cmc	-Critical micelle concentration.
CTAB	-Cetyletrimethylammonium Bromide, C ₁₆ H ₃₃ N(CH ₃) ₃ Br.
DDA	-Dodecylamine, C ₁₂ H ₂₅ NH _{2.}
Dm	-mass fractal dimension, $D_m = -P$ where $I(q) = C q^P$ SAXS data are
	plotted as Intensity vs. q on log-log scales such that power law
	scattering is seen as straight-line segments.
D _S	-Surface fractal dimension, $Ds = 6+P$ where $I(q) = C q^P$ SAXS data
	are plotted as Intensity vs. q on log-log scales such that power law
	scattering is seen as straight-line segments.
EtOH	-Ethanol.
FCC	-Fluid Catalytic Cracking.
g	-Packing parameter, based on the geometry of surfactant molecule
	and is arrived at by taking the ratio of its hydrocarbon core volume,
	V, to the product of its length, $l_{\rm c},$ and effective solvated surface area
	per amphiphilic head group, $a_o (g=V/(a_o I_c))$.
H-bonding	-Hydrogen bonding.
HCI	-Hydrochloric acid.
НК	-Horvath and Kawazoe pore size distribution model.
HMS	-Hexagonal Mesoporous Silica.
HMS-HTx	-Hexagonal Mesoporous Silica, high textural porosity.
HMS-LTx	-Hexagonal Mesoporous Silica, low textural porosity.
Г	-Anionic inorganic precursor.
I+	-Cationic inorganic precursor.
l°	-Neutral inorganic precursor.
IUPAC	-International Union of Pure and Applied Chemistry.
Lα	-Two-dimensional lamellar mesophase.

- L₃ -Bi-continuous, three-dimensional mesophase formed by bilayer structure.
- M⁺ -Metal Cation.
- M41S -Mobil family of Mesostructured silicas.
- MCF -Mesostructured Cellular Foams.
- MCM-41 -Mobil Composition of Matter 41, hexagonal mesophase (member of M41S family).
- MCM-48 -Mobil Composition of Matter 48, cubic mesophase (member of M41S family).
- MCM-50 -Mobil Composition of Matter 50, lamellar mesophase (member of M41S family).

mmol -Millimoles.

- MSU-G -Ultra stable vesicular silicas synthesized with amphiphilic Gemini diamine surfactants of the structure; C₁₂H₂₅NH(CH₂)₂NH₂ under hydrothermal conditions.
- MSU-H -Hexagonal mesostructured silicas synthesized with PEO based surfactants and water-soluble silicates under near neutral assembly conditions.
- MSU-SA -Mesostructured silicas synthesized with amine surfactants and water-soluble silicates under slightly alkaline assembly conditions. (Silicate-Amine).
- MSU-V -Stable mesoporous lamellar silicas with hierarchal vesicular morphologies synthesized with α,ω -diamine surfactants such as 1,12-dodecylediamine.
- MSU-X -Wormhole mesostructured silicas synthesized with PEO based surfactants and TEOS under neutral (N°I°) assembly conditions.
- MSU-X' -Wormhole mesostructured silicas synthesized with PEO based surfactants and water-soluble silicates under near neutral assembly conditions.

nm -Nanometer $(10^{-9}m)$.

NMR -Nuclear Magnetic Resonance.

N°	-Non-ionic amphiphilic PEO based surfactant.
NºIº	-Neutral assembly pathway utilizing H-bonding between PEO based
	surfactants and TEOS.
P/Po	-Relative Pressure, P = pressure, Po = Saturation Pressure.
PEO	-Polyethylene oxide.
ppm	-Part per million.
PXRD	-Powder X-ray Diffraction.
q	- The wave vector q is defined as, q = 4 π sin(20/2) / λ , where 20 is
	the scattering angle.
Q ²	-Incompletely condensed silica sites, SiO ₂ (OSi) ₂ ²⁻ .
Q ³	-Incompletely condensed silica sites, SiO(OSi)3.
Q⁴	-Completely condensed silica sites, Si(OSi) ₄ .
S ⁻	-Anionic amphiphilic surfactant.
S⁺	-Cationic amphiphilic surfactant.
S⁺I ⁻	-Pathway 1, electrostatic assembly between cationic surfactant and
	anionic silica precursors.
S ⁺ X ⁻ I ⁺	-Pathway 3, electrostatic assembly between cationic surfactant and
	cationic silica precursors using halogen ions as mediating
	counterions.
SANS	-Small angle neutron scattering.
SAXS	-Small-angle X-ray scattering.
SBA	-Mesostructured silicas assembled under high acid, low pH
	conditions with TEOS as the inorganic precursor.
SBA-15	-Large pore hexagonal mesostructured silicas assembled under
	high acid, low pH conditions with TEOS as the inorganic precursor
	and tri-block copolymers PEO based surfactants.
SBA-3	-Hexagonal Mesostructured silicas assembled under high acid, low
	pH conditions with TEOS as the inorganic precursor and quaternary
	ammonium surfactants.
SBET	-Specific surface area in m ² /g obtained from the linear part of the
	adsorption isotherm using the Brunauer, Emmett, Teller equation.

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S°	-Neutral amphiphilic amine surfactant.
S°l°	-Neutral assembly pathway between neutral amine surfactants and TEOS.
STSA	-Surfactant-Templated Silica Aerogels.
ТА	-Tallow amine, alkyl-polyamine surfactants of the type
	R(NH(C ₃ H ₆)) _X NH ₂ where R is a variable length alkyl chain (C ₁₄₋₁₈ H ₂₉ . ₃₇) and X = 0.
TDA	-Tallow Diamine, alkyl-polyamine surfactants of the type
	$R(NH(C_3H_6))_XNH_2$ where R is a variable length alkyl chain (C ₁₄₋₁₈ H ₂₉₋₃₇) and X = 1.
TEM	-Transmission Electron Microscopy.
TEOS	-Tetraethylorthosilicate.
TMB	-Trimethylbenzene (C ₉ H ₁₂).
TTA	-Tallow Triamine, alkyl-polyamine surfactants of the type
	R(NH(C ₃ H ₆)) _X NH ₂ where R is a variable length alkyl chain (C ₁₄₋₁₈ H ₂₉₋₃₇) and X = 2.
TTeA	-Tallow Tetraamine, alkyl-polyamine surfactants of the type
	$R(NH(C_3H_6))_XNH_2$ where R is a variable length alkyl chain (C ₁₄₋₁₈ H ₂₉ .
	₃₇) and X = 3.
USY	-Ultrastable Y zeolite.
Vf	-Framework pore volume.
VT	-Total pore volume.
V _{tx}	-Textural (intra-particle) pore volume.
Χ.	-Halogen ion.

Chapter 1

Introduction

1.1 Definitions of Porous Solid

Porous materials are found in a myriad of practical applications encompassing areas throughout society today. These materials find uses as adsorbents, as ion exchange media, in separation and as catalysts or catalytic supports.^{1,2} Though porous solids have various compositions, unvaryingly they are materials that contain accessible void space within their interior structure. Porosity within the interior of a continuous solid is defined as framework porosity. On the other hand, the aggregation or intergrowth of small grains into a solid particle results in the formation of pores between these grains and is defined as intra-particle, or textural porosity. The diameters of textural pores are directly related to the sizes of the grains forming these pores.

Porous solids are classified by their average pore diameter by IUPAC definition.³ Materials with average pores of less than 2.0 nm in diameters are *micro*porous, pores greater than 50 nm in diameter are *macro*porous and pore diameters from 2.0 to 50 nm are mesoporous.

A prominent sub-category of porous solids consists of materials whose framework is composed of an aluminosilica matrix, of which zeolites comprise a large component. Zeolites are crystalline microporous materials with the general

formula of M_x[(AlO₂)_x(SiO₂)_y]•n(H₂O). Many zeolites are quite robust and hydrothermally stable due to their crystalline nature. Pore structures are well defined within crystalline zeolites, however, their pore diameters are limited to the micropore region. This micropore size limitation reduces the use of zeolite molecular sieves to applications appropriate for relatively small molecules. Silica and aluminosilicate gels, on the other hand, have pore diameters within the mesopore range.⁴ The mesopore size distributions of these gels are quite large and unlike zeolites, the inorganic matrix is amorphous. The broad pore size distribution limits the size selectivity of the gels thereby limiting their use in practical applications. Additionally, the amorphous matrix is increasingly susceptible to instability when compared with crystalline zeolites.

1.2 Synthesis of Microporous Zeolites

The microporosity and relatively high surface area of zeolites are utilized extensively in applications as ion exchangers, adsorbents and separation media.² Today, the majority of zeolites are used as water softeners for detergents.⁵ However, their catalytic properties in general and petroleum refining in particular, have fueled their development over the past 50 years.^{5,6,7} Acid catalyzed Fluid Catalytic Cracking (FCC) of common hydrocarbons found in petroleum fractions is highly efficient within the micropores of acidic zeolites such as USY.

Synthetic zeolites are prepared under hydrothermal synthesis conditions from aluminosilicate gels. The first zeolites made were postulated to use

hydrated alkali metal cations as structure directing agents.⁸ Organic cations, such as tetramethylammonium cations in the synthesis of zeolite A,⁹ were later discovered to be effective as framework templates or structure directing agents in preparations of a number of zeolites. Today, there are hundreds of molecular sieves with more than 85 different framework structures classified.¹⁰ The preparation of these structures includes the use of molecular structure directing agents such as organic cations.

Even with the use of a multitude of organic cations as templates, the largest pore zeolites made from aluminosilicate gels have not exceed the 0.74 nm of faujasite. Zeolite molecular sieves are advantageous due to the increase in thermal stability and the attainment of a charged inorganic framework. Larger pore molecular sieves may allow for access to the "bottom of the barrel" fractions in petroleum refining for catalytic (FCC) purposes toward the production of gasoline. Large hydrocarbon molecules contained in this fraction cannot access the pores of conventional zeolites due to their limited size.

1.3 Synthesis of Mesoporous Molecular Sieves

1.3.1 Electrostatic (S⁺I⁻) Assembly of Mesoporous Molecular Sieve Silicas

A significant discovery in the design and synthesis of porous solids was reported in 1992 by researchers at Mobil.^{11,12} These researchers detailed in a series of patents and publications the preparation of a family of molecular sieve

oxides denoted M41S. These aluminosilicate molecular sieves are unique in that they contain pores with uniform sizes (2.0 to 10 nm in diameter) that previously had not been attainable. Mobil researchers used a structure directing species in the assembly of the pore structure, as is done in the synthesis microporous However, where zeolites synthesis utilizes individual or molecular zeolites. species in the structure-directing role, these researchers used assemblies of amphiphilic surfactant molecules in order to increase pore diameters significantly beyond the limits reached in zeolites. The specific class of surfactants used possesses long hydrophobic alkyl chains and hydrophilic guaternary ammonium When dissolved into aqueous solvents, they spontaneously form cations. surfactant assemblies or micelles. Amphiphilic molecules such as long chain quaternary ammonium surfactants $(C_nH_{2n+1}(CH_3)_3N)^+Br$ are able to minimize their energy in solution by forming micelles with their hydrophobic alkyl chain arranged at the interior and the charged head group at the exterior of the micelle.^{13,14} These surfactants can form different mesophases in solution depending on factors such as concentration. One such phase consists of cylindrical or rod-like surfactant micelles.¹⁵ Addition of a basic silica species such as sodium silicate to the surfactant solution and subsequent hydrothermal synthesis conditions resulted in the formation of molecular sieves through charge matching of the cationic surfactant (S⁺) micelle and anionic silica species (I⁻).¹³ The resulting pore structure formed through the electrostatic (S⁺I⁻) pathway illustrated in Figure 1.1 mimics the formation of liquid crystal phases known for these surfactants.¹⁵



Figure 1.1: Mechanism of silicate induced ordering of hexagonally ordered surfactant-silicate structures. Calcination resulting in MCM-41 silica with accessible pore volume.¹³

Mobil researchers were able to tailor mesopore size of the molecular sieves by: a) varying the chain length (C_n) of the surfactant;¹³ b) addition of auxiliary organic agents to swell the micelle array;¹³ or through c) post synthetic treatment to reduce pore size.¹⁶

MCM-41 identifies a subclass of these mesoporous silica that contain onedimensional cylindrical pores packed into a hexagonal array.¹³ Cubic MCM-48 and lamellar MCM-50 mesophases have also been identified and are also consistent with liquid crystal phases known to exist in pure surfactant/water mixtures.¹⁵ Characterization of the mesophases formed in M41S silicas is conclusively done with powder X-ray diffraction. Powder X-ray diffraction patterns of MCM-41 silicas (Figure 1.2A) typically show at least 3 diffraction peaks, the d₁₀₀, d₁₁₀, and d₂₀₀ peaks, that can be indexed to the hexagonal unit cell with a unit cell parameter $a_0=2d_{100}/\sqrt{3}$. MCM-48 (Figure 1.2B) and MCM-50 (Figure 1.2C) also show X-ray diffraction patterns characteristic of the long-range symmetry of the mesophase.

The preparation of ordered pore mesostructures, such as hexagonal MCM-41, by Mobil's pathway involves the use of aqueous solutions of cationic quaternary ammonium surfactants, silicate and aluminate species, and acid or base dependent on the source of silica utilized in the reaction.¹³ A quaternary ammonium surfactant, such as cetyltrimethylammonium bromide, $(C_{16}H_{33}N(CH_3)_3Br, CTAB)$, is dissolved in H₂O, to which is added a sodium silicate solution at a specific I⁻/S⁺ ratio, typically 4.0 for MCM-41. After the



Figure 1.2: Powder X-ray diffraction patterns of M41S silicas. (A) calcined hexagonal MCM-41, (B) calcined cubic MCM-48 and (C) as made lamellar MCM-50.¹³

solution is aged a short period of time at ambient temperatures, the pH of the basic solution is lowered to values from 10-12 with the addition of an acid. The reaction vessel is sealed and heated under autogenous pressure at 100-150 °C for 4 hours to 4 days. The precipitated product is recovered by filtration, air-dried and calcined at temperatures above 500 °C to remove the surfactant species by combustion.¹³

The silica species used is not limited to the use of sodium silicates or water glass but can include colloidal silica such as Ludox[™], fumed silica such as Cab-O-Sil[™], or even molecular silica species such as tetraethylorthosilicate (TEOS). The use of non-basic and non-water soluble silica species, however, requires the use of a base to dissolve colloidal or fumed silicas and to increase the pH to the targeted assembly range. Of note is the ability to substitute heteroatoms such as aluminum for the silica, imparting charge and functionality to the amorphous framework structure.¹³

N₂ adsorption-desorption isotherms of these porous silicas (Figure 1.3) indicate the Type IV isotherms typical for mesoporous materials.¹⁷ Characteristic of mesoporous materials is the sharp increase in the volume of gas adsorbed at relative pressures between 0.2 and 0.6. The adsorption uptake at these relative pressures is due to capillary condensation of the gas within the confined space of the framework mesopores. The relative pressure at which this step occurs is determined by the size of the pore and shifts to higher relative pressures as the pore diameter increases. BET surface areas³ are estimated to



Figure 1.3: N₂ adsorption-desorption isotherm of calcined MCM-41 molecular sieve. (Inset) Corresponding Horvath-Kawazoe pore size distribution curves plotted as normalized volume of N₂ vs. pore diameter (nm). Sample prepared by method described elsewhere.¹³
Figure 1.4: TEM image of calcined MCM-41 silica molecular sieve with 3.3 nm pore diameter. Sample prepared by method described elsewhere.¹³



be approximately 800-1200 m²/g for MCM-41 silicas. Mesopore volumes range from 0.7 to 1.2 cm³/g as indicated by the volume adsorbed at the completion of the capillary condensation step. Pore size distributions are calculated from the adsorption branch of the isotherm using various models. Originally, Mobil modeled their pore sizes using the model of Horvath and Kawazoe.¹⁸ This model (Figure 1.3, inset) has been shown to accurately determine the average pore diameter of cylindrical mesopores of less than 5.0 nm in diameter even though it was originally proposed as a model for microporous materials with slit-like pore geometries.¹⁸

Calcination of the mesostructured silicas removes the surfactant, leaving behind a stable silica framework with open framework pores of uniform diameter. The framework pore structure is clearly visible in TEM images of MCM-41 silicas (Figure 1.4). The left side of the image shows the hexagonal pore structure of the silica as the pores within the particle are oriented parallel to the viewing axis of the microscope. The lamellar pattern on the right side of the image shows the one-dimensional pores laying perpendicular to the viewing axis.

Mobil originally offered two possible mechanisms for the assembly of mesostructured M41S silicas.¹³ The first mechanism described the formation of a liquid crystalline surfactant phase in solution prior to the addition of the inorganic species. Upon the addition of the inorganic species, the silicate anions penetrate solvent regions between the ordered surfactant micelles then condense and polymerize at the cationic surfaces, forming the silica walls and an inorganic replica of the surfactant liquid crystal. At this point, the surfactant could

be removed from the pore channels, resulting in accessible pore volumes of uniform diameter. The second mechanism (Figure 1.1) illustrates cooperative assembly in which the surfactant in solution exists as individual molecules or micelles. Upon the addition of the silicate, the interaction between the silicate and surfactant, coupled with the polymerization and condensation of the silicate species at the interface, induces the formation of the organic-inorganic 'liquid crystalline' phase. Continued condensation of the silicate again results in the formation of a templated inorganic phase with accessible pore volumes upon removal of surfactant.

Stucky and coworkers¹⁹ elaborated on the mechanisms put forth by Mobil for the formation of MCM-41 and identified three important processes. One, there exists multidentate binding between silicate oligomers and the cationic surfactant head groups resulting in, two, the favored polymerization of the silicate species at the micelle interface. Three, as polymerization proceeds, charge density matching occurs between inorganic and organic phases resulting in interfacial surface curvature dependent on the organic to silica ratio. Initially, when the silica interacts with the cationic micelle, the interface of the micelle decreases in its surface curvature due to the shielding affect that the silica imparts to the surfactant head group and the decrease in repulsive forces between head groups at the interface. As condensation and polymerization of the silica matrix proceed, the charge density of the silica species decreases. As charge density decreases, repulsive forces between head groups increase which, coupled with an increase in size of the oligomeric silica species interacting

with the surfactant, results in an interface with increasing surface curvature. The final mesophase formed is directly dependent on the ratio of silica to surfactant, Γ /S⁺.

Further work by Davis^{20,21} showed that during the formation of the MCM-41, the assembly mechanism did not include the formation of the liquid crystal phase prior to addition of the silicate, thereby discounting the first of the two routes Mobil offered as a potential assembly mechanism. Based on ¹⁴N NMR results, they proposed that the silicate anions interact with the randomly ordered cationic surfactant micelles through electrostatic interactions. Polymerization occurs at the surface of the micelles and these "coated" micelles spontaneously pack into a long-range ordered silicate-surfactant array. Further evidence supporting the silicate-induced ordering mechanism is provided by the synthesis of MCM-41 from solutions in which the quaternary ammonium surfactant concentration is below the critical micelle concentration (cmc) for the formation of the hexagonal liquid crystal.

1.3.2 Additional Electrostatic Assembly Pathways to Inorganic Oxides

Stucky clarified and extended the electrostatic assembly approach to the synthesis of mesostructured materials by categorizing four specific electrostatic assembly pathways.²² Pathway 1 (S⁺I⁻) involves the electrostatic interaction between the cationic surfactant micelle (S⁺) and the anionic inorganic species, I⁻, proposed by Mobil.¹³ Pathway 2 (S⁻I⁺) involves the reversed system in which an

anionic surfactant such as an alkylphosphate (S⁻) interacts with the cationic inorganic species (I⁺). Pathway 3 (S⁺X⁻I⁺) and Pathway 4 (S⁻M⁺I⁻) utilize a counter ion mediated route. For instance, Pathway 3 may use halogen ions (X⁻) to mediate interactions between cationic silica species, which occur in strongly acidic (pH<2) solution, and cationic surfactant species.²² Mesoporous silicas synthesized by this pathway are designated SBA materials.²³ Pathway 4 uses alkali metal cations as the mediating counter ion.

1.3.3 Neutral S^ol^o Assembly Pathway to Mesoporous Molecular Sieves

Tanev and Pinnavaia introduced an additional pathway into the assembly of mesoporous silicas utilizing non-electrostatic hydrogen-bonding interactions between surfactant micelles and silica species as the structure directing driving force (S°I°).²⁴ In this pathway, micelles of electrically neutral, long alkyl chain primary amines (S°) are used as the structure directing species in order to assemble mesoporous silicas from molecular inorganic precursors (I°) such as tetraethylorthosilicate (TEOS). H-bonding between the neutral inorganic precursor and the primary amine head group (Figure 1.5) results in the assembly of mesostructured materials designated as HMS for Hexagonal Mesoporous Silica.²⁴ Pore diameters of HMS can be controlled through the use of amine surfactants of different alkyl chain length or by the addition of organic swelling agents in a manner analogous to electrostatic pathways.²⁴

Figure 1.5: Mechanism originally proposed for the neutral S^ol^o assembly of mesoporous molecular sieve HMS silicas. Hydrolyzed silica interacts with isotropic surfactant molecules resulting in spontaneous assembly into micelles. Silica condenses at the surface forming a stable mesostructure.²⁴

(

a

Figure 1.5:



Powder X-ray diffraction patterns of HMS silicas (Figure 1.6) differ from MCM-41 silicas in that they consistently show only one intense X-ray reflection with a broad shoulder at higher angles instead of the numerous peaks common for a hexagonal mesophase. The broadening of the primary peak and shoulder are attributed to scattering from small domains of hexagonally packed pores.^{14,24,25} Though the order of the pores is diminished compared to MCM-

41, the pore size, pore volumes and surface areas are comparable.²⁶ N₂ adsorption-desorption isotherms of HMS silicas (Figure 1.7) reveal Type IV isotherms for mesoporous materials with uptake of N_2 at relative pressures ~0.3. Again, the uptake at these relative pressures is due to capillary condensation of the gas within the confined space of the framework mesopores. An important difference between MCM-41 and HMS silicas, however, is the significant uptake of N₂ at relative pressures above 0.90. These uptakes correspond to the capillary condensation of N₂ within mesopores formed between the grains of HMS silicas as these grains aggregate and intergrow into a particle with a sponge-like texture. Intra-particle, or textural porosity, is independent of the framework porosity within the grain determined by the structure directing surfactant.²⁴ These intra-particle pores are designated textural pores and the uptake of N_2 at high relative pressures is a signature of that textural porosity. Figure 1.8 clearly shows the intra-particle porosity of HMS silicas by TEM. Evident in Figure 1.8A is the sponge-like nature of these mesostructured materials and the resulting void space due to the intergrowth of small grains.



Figure 1.6: Powder X-ray diffraction pattern of calcined HMS molecular sieve silica. Correlation peak at 3.9 nm. Sample prepared by method described elsewhere.⁶⁵



Figure 1.7: N₂ adsorption-desorption isotherm of calcined HMS molecular sieve silica. (Inset) Corresponding Horvath-Kawazoe pore size distribution curves plotted as normalized volume of N₂ vs. pore diameter (nm). Sample prepared by method described elsewhere.⁶⁵

Figure 1.8: A. Low magnification TEM image of HMS molecular sieve silicas showing small mesoporous grains intergrown into a sponge-like particle with intra-particle textural porosity. B. High magnification image of A showing the disordered wormhole pore structure of the silica grains





Figure 1.8B shows the framework structure of uniform pore diameter and the increased disorder as compared to MCM-41 silicas. HMS silicas synthesized at ambient temperatures also experience higher condensation of the silica framework, and therefore higher framework connectivity than electrostatically assembled silicas.²⁴ Framework connectivity is defined as the ratio of fully condensed silica sites ($Q^4 = Si(OSi)_4$) to incompletely condensed silica sites ($Q^3 = SiO(OSi)_3^-$, $Q^2 = SiO_2(OSi)_2^{2-}$), $Q^4/(Q^3+Q^2)$.

1.3.4 Non-ionic N°I° Assembly Pathway to Mesoporous Molecular Sieves

The hydrogen-bonding pathway was later extended to include the bonding that occurred between nonionic polyethylene oxide (PEO) based surfactants (N^o) and molecular silica species (I^o) in the assembly in MSU-X silicas (N^oI^o).^{27,28} Amphiphilic PEO surfactants such as BrijTM or TergitoITM (N^o) contain hydrophilic ethylene ether -(CH₂CH₂O)- segments (EO) connected to a hydrophobic alkyl groups (R) of varying length and have the general formula R_n-O(EO)_xH of an alkyl-PEO surfactant. Again, H-bonding is the structure directing interaction responsible for the assembly of the framework structure. Both mesoporous silicas and aluminas have been prepared via this pathway.^{27,28} PXRD patterns and N₂ adsorption-desorption isotherms yield results similar to both HMS and MCM-41 materials. TEM images of MSU-X silicas distinctly show a disordered

wormhole-like pore structure.²⁷ The wormhole structure is formed from uniform diameter rod-like micelles with no packing order in the inorganic matrix.

The synthesis of wormhole-like pore structures using H-bonding interactions between molecular silica species and other PEO based surfactants has also been successful.²⁹ In addition to the alkyl-PEO surfactants, alkyl-phenyl-PEO surfactants with the basic formula R_n -Ph-O(EO)_mH, such as IGEPAL-RCTM and TRITON-XTM, assemble similar framework pore structures as the alkyl-PEO surfactants. Other suitable PEO based surfactants are the triblock copolymer surfactants such as PluronicTM. These surfactants have the general formula PPO_m-PEO_n-PPO_m where PPO represents the hydrophobic polypropylene oxide segments and can be reversed as in Pluronic-RTM, which is a PEO_n-PPO_m-PEO_n triblock co-polymer.

A fourth basic PEO based surfactant type is derived from the substitution of the hydrogens of ethylene diamine by ethylene oxide and propylene oxide units to form the X shaped, TETRONICTM, molecules with basic formula; ((EO)_n-(PO)_m)₂NCH₂CH₂N-((PO)_m-(EO)_n)₂. The order of the PEO and PPO groups in these molecules may also be reversed to form TETRONIC-RTM. Many of the PEO based surfactants behave similarly to quaternary ammonium surfactants when in solution. These surfactants are also able to minimize their energy in aqueous solutions by spontaneously forming micelles with their hydrophobic segments oriented toward the core of the micelle and their hydrophilic head groups interacting with the aqueous phase at the interface.^{30,31} Liquid

crystalline phases are common for a number of PEO surfactants, yet under neutral assembly conditions the H-bonding interactions between surfactants and silica species form mesophases that are invariably wormhole-like.

1.3.5 Dative Bonding Assembly Pathway to Mesoporous Molecular Sieves

Covalent or dative bonding between the inorganic species and the structure directing organic gives rise to an additional assembly pathway. Dative bonding between the nitrogen atoms of a primary amine surfactant to coordinatively unsaturated transition metal alkoxides has been postulated to be the driving force in the formation of mesostructured niobium and tantalum oxides.^{32,33} Organization into a mesostructured porous oxide occurs under hydrothermal synthesis conditions of 100°-180°C for 4-7 days. Under these conditions the hydrophobic alkyl chain directs the assembly through van der Waals interaction with other alkyl chains, forming micelles. Mesostructured HMS silicas cannot be synthesized at these temperatures with identical surfactants due to relatively weak H-bond interactions. Therefore, the bond between nitrogen and the inorganic species must be stronger than hydrogen bonds lending evidence for covalent bonding. Additional evidence for dative bonding is that the surfactant can only be removed from the mesostructured oxide by extraction into an organic solvent only after the nitrogen-inorganic bond is broken with the use acid.³² Simple solvent extraction is not effective, and calcination causes collapse of the structure.

1.4 Recent Advances in Mesoporous Molecular Sieves

1.4.1 Low pH Conditions with PEO Based Surfactants for the Synthesis of Periodically Ordered Mesostructures

Stucky and coworkers were able to combine their pathway 3 methodology (S⁺X⁻I⁺) with the use of PEO base surfactants in the assembly of periodically ordered mesoporous silicas.^{34,35} The synthesis of these silicas is done at pH values below the isoelectric point of silica (pH~2). At these pH values, the silica source (TEOS) hydrolyzes into silicic acid. Also, the PEO based surfactant in solution has hydronium ions associated with the alkylene oxygen atoms, imparting long-range Coulombic interactions through the mediating halogen anion. This electrostatic pathway (N^oH⁺)(X⁻I⁺) results in the formation of a wide variety of mesophase very much dependant on the choice of surfactant used.³⁵

This high acid, low pH synthesis using large molecular weight surfactants, such as the tri-block copolymers of the Pluronic[™] series, results in materials designated as SBA-15 silicas with pore diameters larger than previously attained for mesostructured silicas.³⁴ Pores up to 25 nm in diameter and of hexagonal symmetry can, without difficulty, be attained. Furthermore, with the addition of organic swelling agents and interfacial modifiers, silicas can be synthesized with spherical pores greater than 35 nm in diameter that resemble foams and are designated as Mesostructured Cellular Foams, MCF. Essential to the synthesize

of these silicas is the use of molecular silica species, for instance TEOS, as in the synthesis pathways using hydrogen bonding interactions.

1.4.2 Metal Complexed PEO Based Surfactants to Synthesize Periodically Ordered Mesostructures

Disordered wormhole-like pore structures are formed under neutral pH assembly conditions using hydrogen bonding N°I° between nonionic (PEO) based surfactants and TEOS.²⁷ Ordered silica mesostructures have more recently been prepared utilizing a modified hydrogen bonding interaction between nonionic surfactant complexes and inorganic reagents. ³⁶ This $(N^{\circ}M^{n+})I^{\circ}$ pathway occurs when certain metal cations are complexed by the nonionic polyethylene oxide surfactants (N°) effectively altering their surfactant packing parameter in solution. The modified surfactant assemblies convey periodic order into the mesophase upon interactions with the inorganic precursor, TEOS (1°), under neutral pH conditions. These ordered mesophases are achieved without sacrificing any of the intrinsically desirable processing advantages of neutral assembly pathways, such as the ease of recovery of the non-ionic surfactant, along with a high degree of silica condensation and framework connectivity associated with neutral pH synthesis.³⁶ As in previous neutral assembly pathways, this pathway depends on the use of expensive molecular silica sources such as TEOS.

1.4.3 Synthesis of Stable Mesostructured Silicas from PEO Based Surfactants and Soluble Silica Sources

Guth and co-workers have reported the preparation of mesostructured silicas using sodium silicate solutions as the silica source and Triton-X 100, an N° surfactant^{37,38} as the structure directing species. These researchers where able to synthesize disordered wormhole-like pore structures over a broad range of pH conditions with X-ray diffraction of the as made material indicating pore structures similar to MSU-X silicas. The retention of the structure was observed up to a calcination temperature of 480 °C, but the complete removal of the surfactant at 600 °C led either to the extensive restructuring of the silica framework or the formation of a completely amorphous material as indicated by the loss of mesoporosity. In contrast, MSU-X mesostructures, synthesized through an N°I° pathway with TEOS, are structurally stable to calcination temperatures in excess of 800 °C.²⁷

Pinnavaia has more recently reported the assembly of mesoporous silicas with pore topologies ranging from disorder wormhole-like³⁹ to hexagonally ordered pore structures⁴⁰ synthesized with PEO based surfactants and sodium silicate solutions. In contrast with Guth, the silicas synthesized through this route produce structures that are stable to the complete removal of the surfactant phase resulting in completely accessible pore volumes. This methodology requires acid neutralization of the hydroxide content of the silicate in the presence of the structure directing surfactant assemblies allowing for the

assembly of the structure at near neutral pH conditions. The framework synthesized has a pore topology that can be either a disordered wormhole framework³⁹ analogous NºIº to conventional assembled MSU-X mesostructures²⁷ and designated MSU-X', or ordered crystalline phases similar to silicas assembled through electrostatic pathways^{34,35} and designated MSU-H silicas⁴⁰. The final pore topology is highly dependent on the surfactant, auxiliary reagents and temperatures used during the reaction. An important result of the near neutral synthesis conditions is the high silica framework connectivity of disordered MSU-X' and hexagonally ordered MSU-H silicas.

1.5 Research Objectives

There are three basic research objectives for which the current work strives to reach. The first objective is to formulate a comprehensible S^oI^o assembly mechanism for the formation of wormhole framework pore structures in HMS silicas using neutral amine surfactants. Included within this objective is determining parameters that directly affect the framework assembly and, consequently, the characteristics properties of these mesoporous silicas. The second objective is to developing a practical methodology to control grain size and textural properties of these mesoporous silicas during synthesis that will directly influence their accessibility and resulting catalytic activity. The third objective is to apply understanding of neutral amine assembly in order to

substitute readily available silica sources for the expensive molecular silica species (TEOS) currently used in the assembly of HMS like silicas.

1.5.1 S° I° Assembly Mechanism

The assembly mechanism for the synthesis of mesostructured silicas through electrostatic pathways has received a significant amount of attention. To date, however, there has been no explanation as to the pore forming mechanism in the assembly of HMS silicas. The disordered pore structure in HMS materials presents a significant problem in putting forth a convincing mechanism. Complicating the problem, there is little literature available dealing with the phase behavior of amines in aqueous systems.⁴¹ However, by developing an understanding of neutral amine surfactant behavior in solution and elucidating how silica precursors interact with these surfactant molecular assemblies, we present a viable explanation of the pore forming mechanism in the assembly of HMS silicas.

The original work of the Mobil group on the electrostatic assembly of hexagonal MCM-41 silicas¹³ has shown that the pore size of the framework could be mediated by controlling the size of the structure-directing surfactant or by incorporating an auxiliary organic solvent as a co-surfactant to swell the micelles. Further studies^{42,43,44,45,46,47} have shown that increases in the assembly temperature or digestion time can also be used to increase the framework pore size and affect the final mesophase formation. In addition, *ex*

situ post-synthesis hydrothermal treatment methods⁴⁸, have been used to expand the pore sizes of electrostatically pre-assembled mesostructures.

Relatively little work has been reported, however, for the pore size mediation of mesostructures assembled through H-bonding interactions between electrically neutral surfactants and inorganic precursors. As in electrostatic pathways, the size can be controlled for both HMS and MSU-X materials through the use of a family of surfactants with different hydrophobic chain lengths.²⁶ Hydrogen bonding pathways normally afford mesostructures with wormhole - like framework structures. The temperature from which HMS silicas can be synthesized is limited due to weak H-bonding interactions. In the case of MSU-X silicas,⁴⁹ controlled pore size expansions up to 2.4 nm have been achieved using a single PEO surfactant simply by increasing the assembly temperature over the range 25 - 65 °C. The pore expansion arises due to temperature-dependent changes in the conformation of the surfactant and, hence, in the amphiphilic character of the surfactant used. Insight into the effects of temperature on the silica framework upon expansion of the pore structure, however, is limited.

The wormhole channel motif is a potentially important structural feature for favorable catalytic reactivity, in part, because channel branching within the framework can facilitate access to reactive sites on the framework walls. A simple method for tailoring the framework pore size of HMS materials in the presence of a single amine surfactant will make them even more attractive for such applications. Accordingly, the present work examines the effect of assembly conditions and post-synthesis modification methods on the pore size

characteristics, framework cross-linking, and particle texture of HMS silicas assembled though a H-bonding $S^{\circ}I^{\circ}$ pathway using dodecylamine as the surfactant (S°) and tetraethylorthosilicate (TEOS) as the inorganic precursor (I°).

1.5.2 Control of Particle Size

HMS silicas, particularly those with a sponge-like particle texture for improved framework access, have found promising applications as heterogeneous catalysts 50,51,52,53,54 and as supports for the immobilization of reagents.^{55,56} HMS wormhole structures can have relatively small fundamental grain sizes (<200 nm), which results in complementary intra-particle, or textural mesoporosity for the more efficient transport of reagents to framework reaction centers.⁵⁷ This catalytically important textural porosity arises from the aggregation of small mesoporous grains through intergrowth or other associative Consequently, textural porosity is dependent on the size. mechanisms. connectivity and surface texture of the fundamental particle, but it is independent of the framework structure of the particles.

The textural mesoporosity of HMS silicas is determined by the polarity of the medium in which the framework is assembled. Highly polar solvents, such as 90:10 (v:v) water - ethanol, characteristically afford wormhole frameworks with fundamental grain sizes < 200 nm and textural mesopores that are comparable to the framework pores in overall volume.⁵⁷ However, solvents of relatively low polarity, e.g., 35:65 (v:v) water - ethanol, promote the growth of large, monolithic particles with little or no textural porosity.

The importance of textural mesopores in enhancing the catalytic activity of HMS materials relative to MCM-41 has been demonstrated for several condensed phase reactions in which access to framework reaction sites may be diffusion limited. Substantially higher conversions have been reported for the peroxide oxidation of various substrates using Ti-^{58,51,52}, V-^{58,51,52,53,54}, Cr-⁵⁸, Mo-⁵⁸, and Mn-⁵⁸ substituted HMS materials compared to analogous compositions of MCM-41. Also, Fe³⁺ exchanged Al-HMS exhibits a higher rate constant for the selective catalytic reduction of NO by NH₃ than does Fe³⁺ exchanged Al-MCM-41⁵⁹. Additionally, Al-HMS is more active for the cracking of cumene⁶⁰ than a compositionally equivalent Al-MCM-41. On the other hand, Ti-HMS has been reported to exhibit *lower* catalytic activity than Ti-MCM-41 for the peroxide epoxidation of α -pinene⁶¹ and the oxidation of aniline⁶².

The discrepancies in assessing the relative catalytic activities of HMS and MCM-41 materials may be linked to differences in textural properties. Although the Ti-HMS used for aniline oxidation was prepared at solvent composition that should have provided a product with high textural porosity, the N₂ adsorption⁶³ properties indicated the *absence* of textural pores. This latter result suggested to us that the textural mesoporosity of HMS materials might be much more sensitive to solvent polarity than previously realized. The present work investigates the factors controlling formation of textural mesoporosity of HMS molecular sieve silicas.

1.5.3 Substituting Sodium Silicate for TEOS in the S^ol^o Assembly of Mesostructured Silicas

Until recently, the assembly of mesostructured silicas relied on the use of either a costly organic reagent, such as the quaternary ammonium salts used in electrostatic pathways, or on expensive molecular inorganic precursors, such as the tetraethylorthosilicate (TEOS) used in H-bonding, dative bonding, and low pH pathways.

Guth and coworkers first reported the synthesis of mesostructured silica by precipitation from a solution combining an inexpensive polyethylene oxide (PEO) based surfactant, Triton-X 100, with low cost sodium silicate^{37,38}. The disordered wormhole pore structure, however, was not stable to complete surfactant removal at calcinations temperatures as high as 600 °C. The first synthesis of stable mesostructured silicas using nonionic polyethylene oxide (PEO) surfactants and water-soluble silica solutions was recently reported by Pinnavaia and coworkers.^{39,40} Their methodology requires acid neutralization of the hydroxide content of the silicate in the presence of the structure directing surfactant assemblies. This allows for the assembly of the structure at near neutral pH conditions and results in a stable oxidic framework.

Extending this methodology to include the use of neutral amine surfactants as structure directors has resulted in stable mesoporous silicas comparable to HMS materials synthesized through a S^ol^o assembly pathway⁶⁴. These MSU-SA (Silicate-Amine) materials have wormhole pore topologies and

small grained, highly aggregated sponge-like particles similar to HMS silicas assembled with TEOS as the silica source. The clusters, or aggregates, possess the high intra-particle or textural porosity characteristic of HMS-HTx⁶⁵ silicas synthesized with dodecylamine (DDA, $C_{12}H_{25}NH_2$) and TEOS. High textural porosity is an attractive property of catalysts and catalytic supports due to the increased access for reagents to reactive sites within the framework pores that these textural pores provide.

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Chapter 2

Neutral (S°I°) Assembly Mechanism

2.1 Abstract

The synthesis of mesoporous molecular sieve HMS silicas by a S°I° pathway proceeds through an assembly mechanism in which the aqueous surfactant initially exists as lamellar liquid crystal colloids. Hydrogen bonding between the silica species (I°) present in solution and the lipid bilayer phase of the surfactant (S°) results in increased surface curvature of the assembly forming wormhole or tubular micelles. The degree of curvature of the silica-surfactant micelle is directly dependent on the I°/S° ratio during synthesis. I°/S° values of 2.0 result in lamellar silica mesophases that are unstable to the removal of surfactant. I°/S° values of 4.0 produce disordered wormhole mesophases with pore diameters of 2.9 nm. Increasing the I°/S° values to 10 causes the disordered wormhole pores to decrease in diameter from 2.9 nm to 2.2 nm. As the pore diameter decreases, the pore wall thickness increases at a constant pore to pore distance.

2.2 Introduction

2.2.1 Synthesis of Mesostructured Silica with Neutral Amine Structure Directors

The synthesis of Ti-HMS¹ and HMS² silicas reported in 1994 and 1995, respectively, by Pinnavaia and Tanev marked the first successful attempt in using hydrogen bonding interactions between the organic structure directing surfactants and inorganic precursors to synthesize mesostructured molecular sieve silicas. These researchers were able to synthesize stable mesoporous silicas with uniform pore diameter by using long alkyl chain primary amine surfactants (S^o) and molecular silica precursors such as tetraethylorthosilicate (TEOS, I^o) in a neutral, or non-electrostatic pathway (S^o I^o). The introduction of this route complemented the initially reported electrostatic assembly method reported by Mobil^{3,4,5,6} in 1992 for the M41S family of silicas along with additional electrostatic pathways put forth by Stucky in 1994.⁷

Electrostatic pathways utilize fundamental Coulombic interactions between long alkyl chain ionic surfactants (S⁺ or S⁻) and charged inorganic species (I⁻ or I⁺) during the assembly of mesostructured oxides. These assembly pathways can occur through direct charge matching such as S⁺I⁻⁵ or through a counter ion mediated pathway using metal cations, M⁺, or halogen anions, X⁻, as the counter ion in the assembly of species of like charge (S⁺X⁻I⁺).⁷ Invariably, the long range Coulombic interactions present in the electrostatic assembly of mesostructured materials result in silicas with uniform pore diameters and long-range periodic pore order.

Though the pore structures of HMS silicas assembled under neutral S°l° conditions exhibit no long-range pore order, it was initially reported that there exists small domains of hexagonally packed pores from which these materials derive their name. Hexagonal Mesoporous Silica.² Tanev and others have reported that the X-ray diffraction spectra of HMS materials, which reveal only one primary diffraction peak and a high angle shoulder, can be interpreted to indicate Bragg scattering with line broadening due to the small size of the hexagonal domains present.^{2,3,8} Though it is now recognized that long-range order is absent in HMS mesostructures, the framework pore properties such as the pore size distribution, pore volume and surface area are guite similar to those seen in the highly ordered M41S⁵ and SBA⁹ families of silicas.¹⁰ Pinnavaia and Bagshaw¹¹ later expanded the H-bonding route in synthesizing molecular sieve oxides to include the interactions between non-ionic polyethylene oxide, N° (PEO), surfactants and TEOS in the synthesis of MSU-X silicas ($N^{\circ}I^{\circ}$) with wormhole-like pore structures.

Most published reports on HMS silicas relate to the physiochemical properties of these molecular sieves and, specifically, how they compare to their electrostatically assembled cousins. Tanev reported HMS silicas have pore structures with pore diameters that are comparable to the uniform diameter seen

in MCM-41 materials.¹⁰ HMS silicas exhibit a considerable increase in the silica framework connectivity over MCM-41 materials, which these researchers attribute to the thicker pore walls reported for HMS silicas.¹⁰ Framework connectivity is defined as the ratio of fully condensed silica sites ($Q^4 = Si(OSi)_4$) to incompletely condensed silica sites ($Q^3 = SiO(OSi)_3$, $Q^2 = SiO_2(OSi)_2^2$), $Q^4/(Q^3+Q^2)$. Also notable is the sponge-like particle texture of the HMS silicas. As a consequence, HMS materials demonstrate significant intra-particle, or textural porosity with large pore diameters detectable by N₂ adsorption.

In contrast with the original definition of pore ordering in HMS silicas, it was later reported that the pore structure formed through S^ol^o assembly is a predominantly disordered wormhole-like pore structure with little to no evidence for even small domains of hexagonally ordered pores.¹² Since these wormhole pore structures have a high degree of branching and disorder, they are believed to form three-dimensional pore networks within the solid matrix. The X-ray diffraction patterns from HMS silicas do not indicate Bragg scattering from small domains of hexagonal pores. Instead the scattering arises from the consistent pore to pore correlation distance of disordered wormhole-like pores with regular pore wall thickness.¹³ Therefore, the pore to pore separation cannot be taken as the lattice parameter, ao, of a hexagonal unit cell as was originally done.2 Instead, the diffraction peak is taken as the pore to pore correlation distance to a first approximation. Therefore, the wall thickness between pores for HMS silicas previously reported are approximately 1.0 nm thick and similar to the thickness of

electrostatically assembled silicas. The increased $Q^4/(Q^3+Q^2)$ ratios of HMS silicas in comparison to electrostatically assembled silicas cannot be attributed to the increased wall thickness. The increase in framework crosslinking is, instead, a result of the lack of charge matching to the surfactant phase. The absence of charge matching combined with the mildly alkaline synthesis conditions favor increased silica condensation.¹⁴

2.2.2 Mechanism of Electrostatic Assembly

Mobil originally offered two possibly mechanisms for the assembly of mesostructured M41S silicas.⁵ The first mechanism described the formation of a liquid crystalline surfactant phase in solution prior to the addition of the inorganic species. Upon the addition of the inorganic species, the silicate anions would penetrate solvent regions between the ordered surfactant micelles then condense and polymerize at the cationic surface forming the silica walls of the ordered material, thus forming an inorganic replica of the surfactant liquid crystal. At this point, the surfactant could be removed from the pore channels resulting in accessible pore volumes with uniform pore diameter.

The second mechanism is based on a cooperative assembly process in which the surfactant in solution exists as individual molecules or micelles. Upon the addition of the silicate, the interaction between the silicate and surfactant, coupled with the polymerization and condensation of the silicate species at the interface, induces the formation of the 'liquid crystalline' phase. Continued
condensation of the silicate results in the formation of an inorganic 'liquid crystalline' replica and accessible pore volumes upon removal of surfactant.

Stucky and coworkers¹⁵ elaborated on the mechanisms put forth by Mobil for the formation of MCM-41 and identified three important processes. One, there exists multidentate binding between silicate oligomers and the cationic surfactant head groups resulting in, two, the favored polymerization of the silicate species at the micelle interface. Three, as polymerization proceeds, charge density matching occurs between inorganic and organic phases resulting in interfacial surface curvature dependent on organic to silica ratio.

Initially, when the silica interacts with the cationic micelle, the interface of the micelle decreases in its surface curvature. This loss of curvature is due to the shielding affect that the silica imparts to the surfactant head group and the decrease in repulsive forces between charged head groups at the interface. As condensation and polymerization of the silica matrix proceed, the charge density of the silica species decreases. As the negative charge density on the silica decreases, repulsive forces between the surfactant head groups increase which, coupled with an increase in size of the oligomeric silica species interacting with the surfactant, result in an interface with increasing surface curvature. The structure of the final mesophase formed is directly dependant on ratio of silica to surfactant, Γ / S^{+} .¹⁵

Work by Davis^{16,17} showed that during the formation of the MCM-41, the assembly mechanism did not include the formation of the liquid crystal prior to the addition of the silicate, thereby discounting the first of the two routes Mobil

offered as a potential assembly mechanism. Based on ¹⁴N NMR results, they proposed that the silicate anions interact with the randomly ordered cationic surfactant micelles through electrostatic interactions. Polymerization occurs at the surface of the micelles. These "coated" micelles spontaneously pack into a long-range ordered silicate-surfactant 'liquid crystal' array. Further evidence supporting the silicate induced ordering mechanism is that hexagonal MCM-41 can be synthesized from solutions in which the quaternary ammonium surfactant concentration is below the critical micelle concentration (cmc) for the formation of the hexagonal liquid crystal.

The degree of framework cross-linking of the molecular sieve silicas synthesized by electrostatic methods is limited due to the number of anionic $(SiO)_3Si-O$ units needed for charge compensation at the interface of the cationic surfactant micelle. Though a sufficient number of additional counter ions are present, such as the halogen anions commonly associated in the ammonium salt, the Q⁴/(Q³+Q²) values of electrostatically assembled mesostructures are generally lower than 2.0. Additionally, the wall thickness between pores of electrostatically assembled silicas are severely restricted due to this necessary charge balancing of the ionic species at the interface.

2.2.3 Mesophase Formation

In classical surfactant chemistry, the formation of mesophases adopted by the surfactant assemblies in aqueous systems is a dynamic and complicated process. However, to a first approximation the mesophase formed is directly dependent on the surfactant packing parameter, g, of the individual amphiphilic

surfactant molecule. The packing parameter, g, is based on the geometry of the molecule and is arrived at by taking the ratio of its hydrocarbon core volume, V, to the product of its length, l_c, and effective solvated surface area per amphiphilic head group, $a_o (g=V/(a_o l_c))$.¹⁸ As the packing parameter increases, the surface curvature of the surfactant assembly decreases and proceeds through distinct phase transitions from spherical (g≤1/3) to cylindrical (1/3<g≤1/2) and finally to lamellar (g=1) surfactant phases.

Stucky and coworkers^{15,19,20,21} were the first to associate this classical micelle behavior of amphiphilic surfactants to the formation of particular mesophases in the synthesis of mesostructured silica. Additionally, by using a variety of quaternary ammonium surfactants, each different in its packing parameter due to variations in head group area (a_o) or hydrophobic volume, V, these researchers were able to successfully synthesize a family of identifiable silica mesophases. The synthesized mesophases correlate directly with the surfactant packing parameters and predicted surface curvature. This understanding of the relationship between the structure directing surfactant and the resulting synthesized silica mesophase contributed greatly to the further design and synthesis of these periodically ordered mesostructured oxides.

To date, however, there has been no explanation as to the pore forming mechanism in the assembly of HMS silicas. The disordered pore structure in HMS materials presents a significant problem in putting forth a convincing mechanism. Complicating the problem, there is little literature available dealing with the phase behavior of amines in aqueous systems.²² However, by

developing an understanding of neutral amine surfactant behavior in solution and elucidating how silica precursors interact with these surfactant molecular assemblies, we present a viable explanation of the pore forming mechanism in the assembly of HMS silicas.

2.3 Experimental

2.3.1 Synthesis of HMS, Variation of I°/S° Ratio

The synthesis of the HMS molecular sieves consisted of dissolving 0.6 g (3.2 mmol, Dilute synthesis) or 1.8 g (9.7 mmol, Concentrated synthesis) of DDA surfactant into 10 mL (170 mmol) of EtOH. An 85 mL (4.7 mole) quantity of H₂O was added to the surfactant/EtOH solution while stirring. Tetraethylorthosilicate (TEOS) was then added to the surfactant solution after 10 minutes while stirring. The amount of TEOS added is varied in order to achieve the desired I°/S° ratios of 2.0, 4.0, 5.0, 7.0 and 10. Increasing EtOH was added with decreasing quantities of TEOS to account for both the decrease in the amount of EtOH released upon hydrolysis of the TEOS and to keep the dilution factor constant. The reaction solution was stirred at ambient temperature for 20 hours with the reaction flask sealed. The initial reaction stoichiometry was as follows:

> Dilute: denoted HMS-DX where $X = I^{\circ}/S^{\circ}$. X SiO₂ : 1 DDA : 93.4 EtOH : 1469 H₂O (X = 4.0-10) Concentrated: denoted HMS-CX where $X = I^{\circ}/S^{\circ}$. X SiO₂ : 1 DDA : 57.6 EtOH : 484 H₂O (X = 2.0, 4.0-10)

The resulting solid product was recovered by filtration, washed with H_2O and allowed to air dry at ambient temperature for 24 hours. Surfactant removal was accomplished by calcination at 630 °C for 4 hours. Calcination to remove the surfactant is chosen instead of ethanol extraction because there was no desire to recover the small amount of surfactant used.

2.3.2 Physical Measurements

Wide-angle powder x-ray diffraction (XRD) patterns were obtained using a Rigaku Rotaflex Diffractometer with Cu K_{α} radiation (λ = 0.154 nm) Counts were accumulated every 0.02 degrees (20) at a scan speed of 1 degree (20)/min.

 N_2 adsorption-desorption isotherms were obtained at -196 °C on a Micromeritics ASAP 2010 Sorptometer using static adsorption procedures. Samples were outgassed at 150 °C and 10⁻⁶ Torr for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear part of the BET plot according to IUPAC²³ recommendations. Pore size distribution was estimated from the adsorption branch of the isotherm by the method of Horvath and Kawazoe.²⁴

TEM images were obtained on a JEOL 100CX microscope with a CeB_6 filament and an accelerating voltage of 120 KV, a beam diameter of approximately 5 μ m and an objective lens aperture of 20 μ m. Sample grids were prepared via sonication of powdered sample in EtOH for 20 min and evaporating 1 drop of the suspension onto a carbon coated, holey film supported on a 3 mm, 300 mesh copper grid.

²⁹Si MAS NMR spectra were recorded on a Varian 400 VRX solid-state NMR Spectrometer at 79.5 MHz under single-pulse mode with a 7-mm Zirconia rotor, a spinning frequency of 4 kHz, pulse width of 8.5 μ s and a pulse delay of 800 seconds. The chemical shifts were externally referenced to talc (-98.1 ppm relative to tetramethylsilane).

2.4 **Results and Discussion**

2.4.1 S⁺/I⁻ Dependant Mesophase Formation

Mobil researchers were originally able to synthesize three specific mesophases in their M41S family of aluminosilicates, these being lamellar MCM-50, cubic MCM-48, and hexagonal MCM-41. They achieved these different phases by varying the inorganic (I⁻) to organic (S⁺) ratio (I⁻/S⁺). Increasing the I⁻/S⁺ values resulted in micelle assemblies with increasing surface curvature. Low I⁻/S⁺ values (~1.0) resulted in assemblies with low surface curvature and subsequently lamellar phases unstable to removal of surfactant. Medium I⁻/S⁺ values (~2) result in assemblies of medium surface curvatures and cubic (Ia3d) phases. High I⁻/S⁺ values (~4) result in assemblies of higher surface curvatures and hexagonal phases. Clearly, the strong electrostatic interactions at the interface between the organic and inorganic phases directly affect the interfacial surface curvature of the surfactant-silica assemblies and consequently, the final inorganic mesophase.

2.4.2 Properties of HMS Synthesized with Increasing I°/S° Values

Unlike charged surfactants, such as quaternary ammonium salts, primary amines, such as dodecylamine (DDA, $C_{12}H_{25}NH_2$), have small effective head group areas, a_o , compared to their hydrophobic volume resulting in a large packing parameter, $g \sim 1.0$, and cylindrical molecular shape. As expected, these molecules adopt a lamellar or lipid bilayer phase (Figure 2.1) in aqueous solutions as is evident by their X-ray diffraction patterns. The original synthesis of HMS silicas utilized I^o/S^o ratios of approximately 4, similar to Mobil's synthesis of MCM-41. These HMS silicas are stable to the removal of the organic phase and the final pore structure exhibits significantly higher curvature than the lamellar organic precursor.

Low $1^{\circ}/S^{\circ}$ values ($1^{\circ}/S^{\circ} = 2.0$) result in lamellar silica-surfactant mesostructures that are not stable to the removal of the surfactant. Figure 2.2 is the X-ray diffraction pattern of an as-made HMS material prepared at an $1^{\circ}/S^{\circ}$ value of 2.0. Evident are 3 peaks indexible to a lamellar mesophase. The low $1^{\circ}/S^{\circ}$ values lead to the formation of an unstable lamellar mesostructure, analogous to MCM-50,

Figure 2.3 shows the powder X-ray diffraction patterns of the calcined samples formed at $1^{\circ}/S^{\circ}$ ratio ranging from 4.0 to 10 and under concentrated reagent conditions. Each pattern shows a single correlation peak at 2.25 degrees 20 with almost no difference as to the position of this peak, indicating the repeat distance between pores within the various samples is relatively independent of the $1^{\circ}/S^{\circ}$ ratio. As the value of the $1^{\circ}/S^{\circ}$ ratio increases, the

A. Dodecylamine, DDA



Figure 2.1: A. Schematic image of long alkyl chain amine (DDA) with high packing parameter, g, and cylindrical shape. B. The lamellar powder X-ray diffraction patterns of an aqueous solution of DDA indicating the formation of, C. A lipid bilayer structure with a 3.6 nm d₀₀₁ spacing.



Figure 2.2: Powder X-ray diffraction pattern of as-made HMS silica assembled at $1^{\circ}/S^{\circ} = 2.0$ under concentrated conditions. Lamellar pattern with d₀₀₁ peaks are labeled. d₀₀₁ = 3.7 nm.



Figure 2.3: Powder X-ray diffraction patterns of calcined HMS molecular sieves assembled under concentrated reagent conditions. Spectra are labeled according to the I^o/S^o synthesis ratio. Each spectra is offset by 2000 cps for clarity.

diffraction peak does decrease in intensity and broadens. These patterns are typical of HMS wormhole structures assembled from long alkyl chain neutral amines as surfactants, the correlation peak indicating the average pore to pore distance in the disordered wormhole framework. Equivalent XRD patterns were obtained for HMS silicas assembled from dilute reagent conditions.

Figure. 2.4 displays N₂ adsorption-desorption isotherms for the HMS samples assembled at $1^{\circ}/S^{\circ}$ ratios of 4.0 to 10. The isotherms of the calcined material show a step increase in the adsorption of N₂ at relative pressures ~ 0.20-0.40 P/Po due to capillary condensation within the framework confined mesopores. Complete saturation of these framework pores occurs at relative pressures of ~0.40-0.50 P/Po. The onset of the capillary condensation occurs at progressively higher P/Po as the 1°/ S° ratio decreases from 10 – 4.0. This is reflected in the Horvath Kawazoe plot (Figure 2.4(Inset)), which calculates a mesopore diameter increase from 2.2 nm to 2.9 nm in the 10 and 4.0 samples respectively. BET surface areas for these silicas range from 900 m²/g for high silica ratios (10) to 1200 m²/g for the silica ratio of 4.0. Table 2.1 summarizes the physiochemical properties for both series of HMS silicas, synthesized in concentrated and dilute reagent conditions.

As the l^o/S^o ratio increases from 4.0 to 10, the pore diameter decreases and the pore to pore correlation peak remains virtually constant, indicating an increased pore wall thickness. This result highlights a considerable difference between H-bonding and electrostatic assembly. In electrostatic assembly the wall thickness is primarily determined by the charge matching of the silicate to



Figure 2.4: N_2 adsorption-desorption isotherms of calcined HMS molecular sieves assembled at I^0/S^0 ratios of 4.0, 5.0, 7.0 and 10 and under concentrated reagent conditions. (Inset) Corresponding Horvath-Kawazoe pore size distribution curves plotted as normalized volume of N_2 vs. pore diameter (nm).

Table 2.1: Physiochemical properties of calcined HMS molecular sieves synthesized at varying $1^{\circ}/S^{\circ}$ ratios under concentrated and dilute reagent conditions.

d ₁₀₀ (nm)	BET SA (m²/g)	V _f	V _T	V _{tx}	V _{tx} / V _f	Pore Diameter HK (nm)	Wall Thickness (nm)
4.0	903	0.46	0.57	0.11	0.25	2.2	1.8
3.8	1018	0.54	0.82	0.28	0.52	2.4	1.4
3.8	1041	0.63	1.22	0.59	0.93	2.6	1.2
3.8	1113	0.74	1.64	0.90	1.21	2.9	0.9
	· · ·						
3.9	934	0.49	0.56	0.07	0.14	2.1	1.8
3.7	1115	0.59	0.75	0.16	0.28	2.5	1.2
3.6	1127	0.66	0.87	0.21	0.32	2.7	0.9
3.7	1057	0.76	0.92	0.16	0.21	3.0	0.7
	d ₁₀₀ (nm) 4.0 3.8 3.8 3.8 3.8 3.8 3.9 3.7 3.6 3.7	d ₁₀₀ BET SA (nm) (nm²/g) 4.0 903 3.8 1018 3.8 1041 3.8 1041 3.8 1113 3.9 934 3.7 1115 3.6 1127 3.7 1057	d ₁₀₀ BET SA (nm) V _f (nm²/g) (m²/g) 4.0 903 0.46 3.8 1018 0.54 3.8 1041 0.63 3.8 1113 0.74 3.9 934 0.49 3.7 1115 0.59 3.6 1127 0.66 3.7 1057 0.76	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

^a[°]Concentrated" HMS silicas were assembled at surfactant concentration of 0.10 M DDA, "Dilute" HMS were assembled at 0.033 M DDA. All silicas were calcined at 600 °C. ^b V_T, total pore volume obtained from the volume of N₂ adsorbed at 0.99 P/Po. ^c V_f, framework pore volume obtained from the volume of N₂ adsorbed at 0.50 P/Po. ^d V_{tx}, textural pore volume obtained from the difference (V_T - V_f). ^e Wall thickness calculated by subtracting the HK pore diameter from the correlation distant as determined by X-ray diffraction.

the surfactant and is independent of the $1/S^+$ ratio. H-bonding assembly allows for a considerable increase in the framework pore wall thickness since the thickness is only limited to the mass transport of the inorganic precursors to interfacial positions between the organic surfactant phases. The increasing wall thickness of the mesostructured silicas with decreasing pore diameters explains why the relative specific surface areas and pore volumes decrease for these silicas as the $1^{\circ}/S^{\circ}$ value increases from 4.0 to 10.

Figure 2.5 shows representative TEM bright field images of the mesoporous silica prepared by neutral S°l° pathway with different ratios of silica to surfactant. Evident in each of the images is the existence of wormhole-like pores of uniform diameter throughout the inorganic matrix and the absence of any long-range order. Figure 2.5A and 2.5B are images of the $1^{\circ}/S^{\circ} = 10$ sample and are representative of the particle morphology and pore structure seen throughout the sample. Figure 2.5A shows individual spherical particles ranging from 100-250 nm in diameter with smooth surfaces. These spherical particles are not of uniform size, but are distinct particles with no evidence of aggregation. Mesopores ~2.2 nm in diameter are evident in Figure 2.5B. Tilt-TEM studies confirm that the morphology is actually spherical. Figure 2.5C and 2.5D are images for the mesostructure prepared at $l^{\circ}/S^{\circ} = 4.0$. Figure 2.5C illustrates the composition of fractal-like particles and highly intergrown clusters that define intra-particle, or textural, porosity in the mesopore range. Figure 2.5D is a higher magnification image of Figure 2.5C that highlights the wormhole-like pore structures that are characteristic of HMS silicas.

Figure 2.5: Bright field TEM images of calcined HMS molecular sieves prepared under concentrated reagent conditions. Figure 2.5 A&B are low and high magnification images, respectively, of HMS assembled at $1^{\circ}/S^{\circ} = 10$. Figure 2.5C&D are low and high magnification images, respectively, of HMS assembled at $1^{\circ}/S^{\circ} = 4.0$. Scale bar 100 nm for A&C. Scale bar 33 nm for B&D.





2.4.3 Mesophase Formation of HMS, S°I°

Long chain primary amines are highly insoluble in aqueous solution²² and readily form lipid bilayer liquid crystalline colloids upon partial solvation using ethanol.²⁵ The addition of TEOS to the surfactant solution results in additional solvation of the surfactant colloids evidenced by decreasing viscosity and increasing transparency of the solution as the hydrolyzed silica species penetrate solvent regions between the micelles of this lamellar surfactant liquid crystalline phase (Figure 2.6). This mechanism is similar to the initial proposal put forth by Mobil researchers as the assembly mechanism for synthesis of M41S silicas⁵ and later discounted by Davis.^{16,17} Hydrogen bonding between silica species and the lamellar surfactant imparts curvature to the surfactant phase resulting in the formation of tubular or wormhole micelles. The silica then condenses and polymerizes at the surfactant surface forming the silica walls and an inorganic replica of the disordered silica phase.

H-bonding interactions between the hydrolyzed silica species and the polar amine head group of the surfactant effectively increases the head group area of the surfactant to include area occupied by the silica species. This increase in area is sufficient to decrease the surfactant packing parameter, which in turn leads to an increase in surface curvature of the micelle assembly. Consequently, this increased surface curvature causes the formation of tubular

Figure 2.6: $S^{\circ}I^{\circ}$ Assembly mechanism for the formation of wormhole molecular sieve HMS silicas. The pure surfactant initially exists in a lipid bilayer liquid crystalline state. Hydrolyzed TEOS species interact with the surfactant surface to increase the surface curvature forming wormhole pores whose diameter is dependent on I°/S° ratio.

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or wormhole-like micelles resulting in the formation of a stable wormhole mesostructure at l°/S° ratios of 4.0-10 (Figure 2.6).

The S°/I° ratio has a direct effect on the mesophase formation in the synthesis of HMS molecular sieves. At low ratios of silica to surfactant ($I^{0}/S^{\circ}=2.0$), there is insufficient silica present to significantly affect the curvature of the lamellar surfactant phase and the resulting mesostructure formed remains lamellar. As the ratio of silica to surfactant increases, the surface curvature of the assembled micelle increases resulting in wormhole micelles and stable mesostructures. Continued increases in the I^{0}/S° ratio result in higher surface curvature and a smaller hydrodynamic radius of the micelle and subsequently a smaller pore.

Though the formation of spherical micelles has not been detected, at high $1^{\circ}/S^{\circ}$ ratios, the surface curvature may increase to the point of forming spherical micelles. The increase in surface curvature of the micelle is due to the increased number of silica species per surfactant, similar to results seen in M41S silicas.⁵ In contrast to M41S silicas, a change in the surface curvature in HMS silicas does not result in changes to distinctly different mesophases beyond the initial ordered lamellar to disordered wormhole phase transition that occurs at $1^{\circ}/S^{\circ} = 4.0$. Instead, the increases in $1^{\circ}/S^{\circ}$ values and subsequent increases in surface curvature result in pores of decreasing diameter, again in contrast to electrostatically assembled mesostructures where the pore diameter is independent of mesophase formation.⁵

Figure 2.7: Bright field TEM image of calcined HMS silicas synthesized under dilute reagent conditions, $1^{\circ}/S^{\circ} = 7.0$ and quiescent conditions showing incomplete disordering of lamellar phase. Figure 2.7A&B low and high magnification image, respectively. Evident in images is the disordered wormhole pore structure along with significant two-dimensional, lamellar character or vesicular morphology.

Figure 2.7:



under owing high dered nellar

Figure 2.7 is a TEM image of HMS silicas synthesized under dilute reagent conditions with an $l^{\circ}/S^{\circ} = 7.0$. Upon addition of TEOS to the surfactant solution, the solution was stirred vigorously for only 5 minutes and then allowed to sit under guiescent conditions for 30 minutes at ambient temperature. By undergoing this process, we hope to impede the transformation from a lamellar surfactant phase to a completely disordered wormhole mesophase. The product was recovered by filtration, dried and calcined. Evident in the micrograph is the original lamellar character of the surfactant imposed on the particle. The particle appears to have considerable disordered wormhole character propagating in three-dimensions, yet clearly evident is the two-dimensional lamellar and possible vesicular character of these silicas. This morphology is representative of the morphology through out the sample. These specific silicas are completely stable to the removal of the surfactant phase. They have pore properties comparable to samples synthesized with stirring for 20 hours at ambient temperatures (Table 2.1, Dilute $1^{\circ}/S^{\circ} = 7.0$). Incomplete mixing of the silica and surfactant phases under quiescent conditions results in only partial disordering of the lamellar pore structure. One reason may be the limited I°/S° ratios at the surfactant interface resulting from diminished mass transport of silica species into solvent regions between surfactant assemblies. The limited I°/S° ratio does not impart sufficient surface curvature to the surfactant interface to form a completely disordered phase and the material retains significant portions of its original lamellar character.



Figure 2.8: ²⁹Si NMR spectra of calcined HMS molecular sieve silicas synthesized under concentrated reagent conditions with I^{o}/S^{o} values ranging from 4.0-10. $Q^{4}/(Q^{3}+Q^{2})$ ratios increase with increasing I^{o}/S^{o} values.

As the pore size decreases with increasing $1^{\circ}/S^{\circ}$ ratio, the wall thickness between pores increases since the pore to pore distance remains constant. The amount of silica forming the wall structure is limited only by the mass transport of neutral silica species into the solvent regions between neutral surfactant micelles. Unlike electrostatic assembly pathways, there is no need for charge compensation of the surfactant micelle and therefore no limitation to the wall thickness. Additionally, the cross-linking of the silica within the wall of HMS materials increases as the walls become thicker. Figure 2.8 shows the ²⁹Si NMR of the HMS silicas synthesized with different ratios of $1^{\circ}/S^{\circ}$. As the ratio increases, the $Q^{4}/(Q^{3}+Q^{2})$ value increases almost two fold. The increased crosslinking is most likely related to the thickness of the wall and therefore to the decreasing ratio of silica at the interface compared to the overall silica within the framework wall structure.

TEM images of all samples in the series consistently show an inorganic matrix with mesopores of uniform diameter. There is no evidence for the existence of long-range order. Instead, all pores appear to be wormhole-like. Wormhole motifs also have been observed for silica and alumina mesostructures obtained by N^OI^O assembly, where N° is a polyoxyethylene surfactant.^{11,26} TEM images also show the existence of 2 distinct particle morphologies (Figure 2.5), spherical at high I°/S° ratios (10), and fractal or sponge-like particles at low I°/S° ratios (4.0).

Spherical HMS particles are formed at high I°/S° ratio systems in both dilute and concentrated reagent conditions. Higher ratios of TEOS may partially

dissolve the surfactant colloids into solution thereby diminishing their diameter and allowing for more complete penetration of silica species between surfactant micelles and complete encapsulation of surfactant species. The complete encapsulation of the surfactant is reflected in the decrease in pH of the system from 8.5 to 6.5 after 20 hours. In contrast, I°/S° ratios of 4.0 witness only a decrease in pH from 8.5 to 8.0 after 20 hours indicating residual surfactant remains in solution. Synthesis of HMS silicas with sponge-like particles textures is directly related to the nucleation from heterogeneous surfactant solutions as will be addressed in the next chapters. At high I°/S° ratios, encapsulation of all surfactant removes the external nucleation sites resulting in monolithic particle growth and may partially explain the synthesis of spherical silica. Additionally, the fact that an amine is used in this synthesis, however, cannot be over looked. It has been shown before that silica spheres of uniform diameter can be synthesized via sol-gel synthesis in alcohol systems in the presence of ammonia and water.²⁷ High volumes of TEOS in a HMS synthesis significantly add to the organic content of the solution. The presence of the basic amines may modify the silica enough to forms spheres. Additionally, mesoporous silica spheres have been synthesized by Unger essentially through electrostatic assembly and a modified the Stöber reaction. 28,29,30

2.5 Conclusion

The assembly of mesostructured molecular sieves by H-bonding interactions between neutral long alkyl chain amine surfactants and molecular

inorganic precursors proceeds through a cooperative assembly process. In this process, a lamellar surfactant phase is transformed into a disordered wormhole mesostructure due to the increase in the surface curvature imparted to the surfactant upon H-bonding of the silica species. As in the electrostatic assembly pathways, the interaction between the inorganic and organic species results in the formation of stable silica mesophases. The addition of the TEOS to the surfactant solution results in the hydrolyzed silica species penetrating solvent regions between the micelles of a lamellar surfactant liquid crystalline phase (Figure 2.6). This mechanism is similar to the initial proposal put forth by Mobil researchers for the assembly of M41S silicas.⁵ Hydrogen bonding between silica species and the lamellar surfactant imparts curvature to the surfactant phase resulting in the formation of tubular or wormhole-like micelles.

Interfacial surface curvature of the surfactant is directly dependant on the ratios of inorganic to organic species (I^{0}/S°) and this curvature results in mesophases with different pore diameters. However, there exist two significant differences in the assembly processes. First, the weak H-bonding interactions between the organic and inorganic phase result in significant disorder in the arrangement of the pore structure. Second, the surfactant packing parameter is determined by the I°/S° ratio. Therefore, the curvature of the $I^{\circ}-S^{\circ}$ interface also is dependent on the I°/S° ratio. This relationship between packing parameter and and surface curvature is manifested in stable wormhole pore structures with pore diameters that are determined by the I°/S° ratio.

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Chapter 3

Textural Mesoporosity and the Catalytic Activity of Mesoporous Molecular Sieves with Wormhole Framework Structures

3.1. Abstract

Three different water - alcohol co-solvent systems were used to assemble mesoporous molecular sieve silicas with wormhole framework structures (denoted HMS silicas) from an electrically neutral amine surfactant (S°) and a silicon alkoxide precursor (1°). The fundamental grain size and associated textural (intra-particle) porosity of the disordered sponge-like structures were correlated with the solubility of the surfactant in the water - alcohol co-solvents used for the S^ol^o assembly process. Polar co-solvents containing relatively low volume fractions of $C_n H_{2n+1}OH$ alcohols (n = 1-3) gave heterogeneous surfactant emulsions that assembled intergrown aggregates of small primary particles with high textural pore volumes (designated HMS-HTx). Conversely, three dimensional, monolithic particles with little or no textural porosity (designated HMS-LTx) were formed from homogeneous surfactant solutions in lower polarity co-solvents. Aluminum substituted AI-HMS-HTx analogs with high textural porosity and improved framework accessibility also were shown to be much more efficient catalysts than AI-HMS-LTx or monolithic forms of hexagonal AI-MCM-41

for the sterically demanding condensed phase alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol. Transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) studies verified the textural differences between wormhole HMS and electrostatically assembled hexagonal MCM-41 and SBA-3 molecular sieves. Power law fits to the scattering data indicated a surface fractal ($D_s = 2.76$) for HMS-HTx, consistent with rough surfaces. A second power law at lower-q indicated the formation of a mass fractal ($D_m = 1.83$) consistent with branching of small fundamental grains and formation of sponge-like particles. Hexagonal MCM-41 and SBA-3 silicas, on the other hand, exhibited scattering properties consistent with moderately rough surfaces ($D_s = 2.35$ and 2.22, respectively) and large particle diameters (>>1 μ m). HMS-LTx silicas showed little or no mass fractal character ($D_m = 2.87$), and no surface fractal scattering.

3.2. Introduction

Several general pathways have been developed in recent years for the assembly of mesoporous molecular sieves. These pathways may be classified according to electrostatic charge matching,^{1,2,3} hydrogen bonding,^{4,5} and dative bonding⁶ interactions at the interface of the structure-directing surfactant micelles and the inorganic framework. The benefits of electrically neutral amine surfactants for the H-bonded assembly of mesostructures have been demonstrated by the properties of silica molecular sieves assembled in the presence of amine surfactants.^{7,8} Originally described as disordered hexagonal molecular silicas and denoted HMS, these latter neutral framework silicas have more recently been shown to possess wormhole-like framework structures^{4,8} rather than the long range hexagonal framework structures characteristic of electrostatically assembled MCM-41 and SBA-3 silicas^{1,3} Nevertheless, the pore size distributions, surface areas, and pore volumes of HMS silicas are similar to those of electrostatically assembled mesostructures. The wormhole channel motif is a potentially important structural feature for favorable catalytic reactivity, in part, because channel branching within the framework can facilitate access to reactive sites on the framework walls. HMS wormhole structures can also have relatively small fundamental grain sizes (<200 nm), which results in complementary textural mesoporosity for the more efficient transport of reagents

to framework reaction centers.⁸ This catalytically important textural porosity arises from the aggregation of small mesoporous grains through intergrowth or other associative mechanisms. Consequently, textural porosity is dependent on the size, connectivity and surface texture of the fundamental grains, but it is independent of the framework structure of the particles.

The textural mesoporosity of HMS silicas is determined by the polarity of the medium in which the framework is assembled. Highly polar solvents, such as 90:10 (v:v) water - ethanol, characteristically afford wormhole frameworks with grain sizes < 200 nm and textural mesopores that are comparable to the framework pores in overall volume.⁸ However, solvents of relatively low polarity, e.g., 35:65 (v:v) water - ethanol, promote the growth of large, monolithic particles with little or no textural porosity.

The importance of textural mesopores in enhancing the catalytic activity of HMS materials relative to MCM-41 has been demonstrated for several condensed phase reactions in which access to framework reaction sites may be diffusion limited. Substantially higher conversions have been reported for the peroxide oxidation of various substrates using Ti-^{9,10,11}, V-^{11,12,13,14}, Cr-¹¹, Mo-¹¹, and Mn-¹¹ substituted HMS materials compared to analogous compositions of MCM-41. Also, Fe³⁺ exchanged Al-HMS exhibits a higher rate constant for the selective catalytic reduction of NO by NH₃ than does Fe³⁺ exchanged Al-MCM-41.¹⁵ Additionally, Al-HMS is more active for the cracking of cumene¹⁶ than a compositionally equivalent Al-MCM-41. On the other hand, Ti-

HMS has been reported to exhibit *lower* catalytic activity than Ti-MCM-41 for the peroxide epoxidation of α -pinene¹⁷ and the oxidation of aniline.¹⁸

The discrepancies in assessing the relative catalytic activities of HMS and MCM-41 materials may be linked to differences in textural properties. Although the Ti-HMS used for aniline oxidation was prepared at a solvent composition that should have provided a product with high textural porosity, the N₂ adsorption¹⁹ properties indicated the absence of textural pores. This latter result suggested that the textural mesoporosity of HMS materials might be much more sensitive to solvent polarity than previously realized. Accordingly, the present work investigates the textural mesoporosity of HMS molecular sieve silicas assembled from co-solvent mixtures of water and three different $C_nH_{2n+1}OH$ alcohols (n = 1 -3). Representative AI - substituted HMS derivatives with relatively high and low textural mesoporosity, designated AI-HMS-HTx and AI-HMS-LTx, respectively, are compared as catalysts, along with AI-MCM-41, for the catalytic alkylation of 2,4-di - tert- butylphenol with cinnamyl alcohol. This sterically demanding condensed phase reaction provides a clear assessment of the role of textural mesoporosity in determining the relative catalytic activities of mesoporous molecular sieves with equivalent framework pore sizes. In addition, SAXS and TEM studies have been used to characterize the textural properties of wormhole HMS materials. Representative hexagonal mesostructures, namely, MCM-41^{20,21} and SBA-3³, as prepared by previously reported electrostatic assembly pathways, have been included in the SAXS studies for comparison.

3.3. Experimental

3.3.1. Synthesis

Solvents of differing polarity for HMS syntheses were prepared by combining different volumes of H_2O and a less polar alcohol co-solvent. A typical reaction series used methanol, ethanol, or propanol as a co-solvent and dodecylamine (abbreviated DDA) as the structure directing surfactant, S^o. The synthesis of a HMS molecular sieves with relatively high or low textural mesoporosity was carried out by first dissolving 1.2 g DDA (6.5 mmol) into the desired volume of alcohol and the diluting the solution to a total volume of 28 mL with water. A 5.0g portion (24 mmol) of the l^o precursor, tetraethylorthosilicate (TEOS), was then added to the surfactant solution under vigorous stirring. The reaction solution was stirred at ambient temperature for 20 h in a sealed flask.

Aluminum - substituted HMS analogs with high and low textural mesoporosities were obtained by first preparing the pure silica mesostructures according to the above procedure in water: ethanol mixtures at volume ratios of 60 : 40 and 50 : 50, respectively. After a reaction time of 20 h, a solution of Al(OCH(CH₃)CH₂CH₃)₃ in 5.0 mL of *sec*-butanol and 5.0 mL of ethanol was added to the HMS reaction mixtures. The reaction mixtures were subsequently heated at 45 °C for an additional 20 h. The as-synthesized HMS and Al-HMS reaction products were filtered, washed with H₂O and air - dried at ambient temperature for 24 h. Surfactant removal from each product was accomplished
by calcination at 630 °C for 4 h in air. The calcination temperature was reached using a ramping rate of 2 °C/min.

Hexagonal SBA-3³ and MCM-41^{20,21} molecular sieve silicas were prepared by electrostatic assembly pathways according to previously reported methods. $C_{16}H_{33}N(CH_3)_3Br$ (CTAB) was the surfactant used in the synthesis of both materials in order to obtain framework pore sizes comparable to the HMS silicas used in this study. Aluminum - substituted MCM-41 was prepared by adding Al(NO₃)₃ to the MCM-41 reaction mixture after 24 h reaction at 100 °C²², and then continuing the reaction for an additional 24 h at 100 °C.

3.3.2. Catalytic Reactions

The alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol was carried out in a 100 mL flask with 1.0 mmol 2,4-di-*tert*-butylphenol (Aldrich) and 1.0 mmol cinnamyl alcohol (Aldrich) using 50 mL isooctane as a solvent. The solution was heated to 60 °C and 500 mg catalyst was added. After a reaction time of 6 h, the catalyst was filtered and extracted with dichloromethane to recover adsorbed reaction products. The solutions from the reaction and the catalyst extraction were combined and distilled to remove the solvent. The products were analyzed by GC (HP 5890) and GC-MS using 1,3-di-*tert*butylbenzene as an internal standard.

3.3.3. Physical Measurements

Wide-angle powder x-ray diffraction (XRD) patterns were obtained using a Rigaku Rotaflex Diffractometer with Cu K_{α} radiation ($\lambda = 0.154$ nm). Counts were

accumulated every 0.02 degrees (2 θ) at a scan speed of 1 degree (2 θ)/min. Shifts in the position of the first correlation peak for HMS samples were taken as being indicative of changes in the average pore - pore separation.

 N_2 adsorption-desorption isotherms were obtained at -196 °C on a Micromeritics ASAP 2010 Sorptometer using static adsorption procedures. Samples were outgassed at 150 °C and 10⁻⁶ Torr for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear part of the BET plot according to IUPAC²³ recommendations. Pore size distribution was estimated from the adsorption branch of the isotherm by the method of Horvath and Kawazoe²⁴. The framework pore volume (V_t) for each mesostructured sample is taken as the volume adsorbed at 0.50 P/Po, whereas the total pore volume (V_t) is the difference (V_t-V_t).

TEM images were obtained on a JEOL 100CX microscope with a CeB_6 filament and an accelerating voltage of 120 KV. Samples were prepared by sonicating the powdered sample for 20 minutes in EtOH, and then evaporating 2 drops onto carbon coated copper grids.

SAXS experiments were conducted at the University of New Mexico/Sandia National Laboratories Small-angle X-ray Scattering Laboratory (http://saxs-comm.unm.edu). Samples approximately 0.07-0.27 mm thick were prepared by sprinkling the powdered samples on adhesive cellophane tape used as windows on a 1.5 cm inner diameter washer. Data were collected and combined for the samples and backgrounds on the Bonse-Hart (0.0003 < q < 0.1

Å⁻¹) and 5 m Pinhole (0.03 < q < 0.7 Å⁻¹) ²⁵ instruments using CuK_{α} radiation. The wave vector q is defined as, q = 4 π sin(2 θ /2) / λ , where 2 θ is the scattering angle. Scattering data from the two instruments is corrected for background, slit smearing, and sample thickness before being combined.

3.4. **Results and Discussion**

3.4.1. Mesostructure Synthesis

In order to better elucidate the relationship between the textural porosity of wormhole HMS molecular sieves and the polarity of the solvent system from which they are assembled, a series of samples were prepared in three different $H_2O - C_nH_{2n+1}OH$ (n = 1, 2, and 3) co-solvents. For each reaction mixture, dodecylamine was the structure - directing surfactant, the surfactant to tetraethylorthosilicate ratio (S^o/l^o) was 0.27, and the concentration of the surfactant was 0.23M. Clear, homogeneous solutions of the structure - directing surfactant were obtained when the alcohol content by volume was $\geq 70\%$ methanol, $\geq 50\%$ ethanol and $\geq 50\%$ propanol. At co-solvent compositions containing lower alcohol concentrations the surfactant formed an emulsion. Thus, at alcohol contents sufficiently high to avoid emulsion formation, the HMS products were nucleated from homogeneous solutions of the surfactant. For co-solvents with lower alcohol concentrations, the products were assembled from heterogeneous mixtures containing the surfactant in emulsion form.

Aluminum - substituted derivatives of HMS for use in catalytic studies (see below) also were prepared from homogeneous and heterogeneous forms of the

surfactant, depending on the choice of the co-solvent composition. The pure silica form of the wormhole mesostructure was formed from either a homogeneous solution (50 : 50 water : ethanol) or from a heterogeneous surfactant emulsion (60 : 40 water : ethanol), and then sufficient aluminum *sec*-butoxide was added to the reaction mixture to achieve 2.0 mole % aluminum incorporation in the framework. This post - assembly procedure for aluminum incorporation made it possible to retain both the wormhole framework structure and the textural properties characteristic of the HMS silica formed from homogeneous and heterogeneous forms of the surfactant. The ²⁷AI MAS NMR spectra of the calcined forms of these AI-HMS derivatives exhibited a single resonance at 54.3 ppm, indicating that all of the aluminum occupied tetrahedral sites in the wormhole framework

Figure 3.1, A and B are representative x-ray powder diffraction patterns for HMS silicas assembled from heterogeneous emulsion and homogeneous solution forms of the surfactant in co-solvents containing 40 % and 50 % ethanol by volume, respectively. The XRD patterns for the products obtained from the two forms of the surfactant are indistinguishable. Both products exhibit an intense reflection at low angle and a broad shoulder near 5 degrees. These patterns are typical of HMS wormhole structures assembled from long alkyl chain neutral amines as surfactants, the correlation peak indicating the average pore to pore separation in the disordered wormhole framework. Equivalent XRD patterns were obtained for HMS silicas assembled from water : alcohol co-solvents



Figure 3.1: Powder x-ray diffraction patterns of calcined HMS silicas assembled from (A) heterogeneous emulsion and (B) homogeneous solution forms of a dodecylamine surfactant in co-solvents containing 40 % and 50 % ethanol by volume, respectively. Each sample was prepared at ambient temperature from reaction mixtures containing 0.23 mole/L of dodecylamine and a surfactant / TEOS (S°/I°) ratio of 0.27. As is explained later in the text, sample (A) has a high textural mesoporosity (denoted HMS-HTx) and sample (B) has a relatively low textural mesoporosity (denoted HMS-LTx), but the XRD patterns are indistinguishable. Samples are offset 2000 (cps) for clarity.

containing methanol and propanol, regardless of the homogeneity of the initial surfactant solution. The same XRD features also were obtained for the AI-HMS derivatives prepared from heterogeneous and homogeneous forms of the surfactant.

Although the HMS molecular sieves formed from a heterogeneous surfactant emulsion or from a homogeneous surfactant solution cannot be distinguished by XRD, the N₂ adsorption properties of the products obtained from these fundamentally different forms of the surfactant differ dramatically. Figure 3.2, A and B are representative N₂ adsorption - desorption isotherms for HMS silicas prepared from a surfactant emulsion and a surfactant solution, wherein the ethanol content of the co-solvent was 40% and 50% by volume, respectively. Filling of the framework confined mesopores occurs in the partial pressure range 0.15 - 0.30 for both samples, but only the product formed from the heterogeneous surfactant emulsion shows an additional capillary condensation at partial pressures > 0.90 due to the filling of textural mesopores 4,8 . This characteristic signature of textural mesoporosity is observed for all HMS materials assembled from heterogeneous emulsions of the amine surfactant in water : alcohol co-solvents, including co-solvents containing methanol and propanol. In contrast, the HMS products obtained from homogeneous solutions of the surfactant showed little or no hysteresis behavior in the textural mesopore region.

Table 3.1 provides the total pore volume (V_t), framework pore volume (V_f), and textural pore volume (V_{tx}), along with the framework pore diameter and BET



Figure 3.2: N₂ adsorption-desorption isotherms for calcined HMS silicas assembled from heterogeneous emulsion and homogeneous solution forms of a dodecylamine surfactant in co-solvents containing 40 % and 50 % ethanol by volume, respectively. Sample A has high textural mesoporosity (HMS-HTx) as indicated by the hysteresis loop at partial pressures >0.90, whereas sample B has low textural mesoporosity (HMS-LTx). The isotherms are offset vertically by 100 cm³/g, STP for clarity.

	ප්	Vol % Alc.	۹. >	ہ <	< ^{بر م}		Pore Diameter	BET SA
sample	solvent	Co-solvent	(cc/g)	(cc/g)	(cc/g)	Vtx / Vf	HK (nm)	(m²/g)
HMS-HTx	CH ₃ OH	40	1.72	0.82	0.90	1.10	3.25	1061
HMS-HTx	CH ₃ OH	50	1.81	0.73	1.08	1.48	3.01	1041
HMS-HTx	CH ₃ OH	60	1.20	0.76	0.44	0.58	2.82	1005
HMS-LTx	CH ₃ OH	70	0.59	0.57	0.02	0.04	2.31	1106
HMS-HTx	C ₂ H ₅ OH	30	1.67	0.73	0.94	1.29	2.83	1054
HMS-HTx	C ₂ H ₅ OH	40	1.41	0.80	0.61	0.76	3.38	1021
HMS-LTx	C ₂ H ₅ OH	50	0.95	0.90	0.05	0.06	3.06	1075
HMS-LTx	C ₂ H ₅ OH	60	0.93	0.88	0.05	0.06	2.50	1175
HMS-HTx	C ₃ H ₇ OH	20	1.74	0.76	0.98	1.29	2.70	1140
HMS-HTx	C ₃ H ₇ OH	30	1.28	0.72	0.56	0.78	2.66	1160
HMS-HTx	C ₃ H ₇ OH	40	0.75	0.59	0.16	0.27	2.15	1300
HMS-LTx	C ₃ H ₇ OH	50	0.62	0.60	0.02	0.03	2.10	1179
AI-HMS-HTx	C ₂ H ₅ OH	40%	1.17	0.80	0.37	0.46	3.4	006
AI-HMS-LTx	C ₂ H ₅ OH	50%	0.90	0.80	0.10	0.12	3.3	980
AI-MCM-41			0.95	0.85	0.10	0.11	3.3	1036

Table 3.1: Textural properties of calcined HMS molecular sieves assembled in water - alcohol co-solvents and calcined

 $^{\rm b}$ V_t, total pore volume obtained from the volume of N₂ adsorbed at 0.99 P/Po. ^c V_t, framework pore volume obtained from the volume of N₂ adsorbed at 0.50 P/Po. ^d V_x, textural pore volume obtained from the difference (V_t - V_f). -)

surface area, for HMS derivatives assembled from different water : alcohol cosolvent compositions. The table includes for comparison the analogous values for a hexagonal AI-MCM-41 with a comparable framework pores size. For all of the HMS products assembled from homogeneous surfactant solutions, namely, in co-solvents containing \geq 70% methanol, \geq 50% ethanol and \geq 50% propanol, the total pore volume is expressed almost entirely as framework porosity and little or no textural porosity (< 5% as V_{tx}). These HMS derivatives with low textural porosity, which we denote HMS-LTx, resemble electrostatically assembled MCM-41 in their pore volume distributions. However, for the mesostructures assembled from surfactant emulsions, at least 20%, and more typically 40 - 60%, of the total pore volume arises from textural mesopores. Significantly, neither the framework pore volume nor the framework pore size is compromised in these high textural pore derivatives. In fact, the framework pore size, as well as the textural porosity generally increases with decreasing alcohol content of the cosolvent. We denote these high textural porosity materials HMS-HTx.

We consider next the potential importance of textural mesoporosity on the catalytic properties of HMS molecular sieves.

3.4.2. Catalysis Studies

Al-MCM-41 recently has been shown to be an effective solid acid catalyst for the alkylation of 2,4-di-*tert*-butylphenol (2,4-DTBP) by cinnamyl alcohol (Cin-OH) to yield a flavan (Reaction 1).²⁶

We selected this reaction for evaluating the catalytic significance of textural mesoporosity in HMS mesostructures, in part, because it is a sterically

Reaction 1: Acid catalyzed alkylation of 2,4 DTBP with cynnamyl alcohol.



demanding condensed phase transformation and potentially susceptible to diffusion limitations arising from restricted access to the active acid sites in the framework. Also, cinnamyl alcohol self-degrades to unwanted side products, such as the corresponding symmetric ether²⁷, under strong acid catalytic conditions. Consequently, the selectivity to flavan is an indicator of the effectiveness of the desired reagent pairing and conversion at the moderately acidic sites within the framework mesopores.

Table 3.2: Alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol in the presence of Al-HMS and Al-MCM-41 catalysts^a.

Catalyst (2.0 mol % Al)	Conversion (%)	Selectivity (%)	Flavan Yield (%)
AI-HMS-HTx	56.5	74.2	41.4
AI-HMS-LTx	49.1	69.3	34.0
AI-MCM-41	47.2	71.8	33.9

^aReaction conditions: 60 °C, 6 h, 500 mg catalyst, 50 mL isooctane

The catalytic properties of Al-HMS-LTx and Al-HMS-HTx, along with those of Al-MCM-41 for comparison are summarized in Table 3.2. These mesostructures have nearly the same framework pore volume (0.80 - 0.85 cc/g) and the same framework aluminum content (2.0 mole %), as indicated by the data presented in Table 3.1. They also have the same average framework pore size (3.3 - 3.4 nm), although the pore distribution is somewhat broader for the Al-HMS derivatives than for Al-MCM-41 (see Figure 3.3). The incorporation of aluminum into the framework of HMS-HTx reduces the textural pore somewhat, perhaps due to Ostwald ripening at the elevated temperatures used to achieve alumination (c.f., experimental section). Nevertheless, the textural pore volume is almost four times larger for Al-HMS-HTx than for Al-HMS-LTx and Al-MCM-41.

The conversion of cinnamyl alcohol in all cases is 100%, but the conversion of phenol is considerably lower. Al-HMS-LTx affords the desired flavan in 47.2% yield, comparable to the yield obtained with Al-MCM-41 (49.1%). On the other hand, Al-HMS-HTx provides a flavan yield (56.5%) that is 1.20 times as large as the yield obtained with Al-HMS-LTx and 1.15 times larger than the yield obtained with Al-MCM-41. Factors other than textural mesoporosity may contribute to the differences in the catalytic efficiencies of HMS and MCM-41 mesostructures. These two types of structures (wormhole vs. hexagonal frameworks) are assembled by fundamentally different mechanisms (H bonding vs. electrostatic assembly). Consequently, the acidic centers may differ in intrinsic strength and accessibility, even though the framework walls are amorphous for both structure types.



Figure 3.3: Horvath and Kawazoe pore size distribution plot for calcined samples of 2% Al-substituted HMS and MCM-41 molecular sieves: (A) Al-MCM-41, (B) Al-HMS-LTx, and (C) Al-HMS-HTx. The average framework pore size is 3.35 ± 0.05 nm for each sample.

However, the substantially greater catalytic activity for AI-HMS-HTx compared to AI-HMS-LTx can only be attributed to the four-fold larger textural pore volume, which is important in providing reagent transport to the framework active sites.

3.4.3. TEM and SAXS Studies

TEM images of HMS-HTx and HMS-LTx silicas, prepared with 40 % and 50 % ethanol co-solvent, respectively, illustrate the differences in the sizes and morphologies of particles for these two classes of HMS mesostructures (see Figure 3.4). Analogous images are observed for all HMS derivatives with high and low textural mesoporosities, regardless of the water : alcohol co-solvent system used for the S^ol^o assembly process. A HMS-HTx derivative consists of fundamental grains intergrown into a sponge-like particle texture with a rough, uneven surface (Figure 3.4A). The intergrowth of small primary grains results in aggregates with significant extra-framework, intra-particle void space consistent with the textural mesoporosity observed in N_2 adsorption (Figure 3.2A). Conversely, the HMS-LTx silicas (Figure 3.4C) obtained from co-solvents of lower polarity have fundamental particle sizes of ~ 250 nm or larger. These large, monolithic particles have smoother surfaces and a Euclidean or three-However, all HMS-HTx and -LTx derivatives have dimensional geometry. disordered wormhole - like frameworks, as represented by the higher magnification TEM images (see Figure 3.4B&D, respectively).

Small angle scattering of both X-rays (SAXS) and neutrons (SANS) has been used quite extensively in probing the fractal dimensions, particles sizes and various other structural parameters of porous silicas^{28, 29} and micelles confined

Figure 3.4: TEM images of calcined HMS materials assembled from heterogeneous emulsion (HMS-HTx, A. Low magnification, B. High magnification) and homogeneous solution (HMS-LTx, C. Low magnification, D. High magnification) forms of a dodecylamine surfactant in co-solvents containing 40 % and 50 % ethanol by volume, respectively.





in porous silica.³⁰ In addition, several small-angle scattering studies have been reported for surfactant assembled mesostructured silicas.^{31, 32, 33, 34, 35} SAXS also has recently been used to describe the unique mass fractal character of Surfactant -Templated Silica Aerogels (STSA)³⁶ with a hexagonal MCM-41 framework structure (see below). In order to obtain more incisive insights into the texture of wormhole HMS-HTx and -LTx derivatives in comparison to hexagonal mesostructures, we examined the SAXS scattering over a wide q-range, 0.0003 < q < 0.7 Å⁻¹. Over this q-range, we can attempt to determine the surface and mass fractal dimensions of the materials by analyzing the transition region between surface and mass fractal power law scattering.

Small-angle scattering provides a direct measure of the fractal nature of matter³⁷ over many decades in length scale, 1/q. This inverse relationship means that scattering by small feature sizes is observed at large q values and conversely, large feature sizes are probed at small q values. For example, the smallest features giving small-angle scattering intensity in the present case are the framework pores, whereas the large features contributing to the scattering are the porous particles themselves.

Fractal objects produce power law scattering, $I(q) = C q^P$, where C is a constant and P is the power²⁸. SAXS data are plotted as Intensity vs. q on loglog scales such that power law scattering is seen as straight-line segments. Objects that scatter as P = -4 (Porod scattering) have a non-fractal surface morphology. Power laws where $-4 \le P \le -3$ are indicative of surface fractal

structure where the surface fractal dimension $D_S = 6+P$. The surface area of a surface fractal scales as A ~ r^{D_S} , where r is the size of the particle. Power laws where $-3 \le P \le -1$ are indicative of mass fractal structure where the mass fractal dimension $D_m = -P$. Mass fractals are porous aggregates of primary particles for which the mass scales as M ~ r^{D_m} . Power laws where P < -4 are indicative of diffuse interfaces.³⁸

We first consider the small angle scattering characteristics of hexagonal mesostructured silicas formed through general electrostatic assembly pathways, in particular MCM-41 20,21,39 and SBA-3 3 . SAXS data, along with a least squares fit to the power-law, are plotted in Figure 3.5. The curve for MCM-41 has been offset by a factor of 10^2 across the entire q range for clarity. Power-law scattering is seen in the low-q region with no evidence of a surface to mass fractal scattering transition. Multiple orders of correlation peaks are evident at high-q in both samples. A least squares fit to the power-law scattering at mid-q (q lower than the correlation peaks) yields an exponent of -3.78(3) for SBA-3 and -3.62(2) for MCM-41, where the numbers in brackets are the standard deviation on the last figure. This implies that the surfaces of the primary particles are fractal with moderate roughness and a surface fractal dimension of 2.22 for SBA-3 and 2.38 for MCM-41(see table 3.3).

The multiple correlation peaks evident in the scattering curves of MCM-41 and SBA-3 indicate that the pores are well ordered. Both curves are consistent with the hexagonal array of framework pores seen in TEM images. MCM-41 is



Figure 3.5: SAXS data for the hexagonal molecular sieve silicas SBA-3 and MCM-41 plotted as I(q) vs. q on log-log scales. The curve for MCM-41 has been offset by a factor of 10^2 counts across the entire range for clarity. The solid lines are fits to a power law equation, $I(q) \sim q^P$.

the best - ordered structure with four correlation peaks and a d_{100} peak at 3.55 nm. Three correlation peaks are evident in SBA-3 with a d_{100} peak 3.51 nm.

	HMS-HTx	HMS-LTx	SBA-3	MCM-41	STSA⁵
Ds	2.76	<2.00	2.22	2.35	2.0
Dm	1.83	2.87	NA	NA	1.0

Table 3.3: Summary of SAXS parameters for mesostructured molecular sieves^a.

 ${}^{a}D_{s} = 6 + P$, where P is the power-law slope of the mid-q (surface scattering) region. $D_{m} = -P$, where P is the power-law slope of the low-q region. b Surfactant-Templated Silica Aerogel⁴².

The SAXS data, along with the least squares fit to the power-law, for HMS materials are shown in Figure 3.6, along with the scattering curve of MCM-41 for comparison. Again, the curves are offset from each other by a factor of 10². The SAXS data for both HMS samples show a transition between two different power law scattering regimes. The mid-q power law is attributed to surface scattering from the primary particles, the low-q power law to scattering from mass fractal aggregates. The transition region occurs relative to the length scale of the primary grain or particle. HMS-HTx displays a transition region at higher q than seen in HMS-LTx, indicating significantly smaller primary particle sizes.

HMS-HTx has a $D_s = 2.76$ over about a decade of q, the highest surface fractal dimension of any of the samples studied. It was also possible to estimate the mass fractal dimension of the particle aggregate from the power-law



Figure 3.6: SAXS data for the molecular sieve silicas HMS-HTx, HMS-LTx and MCM-41 plotted as I(q) vs. q on log-log scales. The curves have been offset from each other by a factor of 10^2 counts across the entire range for clarity. The solid lines are fits to a power law equation, $I(q)-q^P$.

scattering on the low-q side of the crossover ($D_m = 1.83$). This latter value should be treated with some caution because the fit is over less than one decade of data. However, it is consistent with the clustering (intergrowth) of small mesostructured primary grains into larger textured aggregates, as observed in the TEM images. In addition, this SAXS result supports the conclusion that the higher catalytic activity of a HMS-HTx compared to a HMS-LTx analog is primarily a consequence of improved molecular access to the pores of the wormhole framework.

The SAXS curve for HMS-LTx exhibits power-law scattering with a slope of -4.39. Such a steep slope of the power-law scattering has previously been seen in semi-crystalline polymer samples that have a graded electron density at the surface due to a crossover between crystalline and amorphous regions.³⁸ This behavior also was observed for a separate HMS sample with a smooth spherical surface, as judged by TEM. A linear fit to the low-q side of the crossover point yielded $D_m = 2.87$. This is a mass fractal that is approaching the value of $D_m = 3.00$, as expected for a three-dimensional object. Again, the fit to the scattering data is over less than a decade of q. These SAXS data, however, are consistent with the TEM images showing continuous (monolithic) threedimensional particles. Thus, we can conclude that HMS-LTx is composed of larger primary particles with a surface fractal dimension that is lower than HMS-HTx, but a higher mass fractal dimension. These factors contribute to a material with considerably less textural porosity than HMS-HTx, though the primary

particles in either case are not as large as those found in either MCM-41 or SBA-3.

The significant textural porosity of HMS-HTx materials arises from a combination of the high surface texture and low mass fractal dimension of the porous silica aggregates. The hexagonally ordered materials prepared via electrostatic assembly pathways possessed particles larger than can be determined by the SAXS instrumentation used. Even though each of these materials does possess a moderate surface roughness, the lack of textural pore volume can be attributed to the large monolithic particles. Similarly, the smooth particle nature of the HMS-LTx material, combined with the non-fractal aggregation of the primary particles explains the lack of textural pore volume in this material.

Recent small angle scattering studies have shown that MCM-41 silicas synthesized through a modified aerogel technique³⁹ retain not only a high degree of framework pore order, but also form a low dimensional mass fractal monolith.³⁶ These Surfactant-Templated Silica Aerogels (STSA) upon supercritical solvent extraction and subsequent calcination, retain significant textural pore volume due to the low mass fractal dimension ($D_m = 1.0$) of the materials. Though the primary particles of STSA can be larger than those of HMS-LTx and the surfaces smooth ($D_s = 2.0$), their growth into a low dimension mass fractal ($D_m = 1 \text{ vs.} = 2.87$) results in significant intra-particle porosity (Table 3.3).

The analysis of the high-q (small feature size) region of the SAXS gives information about the framework pore sizes and separations. The HMS samples show only a single, broad correlation peak and no higher order reflections, in accord with the wide-angle XRD results. The presence of only one correlation peak indicates that a pore-pore correlation exists due to the more or less uniform pore diameter and wall thickness, but that the pores are not arranged in a periodic array. An additional feature is evident in the data on the high-q side of the correlation peaks in both HMS samples, but it cannot be indexed as a higher order reflection. We believe that this small angle scattering feature arises from the worm-like framework pores. A quantitative analysis is in progress and will be reported elsewhere.

3.5. Conclusion

The textural properties of HMS molecular sieves with wormhole framework structures are determined by the physical state of the neutral amine surfactant used to direct the S^ol^o assembly process. Homogeneous solutions of the structure - directing surfactant in water : alcohol co-solvents containing relatively high volume fractions of alcohol (i.e., \geq 70% methanol, \geq 50% ethanol or \geq 50% propanol) completely dissolve the surfactant and allow for the formation of HMS-LTx derivatives with low textural pore volumes (< 0.1 cc/g). The uniform nucleation and growth of HMS-LTx derivatives from these homogeneous surfactant solutions results in monolithic particles with smooth surfaces, as judged by TEM and SAXS. The textural properties of HMS-LTx derivatives are

similar to those of hexagonal MCM-41 and SBA-3 mesostructures assembled through electrostatic assembly pathways.

Increasingly polar co-solvent compositions partition the surfactant between homogeneous solution and emulsion forms. These heterogeneous mixtures of the surfactant afford HMS-HTx derivatives in which the textural mesoporosity can be as high as 1.1 cc/g without compromising the framework pore volume or framework pore size. The strong correlation between high textural mesoporosity and surfactant heterogeneity suggests that primary HMS particles are not nucleated from the homogeneous solution phase of the surfactant mixture, but that they form and intergrow at the surface of colloidal particles of the free surfactant in emulsion form. As the primary particles undergo further intergrowth and deplete the emulsion, voids reminiscent of the segregated surfactant form within the aggregates and give rise to the high intraparticle textural mesoporosity. That the primary particles grow non-uniformly is supported by the high surface fractal dimension ($D_s = 2.7$) and low mass fractal dimension ($D_m = 1.83$) obtained from the SAXS studies.

Finally, the results of the present study clearly show that the catalytic activity of a HMS molecular sieve for a sterically demanding condensed phase reaction, such as the alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol, is greatly dependent on the textural mesoporosity available for transporting reagents to the framework mesopores. An Al-HMS-HTx derivative affords up to 1.20 times more alkylation product than either Al-HMS-LTx or MCM-41 with the same aluminum content and framework pore size. The assembly of a

catalytically superior HMS-HTx derivative, as opposed to a less active HMS-LTx form, is very sensitive to the alcohol content of the co-solvent. A change in alcohol content as low as 10 % by volume can decide the difference in textural mesoporosity and catalytic performance properties. Previously reported discrepancies in the catalytic activities of HMS molecular sieves, in comparison to MCM-41^{17,18}, most likely were a consequence of differences in the co-solvent dependent textural mesoporosities. Thus, care must be exercised in selecting the alcohol composition of the co-solvent during the synthesis of a HMS molecular sieve catalyst with high textural porosity and catalytic activity. The catalytic importance of textural mesoporosity can also be anticipated for electrostatically ordered mesostructures, such as the STSA³⁶ forms of MCM-41.

3.6. References

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Chapter 4

Pore Size Modification of Mesoporous HMS Molecular Sieve Silicas with Wormhole Framework Structures

4.1 Abstract

Wormhole-like HMS silica molecular sieves with average framework pore sizes in the range 2.9 to 4.1 nm were assembled from 4:1 molar mixtures of TEOS as the inorganic precursor (I°) and dodecylamine as the structure-directing surfactant (S°) in 63 : 27 (v/v) water : ethanol. Increasing the assembly temperature from 25 °C to 65 °C resulted in an increase in the Horvath -Kawazoe pore size (from 2.9 to 4.1 nm). Also, the ratio of fully cross-linked (Q⁴) to incompletely cross-linked (Q^3) SiO₄ sites (Q^4/Q^3) increased more than 2 fold from 1.96 to 4.26 with little or no change in the framework wall thickness (~1.0 nm). Analogous results were obtained for HMS mesostructures assembled at an 1°/S° ratio of 10. Post - synthesis remodeling of as-made HMS mesostructures through digestion in hot distilled water resulted in comparable expansions in the framework pore sizes. The pore expansion process, whether achieved through an increase in the direct assembly temperature or through post-synthesis remodeling in distilled water, is consistent with a mechanism based on temperature - dependent changes in the polarity of the S°I° interface and

concomitant changes in the surfactant packing parameter, and self - swelling of the structure - directing micelle.

4.2 Introduction

The supramolecular assembly of mesoporous molecular sieves can be achieved through various types of interactions at the micelle - solution interface. Electrostatic charge matching^{1,2,3}, H-bonding^{4,5} and dative bonding interactions⁶ between the organic structure director and the inorganic precursor have all been successfully utilized in the formation of mesostructured materials. The original work of the Mobil group on the electrostatic assembly of hexagonal MCM-41 silicas¹ has shown that the pore size of the framework could be mediated by controlling the size of the structure - directing surfactant or by incorporating an auxiliary organic solvent as a co-surfactant to swell the micelles. Further studies^{7,8,9,10} have shown that increases in the assembly temperature or digestion time can also be used to increase the framework pore size. Increases in the assembly temperature can lead to decomposition of the quaternary ammonium ion surfactants^{7,10} through either reaction with OH⁻ to yield neutral amines or by Hoffman degradation to yield alkenes. Both long chain amines and alkenes are efficient swelling agents and can act as auxiliary surfactants in increasing framework pore sizes. In addition, ex situ post-synthesis hydrothermal treatment methods¹¹, have been used to expand the pore sizes of electrostatically pre-assembled mesostructures by an analogous mechanism.

Relatively little work has been reported, however, for the pore size mediation of mesostructures assembled through H-bonding interactions between

electrically neutral surfactants and inorganic precursors. Assembly pathways based on H bonding are generally designated either S^ol^o or N^ol^o, where l^o is the inorganic precursor (typically an alkoxide) and S^o or N^o is the surfactant (typically an amine or a nonionic PEO-based surfactant, respectively). These pathways normally afford mesostructures with wormhole - like framework structures. HMS⁴

and MSU-X⁵ silicas assembled from electrically neutral amines and nonionic diand tri-block surfactants, respectively, are examples of wormhole framework mesostructures. As expected, pore size control can be achieved for both HMS and MSU-X materials through the use of a family of surfactants with different hydrophobic chain lengths.^{4,12} In the case of MSU-X silicas,¹³ controlled pore size expansions up to 2.4 nm can also be achieved using a single PEO surfactant simply by increasing the assembly temperature over the range 25 - 65 °C. Additionally, the pore sizes of MSU-X materials can be expanded through *ex situ* post synthesis thermal treatments.^{14,15} These pore expansion processes arise due to temperature-dependent changes in the conformation of the surfactant and, hence, in the amphiphilic character and size of the surfactant.

Reliable methods for the pore size mediation of a HMS mesostructure assembled from a single amine surfactant, however, are generally lacking. The use of an auxiliary organic solvent as a co-surfactant, such as 1,3,5trimethylbenzene (TMB), can lead to either an increase or a decrease in the framework pore diameter, depending on whether the co-solvent resides in the hydrophobic interior or the hydrophilic palisade region of the micelle.¹⁶

Incorporating ethanol as a co-solvent has been found to decrease HMS pore diameters¹⁷ because this co-solvent binds primarily at the palisade region of the micelle and decreases the surfactant packing parameter. A high concentration of ethanol (>50 vol %) also promotes the undesirable nucleation of large monolithic particles that limit framework accessibility.¹⁸ It has been noted qualitatively¹¹ that the pore size of HMS could be enlarged through an *ex situ* hydrothermal treatment of the pre-dried, as - made mesostructure in H₂O at 100 °C. Subsequent results¹⁵ indicate that post synthesis hydrothermal treatment causes a significant decrease in the X-ray diffraction intensity and a broadening of the N₂ adsorption step, suggesting an accompanying loss in the integrity of the wormhole framework structure.

HMS silicas, particularly those with a sponge-like particle texture for improved framework access,¹⁸ have found promising applications as heterogeneous catalysts^{19,20} and as supports for the immobilization of reagents.²¹ A simple method for tailoring the framework pore size of HMS materials in the presence of a single amine surfactant could make them even more attractive for such applications. Accordingly, in the present work we have examined the effect of assembly conditions and post-synthesis modification methods on the pore size characteristics, framework cross-linking, and particle texture of HMS silicas assembled though a H-bonding S^oI^o pathway using dodecylamine as the surfactant (S^o) and tetraethylorthosilicate (TEOS) as the inorganic precursor (I^o).

4.3 Experimental

4.3.1 Direct Assembly of HMS Silicas

Dodecylamine (DDA, 4.9 mmole) was dissolved in 5.0 mL of ethanol and 45 mL of H₂O was then added to afford a 90:10 (v/v) H₂O : EtOH solution of the surfactant. The surfactant solution was heated to the desired reaction temperature and tetraethylorthosilicate (TEOS, 20 or 49 mmol) was added to give a reaction mixture with an $1^{\circ}/S^{\circ}$ ratio of 4.0 or 10, respectively. For the reaction mixture containing 20 mmol TEOS, an additional 7 mL of EtOH was added to account for the difference in ethanol released upon TEOS hydrolysis between the two mixtures. The reaction flask was sealed and shaken at 220 rpm in a heated water bath at the desired synthesis temperature for 20 hours. The synthesis temperatures were varied from 25 - 85 °C in 10-degree increments. The resulting white precipitates were filtered, washed with copious amounts of H₂O and allowed to air dry at room temperature for 24 hours. The surfactant was removed by calcination in air at 600 °C for 4 hours. The final composition of the assembly medium was 63 : 27 (v/v) water : ethanol and the reaction stoichiometries were as follows:

4 (10) TEOS : 1 DDA : 41.5 (17.5) EtOH : 510 H₂O

4.3.2 Post - Synthesis Remodeling of HMS Silicas

As-made HMS wormhole silica molecular sieves were subjected to a post synthesis modification treatment to remodel the framework pore topology. In one series of experiments, an as-made product was first assembled at 25 °C and a reaction stoichiometry $I^{\circ}/S^{\circ} = 4.0$, recovered from the mother liquor, washed with two 150 - mL portions of H₂O, and then remodeled by heating at 65 °C for 1-5 days in distilled H₂O. The remodeled products were filtered, washed with copious amounts of H₂O, and allowed to air dry at room temperature for 24 hours. The surfactant was then removed by calcination in air at 600 °C for 4 hours.

In a second experiment, an as-made HMS silica with a spherical particle morphology was assembled at an $1^{\circ}/S^{\circ}$ ratio of 8.0 and then examined by TEM before and after framework remodeling in distilled water. In order to prepare the as-made product, DDA (3.4 mmole) was dissolved in 10 mL of ethanol, and then 90 mL of H₂O was added to afford a 90 : 10 (v/v) H₂O : EtOH solution of the surfactant. TEOS (27.6 mmole) was added to the surfactant solution and the flask was sealed and shaken at 220 rpm in a H₂O bath at 25 °C for 20 hours. The final composition of the reaction medium was 85 : 15 (v/v) water : ethanol and the reaction stoichiometry is as follows:

8 TEOS : 1 DDA : 50.4 EtOH : 1471 H₂O

After 20 hours of reaction time the product was washed with two 150 mL portions of H_2O and then heated in 60 mL of distilled water at 65 °C for 4 days. The product was then filtered, washed with H_2O and allowed to air dry at room temperature for 24 hours. The surfactant was removed by calcination in air at 600 °C for 4 hours.
4.3.3 Physical Measurements

Wide-angle powder x-ray diffraction (XRD) patterns were obtained using a Rigaku Rotaflex Diffractometer with Cu K_{α} radiation ($\lambda = 0.154$ nm). Counts were accumulated every 0.02 degrees (2 θ) at a scan speed of 1 degree (2 θ)/min.

 N_2 adsorption-desorption isotherms were obtained at -196 °C on a Micromeritics ASAP 2010 Sorptometer using static adsorption procedures. Samples were outgassed at 150 °C and 10⁻⁶ Torr for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear part of the BET plot according to IUPAC²² recommendations. Pore size distribution was estimated from the adsorption branch of the isotherm by the method of Horvath and Kawazoe.²³

TEM images were obtained on a JEOL 100CX microscope with a CeB₆ filament and an accelerating voltage of 120 KV, a beam diameter of approximately 5 μ m and an objective lens aperture of 20 μ m. Sample grids were prepared via sonication of powdered sample in EtOH for 20 min and evaporating 1 drop of the suspension onto a carbon coated, holey film supported on a 3 mm, 300 mesh copper grid.

 29 Si MAS NMR spectrums were recorded on a Varian 400 VRX solid-state NMR Spectrometer at 79.5 MHz under single-pulse mode with a 7-mm zirconia rotor, a spinning frequency of 4 kHz, pulse width of 8.5 μ s and a pulse delay of 800 seconds. The chemical shifts where externally referenced to talc (-98.1 ppm relative to tetramethylsilane).

4.4 Results

4.4.1 Assembly of HMS Framework Structures

The S^ol^o assembly of HMS molecular sieve silicas with wormhole framework structures was accomplished using dodecylamine (abbreviated DDA) as the structure directing surfactant, S^o, and tetraethylorthosilicate (TEOS) as the inorganic precursor, I^o. The effect of the assembly temperature over the range 25-85 °C was assessed at two silica to surfactant reaction ratios, namely I^o/S^o = 4.0 and 10.

Figure 4.1 provides the x-ray powder diffraction patterns for the calcined HMS derivatives formed at different assembly temperatures and an I°/S° stoichiometry of 4.0. Each sample exhibited a single low angle reflection indicative of the average pore-pore correlation distance. As the synthesis temperature increased, the pore-pore correlation distance systematically increased from a low of 3.8 nm at 25 °C to a maximum value of 5.1 nm at 65 °C. An analogous increase in the pore- pore correlation distance with increasing assembly temperature was also observed for a reaction stoichiometry of I°/S° = 10. Samples assembled at 75 °C and 85 °C, however, gave diffraction patterns (not shown) with greatly reduced XRD intensity. The loss of a well - expressed pore - pore correlation peak indicated that the wormhole framework structure is largely lost at these higher assembly temperatures due to thermal motions that severely disorder H-bonding interactions at the micelle - solution interface.



Figure 4.1: Powder X-ray diffraction patterns of calcined HMS silicas assembled from dodecylamine (S^o) as the structure - directing surfactant and TEOS as the inorganic precursor (I^o) at temperatures in the range 25 °C - 65 °C and a reaction stoichiometry $I^{o}/S^{o} = 4.0$.

Figures 4.2 and 4.3 show the N₂ adsorptions isotherms and Horvath and Kawazoe (HK) pore size distributions, respectively, for calcined HMS silicas assembled over the temperature range $25^{\circ} - 65 \,^{\circ}$ C and $1^{\circ}/S^{\circ} = 4.0$. The samples exhibit type IV isotherms (Figure 4.2) as expected for mesoporous silica. Filling of the framework-confined mesopores occurred at P/P_o = 0.2 - 0.5. The shift to higher relative pressures indicates an increase in framework pore size with increasing assembly temperature. Additionally, each sample displayed a significant uptake of N₂ at high relative pressures (P/Po > 0.90), a signature of a high degree of textural porosity.¹⁸

As can be seen from the Horvath - Kawazoe plots in Figure 4.3, the pore size increased systematically with increasing temperature from 2.9 nm at 25 °C to a 4.1 nm at 65 °C, a 41% increase. At 45 °C, the pore size distribution was narrowest, indicating an optimum temperature for HMS assembly with DDA. It is noteworthy that the maximum HK pore diameter achieved for these materials (4.1 nm) is greater than the d_{001} spacing found for the lipid bilayer phase that DDA forms in a water-alcohol solution (3.6 nm). The trend to larger framework pores with increasing assembly temperature also was observed for HMS wormhole silicas assembled at $1^{\circ}/S^{\circ} = 10$.

²⁹Si MAS NMR spectra of the as-made HMS derivatives assembled at $I^{\circ}/S^{\circ} = 4.0$ (Figure 4.4) show that increasing the assembly temperature increases the fraction of fully cross-linked Q⁴, <u>Si</u>(OSi)₄, tetrahedra (~110 ppm) in



Figure 4.2: N₂ adsorption-desorption isotherms for calcined HMS silicas assembled at temperatures in the range 25 °C - 65 °C and a reaction stoichiometry $1^{\circ}/S^{\circ} = 4.0$. The isotherms are offset vertically by 200 cm³g⁻¹ STP for clarity.



Figure 4.3: Horvath and Kawazoe pore size distribution plots for calcined HMS silicas assembled at temperatures in the range 25 °C - 65 °C and a reaction stoichiometry $I^{o}/S^{o} = 4.0$.



Figure 4.4: ²⁹Si MAS NMR spectra of calcined HMS silicas assembled at 25 $^{\circ}$ C - 65 $^{\circ}$ C and a reaction stoichiometry $I^{\circ}/S^{\circ} = 4.0$. Resonances near -98 and -110 ppm are assigned to Q³ and Q⁴ silica environments, respectively.

comparison to the Q^3 , $HOSi(OSi)_3$, sites (~98 ppm). The Q^4/Q^3 ratio increased from a value of 1.96 at 25 °C to 4.26 at 65 °C, corresponding to 66% and 81% of all SiO₄ sites being fully cross-linked, respectively. The NMR spectra for the calcined versions of the samples assembled at 25 and 65 °C were virtually indistinguishable (not shown), indicating that the extent of framework crosslinking achieved upon calcination was independent of the degree of crosslinking in the initial as-made mesostructures. For both calcined samples, the peak centered at near 110 ppm broadened significantly due to the formation of a range of Q^4 sites. Although this broadening made quantitative analysis of the Si siting difficult, the retention of some Q^3 sites in the calcined derivatives was clearly indicated by a shoulder at 98 ppm.

Table 4.1 summarizes the effect of assembly temperature on the structural properties of the HMS silicas assembled at $1^{\circ}/S^{\circ}$ ratios of 4.0 and 10 and temperatures in the range 25 - 65 °C. Clearly, the X-ray correlation distances and framework pore diameters increase with assembly temperature for both reaction stoichiometries ($1^{\circ}/S^{\circ} = 4.0$ or 10). Subtraction of the HK pore size from the observed pore - pore correlation distance shows that the pore wall thickness is essentially independent of the assembly temperature, though the wall thickness is substantially larger for the mesostructures assembled at $1^{\circ}/S^{\circ} = 10$ (1.6 ± 0.2) than at $1^{\circ}/S^{\circ} = 4.0$ (0.9 ±0.1 nm). The thicker framework walls are associated with lower specific BET surface areas, pore volumes, and framework pore diameters, as expected. Also, the BET surface areas show the expected decrease with increasing pore diameter increases at constant pore volume.

Assembly Temp., °C	lº/Sº (mol/mol)	d- spacing (nm)	HK Pore diameter (nm)	Wall Thickness [⊵] (nm)	Surface Area (m²/g)	Framework Pore Volume (cm ³ g ⁻¹)
25	4.0	3.8	2.9	0.9	1121	0.78
35	4.0	4.1	3.2	0.9	1025	0.80
45	4.0	4.2	3.4	0.8	938	0.81
55	4.0	4.6	3.7	0.9	888	0.82
65	4.0	5.1	4.1	1.0	780	0.75
25	10	3.7	2.3	1.4	1069	0.44
35	10	4.0	2.3	1.7	747	0.43
45	10	4.0	2.6	1.4	697	0.42
55	10	4.6	3.0	1.6	666	0.39
65	10	5.0	3.2	1.8	644	0.31

 Table 4.1: Structural Properties of Calcined HMS Molecular Sieves Prepared by

 S°I° Assembly ^a

^a All mesostructures were prepared from TEOS as the inorganic precursor (I^o), dodecylamine as the structure-directing surfactant (S^o) and calcined at 600°C. ^b Wall thickness was calculated by subtracting the HK pore diameter from XRD d-spacing. The framework pore volume was obtained from the volume of N₂ adsorbed in pores less than 5.0 nm in diameter.

4.4.2 Post-Synthesis Remodeling of As-Made HMS Wormhole Frameworks

In order to more fully explore the possibility of remodeling the framework pore size of an as-made HMS through post-synthesis treatment^{11,15}, a mesostructure was assembled at 25 °C ($1^{\circ}/S^{\circ} = 4.0$), washed free of mother liquor, and then digested in distilled water at 65 °C for 1-5 days. In this procedure it was important that the initial as-made mesostructure was washed free of the original mother liquor prior to being remodel in distilled water. A significant loss of pore structure occurred if the as-made mesostructure was allowed to digest in the ethanol-containing mother liquor. It appears that the presence of ethanol in the mother liquor increased the solubility of the pore-filling surfactant at elevated temperatures and this compromised the integrity of the remodeled mesostructure.

As in the case of HMS derivatives formed by direct assembly, the XRD patterns and N_2 adsorption-desorption isotherms for the remodeled mesostructures were consistent with the retention of the mesoporous wormhole framework and sponge-like particle morphology. The relevant structural parameters for the calcined products are provided in Table 4.2. A substantial increase in pore to pore correlation distance (d-spacing) from 3.8 to 4.6 nm was realized after only 1 day of digestion, followed by a more gradual increase to 5.3 nm after 5 days. Also, an overall pore expansion of 1.5 nm was achieved,

somewhat larger than the 1.2 nm expansion afforded through direct assembly at 65°C due to the lack of ethanol in the digestion liquor.¹⁷

Reaction Time	d-spacing	HK Pore Size	Wall Thickness	Surface Area (m²/g)	Framework Pore Vol. (cm ³ g ⁻¹)
(days)	(nm)	(nm)	(nm)		
0	3.8	2.9	1.0	1121	0.78
1	4.6	3.7	0.9	747	0.64
2	4.9	4.1	0.8	697	0.67
3	5.1	4.1	1.0	666	0.65
5	5.3	4.4	0.9	644	0.64

 Table 4.2:
 Structural Properties of HMS Mesostructures Remodeled through

 Post-Synthesis Treatment at 65 °C^a

^a The initial as-made mesostructure (reaction time = 0 days) was assembled from TEOS and DDA at 25°C and a reaction stoichiometry $I^{\circ}/S^{\circ} = 4.0$.

The remodeling of the above HMS mesostructure in distilled water at 65°C was further manifested by an increase in the framework crosslinking. The Q⁴/Q³ cross-linking parameter prior to calcination increased from an initial value of 1.96 to a value of 4.1 after 5 days of digestion at 65 °C. Although previously reported post-synthesis treatments of as-made HMS silicas at 100 °C resulted in the loss of pore uniformity and the partial collapse of the mesostructure, ¹⁵ remodeling at 65 °C substantially improved both the framework pore size and framework crosslinking. Apparently, the thermal disorder at 100 °C disrupted the hydrogen bonding interactions at the micelle interface and caused structural collapse. At 65 °C, the hydrogen bonding interactions were sufficient to retain the wormhole

structure and allow remodeling of the framework walls and the expansion of the pore size.

We also investigated the framework remodeling of a HMS mesostructure assembled at 25 °C and a reaction stoichiometry $1^{\circ}/S^{\circ} = 8.0$. At this reaction stoichiometry, the wormhole framework prevailed, but the particles were monolithic and spherical in comparison to the fractal or sponge-like particles¹⁸ obtained at $1^{\circ}/S^{\circ} = 4.0$. Digesting the as-made mesostructure in distilled water at 65 °C for 4 days increased the pore-pore correlation distance from 4.1 nm to ~7.1 nm. As shown by the nitrogen isotherms and pore size distribution curves in Figures 4.5 and 4.6 respectively, this increase in correlation distance was accompanied by an increase in the framework pore size from 2.5 to 4.4 nm. In addition, the Q⁴/Q³ cross-linking parameter increased from 1.77 to 3.87 upon remodeling.

The TEM images of this remodeled sample provided insight into the remodeling mechanism. As seen in Figure 4.7A, the initial as-made mesostructure consists of sub-micron, spherical monolithic particles. Though the spheres are not uniform in size, they are clearly independent particles and discriminate in shape. The framework mesopores are wormhole-like throughout each particle (Figure 4.7B). There appears to be some spatial orientation of the pores within the particles, as suggested by the concentric rings within the spherical particles (Figure 4.7A). The remodeled mesostructure, however, clearly shows Ostwald ripening of the amorphous silica as the spheres became inter-grown (Figure 4.7 C, D).



Figure 4.5: N₂ adsorption-desorption isotherms for a HMS mesostructure prepared by direct assembly (25 °C, $I^{\circ}/S^{\circ} = 8.0$) and for the corresponding mesostructure remodeled by digestion in distilled water (65 °C, 4 days). Samples offset 100 cm³/q. STP for clarity.



Figure 4.6: Horvath and Kawazoe pore size distribution plots for a HMS mesostructure prepared by direct assembly (25 °C, $1^{\circ}/S^{\circ} = 8.0$) and for the corresponding mesostructure remodeled by digestion in distilled water (65 °C, 4 days).

Figure 4.7: TEM images of HMS particles: (A , B) spherical particles prepared by direct assembly (25 °C, $1^{\circ}/S^{\circ} = 8.0$) and (C & D) the corresponding mesostructure showing evidence for Ostwald ripening after being remodeled by post-synthesis treatment in distilled water at 65 °C for 4 days. Scale bars correspond to 100 nm in images A & C and to 33 nm for images B & D.



Figure 4.7:

4.5 Discussion

In the absence of TEOS, dodecylamine forms a lipid-like bilayer phase in a water - alcohol solution at ambient temperature as evidenced by a lamellar Xray diffraction pattern corresponding to a basal spacing $d_{001} = 3.6$ nm. The lamellar surfactant structure is consistent with a small amine head group area (a_0) and a surfactant packing parameter²⁴, $g = V/(I \cdot a_0)$, near 1.0. Upon the addition of TEOS to the surfactant solution, a wormhole-like HMS mesostructure is formed via $I^{\circ}S^{\circ}$ assembly. The transformation from a lamellar to a wormhole structure arises due to H-bonding interactions between the amine head group and the silica precursors formed through TEOS hydrolysis increasing the surface curvature of the surfactant micelle.

In the present work we have shown that one can substantially mediate the pore size, framework wall thickness, and framework crosslinking of HMS molecular sieve silica simply by controlling the assembly temperature and reaction stoichiometry. In general, increasing the assembly temperature from 25 $^{\circ}$ C to 65 $^{\circ}$ C increases the framework pore size by about 40% (from 2.8 to 4.1 nm at $1^{\circ}/S^{\circ} = 4.0$ and from 2.3 to 3.2 nm at $1^{\circ}/S^{\circ} = 10$) when the solvent composition is maintained at a water : ethanol ratio of 63 : 27 (v/v). Above ~65 $^{\circ}$ C, however, thermal disorder begins to disrupt mesostructure formation, and there is no benefit to further increasing the assembly temperature.

For HMS assembly temperatures in the range 25 °C to 65 °C, where the wormhole structure is well - expressed, the framework cross-linking improves substantially with increasing temperature. For example, the fraction of totally cross-linked Q⁴ sites increases from 66% to 81% as the assembly temperature is increased from 25 °C to 65 °C. As indicated by similarities in ²⁹Si MAS NMR spectra, the calcination of HMS silicas at 600 °C tends to level the Q⁴/Q³ values, regardless of the initial framework crosslinking achieved under assembly conditions. It is especially notable, however, that the calcined versions of samples assembled at 65 °C are stable to boiling water at 100 °C for 6h, whereas the calcined form of HMS assembled at 25 °C experiences structural collapse under these conditions, as judged by XRD. That is, an as-made HMS mesostructure with an initially high Q⁴/Q³ cross-linking value exhibits better hydrothermal stability upon calcination than a calcined HMS with an initially low Q^4/Q^3 value. This difference in structural stability occurs even though the Q^4/Q^3 values for the final calcined derivatives may be guite similar. This suggests that the overall Q⁴/Q³ value is not a reliable predictor of structural stability. Other factors, such as the siloxane ring stain induced upon silanol condensation, may also influence framework stability.

Increasing the l°/S° reaction stoichiometry for HMS assembly adds more silica to the framework walls, resulting in an increase in average wall thickness from 0.9 ±0.1 nm at $l^{\circ}/S^{\circ} = 4.0$ to 1.6 ± 0.2 nm at $l^{\circ}/S^{\circ} = 10$. The 2.5-fold increase in silica to surfactant ratio, however, also is accompanied by a decrease in framework pore size (c.f., Table 4.1). The increases in framework wall thickness

with increasing reaction stoichiometry, as well as the increases in framework pore size and framework cross-linking with increasing assembly temperature, are consistent with an electrically neutral I^0/S^0 assembly pathway based on H-bonding interactions at the surfactant micelle - silica interface. The absence of charge matching requirements between the surfactant and the silica framework places no constraints on the Q^4/Q^3 siting of SiO₄ tetrahedra and this allows more silica to be condensed into the framework walls under the influence of mass action.

The mechanism leading to an increase in framework pore size with increasing assembly temperature is related to changes in the polarity of the I°S° interface and, consequently, a decrease in H-bonding at the interface. As the assembly temperature is increased, the framework crosslinking is enhanced through further condensation of silanol groups, leading to a reduction in the framework polarity. The degree of H-bonding, along with the hydration of the amine head group, decreases as the polarity of the interface decreases. This leads to an increase in the surfactant packing parameter (g) with decreasing effective head group area (a_0) and, therefore, to an increase in the framework pore diameter as the interfacial curvature decreases. The maximum pore diameter attained in these materials (4.4 nm) is significantly larger than twice the surfactant molecule length of approximately 1.6 nm. There is, therefore, the likelihood that the decreasing degree of H-bonding between the silicate wall and the surfactant molecules at elevated temperatures results in a fraction of the surfactant molecules migrating to the micelle core. The hydrophobic nature of

the non-H-bonded alkylamine causes the molecule to penetrate the core and expand the micelle analogous to electrostatic pore expansion mechanisms.¹⁰ The pore expansion process is, consequently, a combination of the decreasing interfacial curvature due to an increasing average surfactant packing parameter coupled with the alkylamine swelling of the micelle with increasing temperature.

Although pore expansion in HMS may involve micelle swelling, it is initiated through a fundamentally different event. For MCM-41 and related electrostatically assembled mesostructures, increases in the assembly temperature does not fundamentally alter the framework charge. Instead, partial degradation of the quaternary ammonium ion surfactants leads to the formation of neutral amines and alkenes that act as auxiliary surfactants and increase the framework pore size by expanding the micelle.⁷⁻¹¹ In the case of MSU-X mesostructures, the temperature - dependent pore expansion is attributable to changes in the conformation of the PEO segment of the nonionic surfactant and, hence, to an increase size of the surfactant.^{14,15} For HMS silicas, however, it is the decrease in H-bonding interactions between the silica and the surfactant that initiates an increase in the micelle diameter and the expansion of framework pores.

An analogous pore expansion mechanism based on temperature dependent changes in the polarity of the I^oS^o interface accounts for the framework remodeling that occurs upon post-synthesis treatment of as-made HMS mesostructures in hot distilled water. The substantial increase in

framework pore size (c.f., Table 4.2) and enhancement in Q⁴/Q³ cross-linking that occurs upon post-synthesis treatment at 65 °C is almost certainly a consequence of the reduction in interfacial H-bonding and polarity at the remodeling temperature. As the interface becomes less polar and the packing parameter increases, the surfactant becomes partitioned between the micelle interface and the micelle core, and the increase in micelle size is reflected in the framework pore size.

The transport of silica in the remodeling process occurs through dissolution and re-precipitation, as evidenced by the Ostwald ripening of the mesostructured particles under remodeling conditions (c.f., Figure 4.7). Localized dissolution of the silica matrix during thermal treatment is most likely to occur in regions of high surface curvature such as at the intersections of pores within the wormhole network.²⁵ The presence of the basic amine at these intersections promotes this localized dissolution of the silica. H-bonding controls the reprecipitation and reforming of the silica at the micelle interface, resulting in an expansion of the pore diameter.

4.6 **References**

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Chapter 5

Neutral Assembly of Mesostructured Silicas With Alkyl-Diamine Surfactants

5.1. Abstract

The synthesis of mesoporous silicas has been accomplished through Hbonding assembly pathways using alkyl-diamine surfactants of the type RNH(CH₂)₃NH₂ where R is composed of mixtures of alkyl chains of varying lengths (C₁₄₋₁₈H₂₉₋₃₇). Tallow Diamine (TDA) surfactants behave comparably to primary amines in the synthesis of HMS like molecular sieves with wormhole-like frameworks and uniform framework pores of 4.0-5.0 nm in diameter. Increasing the l°/S° ratio during synthesis shifts the framework structure from a lamellar organic mesophase to a wormhole phase by increasing the surface curvature of the micelle array. Structures with high intra-particle textural porosity can be synthesized from heterogeneous reaction mixtures simply by increasing the solvent polarity. Both of these properties are characteristic of H-bonding assembly and seen in the synthesis of HMS silicas with primary amines. Moreover, increasing amine functional units per molecule at the interface of the micelle allow for the synthesis of MSU-G like molecular sieves under hydrothermal conditions. Small, vesicular particles are formed with $Q^4/(Q^3+Q^2)$ values as high as 6.0 with TDA surfactants. These silicas have framework pore

volume comparable to MSU-G (0.39 mL/g), yet they have extremely high intraparticle porosity (2.09 mL/g).

5.2. Introduction

Research into the synthesis of mesostructured molecular sieves utilizing surfactant micelles as structure directors in the assembly of the inorganic frameworks has received extensive interest since Mobil first reported this discovery in 1992.¹ These researchers utilized assemblies of long alkyl chain quaternary ammonium surfactants, or micelles, to assemble anionic silicate species into inorganic 'liquid crystalline' phases designated M41S silicas. Strong Coulombic interactions between the cationic surfactant micelles (S⁺) and the anionic silicate species (I) drive the electrostatic assembly mechanism $(S^{+}I)$ forming ordered pore structures with amorphous silica walls. The stable silica framework allows for the removal of the surfactant species by calcination resulting in periodically ordered mesopores of 2.0 to 10 nm in diameter. Originally three mesophases were identified and labeled. Lamellar MCM-50 is unstable to the removal of surfactant and collapses upon calcination. MCM-41 silicas, which possess hexagonal framework pore symmetry, and MCM-48 silicas with cubic (Ia3d) pore symmetry, however, are stable to the complete removal of the organic surfactant phase.¹ The open framework pore structures are completely accessible and of uniform diameter. The high surface area makes these materials highly desirable for use in a number of applications such as for adsorption, separation and catalysis.

Tanev and Pinnavaia first reported the use of neutral surfactants to assemble mesoporous silicas identified as HMS materials from molecular silica precursors such as tetraethylorthosilicate (TEOS).^{2,3} As in electrostatic assembly reactions, the structure directing agent is a surfactant micelle. The surfactant, in this case however, is a neutral long alkyl chain primary amine such as dodecylamine (DDA, $C_{12}H_{25}NH_2$). The interfacial interaction between surfactant micelle and silica species is hydrogen bonding (S° I°) instead of the Coulombic interactions used in electrostatic assembly pathways.³ The structured silicas are less ordered than mesoporous molecular sieves synthesized through electrostatic pathways, yet HMS silicas have comparable framework pore characteristics and they exhibit an increase in the silica framework connectivity when compared to M41S silicas.⁴ Additionally, as a consequence of its sponge-like particle nature, HMS materials can demonstrate significant intra-particle, or textural porosity, which improves accessibility to surface sites within the framework. A direct consequence of this improved access is an increase in catalytic activity of HMS silicas when compared to large, monolithic mesoporous silicas absent any textural porosity, especially in condensed phase reactions where diffusion plays a limiting role.⁵

Amine based H-bonding assembly was also utilized in the synthesis of stable mesoporous lamellar silicas with hierarchal vesicular morphologies designated MSU-V.^{6,7} Using α, ω -diamine surfactants such as 1,12-dodecylediamine (H₂N(CH₂)₁₂NH₂), Tanev was able to utilize the dominant

lamellar character of the surfactant species to synthesize the first 'lamellar' silicas that are stable to the complete removal of the surfactant. The mechanism of formation was postulated as being biomimetic, in which the transport of inorganic reagents to form the framework structure occurred through processes analogous to biological transport across membranes.⁶ This hypothesis was developed to explain the formation of the resultant vesicle structure of the product and the belief that the surfactant in solution also existed in a vesicular phase. Studies on similar amine surfactants suggest the final vesicle morphology is a result of the curvature induced into the lamellar surfactant system upon the addition of the inorganic silica species.⁸

Kim adopted a modified H-bonding route to assemble 'lamellar' silicas using amine surfactants.⁹ Instead of using an α,ω -diamine surfactants as the structure directing surfactant, they used an amphiphilic Gemini diamine surfactant of the structure; C₁₂H₂₅NH(CH₂)₂NH₂ in the assembly of ultra stable vesicular silicas designated MSU-G. As with monoamine head group surfactants, the diamine surfactants form lipid bilayer phases in aqueous solutions. Upon the addition of the silicate species, the curvature imparted to the surfactant through H-bonding results in the assembly of a wormhole pore structure similar to HMS silicas synthesized with monoamine surfactants. Heating the aged synthesis solution to 100 °C for 2 days, though, causes the silicate to restructure into particles with a distinct vesicular morphology.⁹

Elevated temperatures decrease the H-bonding between the amine surfactants and the silicate wall, resulting in an interface with less surface curvature. The decrease in surface curvature in primary amine surfactant-silica systems manifests itself in an increase in framework pore diameters. Above 65 °C, however, significant loss of H-bonding does not allow for stable mesostructured silica to form. A surfactant species with two amine functional units at its hydrophilic head group adds considerable stability to the total Hbonding occurring at the interface allowing for the use of increased synthesis temperatures. Decreasing H-bonding interactions between Gemini surfactants and silica species also exhibits decreases in surface curvature with increased synthesis temperatures. However, instead of changes in pore diameter, the decreasing surface curvature manifests itself in a mesophase change from disordered wormhole at ambient temperatures to cross-linked lamellar vesicles under hydrothermal conditions. Additionally, synthesis under hydrothermal conditions result in a significant increase in the framework cross-linking of the silica wall as judged by the ratio of fully cross-linked silica sites $(Q^4 = Si(OSi)_4)$ to incompletely condensed silica sites $(Q^3 = SiO(OSi)_3, Q^2 = SiO_2(OSi)_2)$ $Q^4/(Q^3+Q^2)$. MSU-G silicas commonly have $Q^4/(Q^3+Q^2)$ values greater than 6 for the non-calcined materials.⁹ This value is three to four times larger than seen for MCM-41 type silicas and two to three times larger than for HMS silicas synthesized under ambient temperature conditions.⁴ The high framework crosslinking in walls roughly 3.0 nm thick allow these vesicles to display the highest

hydrothermal stability yet seen in mesostructured silicas. MSU-G silicas have been shown to be stable in boiling H_2O for more than 7 days.⁹

Of great interest is the growth of mesopores oriented perpendicular to the pillared layer, creating a three-dimensional pore structure desirable for mass transport in catalytic and other applications.⁹ The structure appears similar to that of a surfactant transition phase between purely two-dimensional L_{α} and a three-dimensional L_3 phase.¹⁰ Though three-dimensional like that of an L_3 phase, the clearly lamellar character is closer in appearance to a two-dimensional phase, yet it is completely stable to the complete removal of the surfactant phase. Unlike the micron sized MSU-V silicas synthesized earlier, the MSU-G silicas are submicron in size and do not appear to intergrow to any detectable level, therefore providing highly stable silicas with improved access to framework surface sites.⁹

Unfortunately, in both MSU-V and MSU-G silicas, the structure directing surfactants are not commercially available and, therefore, the synthesis of these silicas is costly. In the case of MSU-V, the structure directing α,ω -diamine surfactants with alkyl chains greater than 14 carbon atoms are large enough to form mesoporous silicas, but they need to be synthesized in high purity to be useful. Likewise, neutral Gemini surfactants also are not commercially available and must also be synthesized prior to use in assembly experiments. A readily available and inexpensive amine surfactant similar in structure to the Gemini

surfactants would be of great interest for the synthesis of mesostructured silicas of high quality.

The surfactant of choice is the neutral diamine surfactants received from Tomah³ Products, Inc. These particular amine surfactants have the structural formula (Figure 5.1) R(NH(CH₂)₃NH₂. R is a straight alkyl chain with 14-18 carbon atoms ($C_{14-18}H_{29-37}$), 60% of which are C_{16} chains. Each nitrogen functional unit has a straight chain propylene spacer ($C_{3}H_{6}$).



Figure 5.1: Tallow diamine surfactant received from Tomah³ Products, Inc. R is a straight alkyl chain with 14-18 carbon atoms ($C_{14-18}H_{29-37}$).

A series of experiments similar to those performed earlier in the synthesis HMS silicas are described in this chapter based on the use of these long alkyl chain (tallow) diamine molecules as the structure directing surfactant. These experiments where carried out in order to determine the feasibility of using this surfactant in the neutral assembly of mesostructured materials similar to HMS silicas. Additionally, attempts are made to synthesize MSU-G like silicas at temperatures unattainable to primary amine surfactants in order to capitalize on the presence of multiple amine functional units at the head group of the TDA surfactant. It is hoped that these commercially available surfactants will allow for the syntheses of hybrid mesostructures that contain properties unique to HMS and MSU-G silicas.

5.3. Experimental

5.3.1. Synthesis of HMS Like Silicas with TDA at Varying Solvent Compositions

Tallow diamine (TDA, MW 298 g/mole, 2.1 g, 7.0 mmol) was dissolved in ethanol. H_2O was added to provide a initial (v/v) EtOH : H_2O solution ranging from 10 – 70% (v:v) ethanol and a 0.23 M surfactant mixture. Tetraethylorthosilicate (TEOS, 7.3 g, 35 mmol) was added to the stirred surfactant solutions making the l^o/S^o ratio equal to 5.0. The reaction flask was sealed and shaken at 220 rpm in a heated water bath at 45 °C for 20 hours. The initial reaction stoichiometries were as follows:

1 TEOS : 0.20 TDA : 1.36 -9.50 EtOH : 13.18 -41.70 H₂O

5.3.2. Synthesis of HMS Like Silicas with TDA at Varying I°/S° Values

TDA (2.1 g, 7.0 mmole) was dissolved in 9.0 mL of ethanol and 21 mL of H_2O is added to give a 30% (v:v) ethanol solution and a 0.23 M surfactant mixture. TEOS was added, along with ethanol, to the stirred surfactant solution to give I^0/S^0 ratios of 3.0, 4.0, and 5.0. Enough ethanol was added with decreasing amounts of TEOS to keep the dilution factor and the final ethanol content constant. The reaction flask was sealed and shaken at 220 rpm in a water bath at 45 °C for 20 hours. The initial reaction stoichiometries were as follows:

3-5 TEOS : 1 TDA : 22 EtOH : 167 H₂O

Final solvent composition is 45% (v:v) ethanol.

5.3.3. Synthesis of MSU-G Like Silicas with TDA at Increasing Assembly Temperatures

TDA (2.1 g, 7.0 mmol) was dissolved in 7.0 mL of ethanol and 41 mL of H_2O was added to the surfactant solution to yield an initial 15% v:v ethanol solution and 0.15 M surfactant mixture. TEOS (6.1 g, 29 mmol) was added to the surfactant solution with stirring to give an I^0/S° ratio of 4.18. The reaction flask was sealed and shaken at 220 rpm at 20 °C for 30 min and then in a water bath at 20 °C, 45 °C, or 100 °C for 48 h. Only the reaction at 100 °C yielded MSU-G like silicas. Lower temperature synthesis yield wormhole-like products similar to HMS silicas. The initial reaction stoichiometries are as follows:

1 TEOS : 0.24 TDA : 4.10 EtOH : 77.7 H₂O

In each series of experiments, the resulting white products were recovered by filtration, washed with copious amounts of H_2O and allowed to air dry at room temperature for 24 h. Though the surfactants can be completely removed by ethanol extraction, the surfactants were removed by calcination in air at 600 °C for 4 h, because there was no desire to recover the template.

5.3.4. Physical Measurements

Wide-angle powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Rotaflex Diffractometer with Cu K_{α} radiation ($\lambda = 0.154$ nm). Counts were accumulated every 0.02 degrees (20) at a scan speed of 1 degree (20)/min.

 N_2 adsorption-desorption isotherms were obtained at -196 °C on a Micromeritics ASAP 2010 Sorptometer using static adsorption procedures.

Samples were outgassed at 150 °C and 10⁻⁶ Torr for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear part of the BET plot according to IUPAC¹¹ recommendations. Pore size distribution was calculated from the adsorption branch of the isotherm by the method of Horvath and Kawazoe¹².

TEM images were obtained on a JEOL 100CX microscope with a CeB₆ filament and an accelerating voltage of 120 KV, a beam diameter of approximately 5 μ m and an objective lens aperture of 20 μ m. Sample grids were prepared via sonication of powdered sample in EtOH for 20 min and evaporating 1 drop of the suspension onto a carbon coated, holey film supported on a 3 mm, 300 mesh copper grid.

 29 Si MAS NMR spectra were recorded on a Varian 400 VRX solid-state NMR Spectrometer at 79.5 MHz under single-pulse mode with a 7-mm Zirconia rotor, a spinning frequency of 4 kHz, pulse width of 8.5 μ s and a pulse delay of 800 seconds. The chemical shifts where externally referenced to talc (-98.1 ppm relative to TMS, tetramethylsilane).

5.4. **Results and Discussion**

Supramolecular assembly reactions comparable to those performed previously for the preparation of HMS silicas from DDA were carried out in order to determine the feasibility of using a diamine surfactant for the neutral assembly of mesostructured silicas. Of particular interest were two properties characteristic of mesostructures made by neutral assembly pathways using

amine surfactants. One property concerned the nucleation and intergrowth of small mesostructured grains and, hence, the corresponding textural or intraparticle porosity of the mesostructured silica. Managing the polarity of the solvent and, therefore, the homogeneity of the reaction mixture controls the nucleation and intergrowth of small mesostructured grains. The second property concerned the surface curvature of the organic-inorganic interface, which determines the framework pore size, through controlling the number and/or size of the silica species at the temperature dependent H-bonding interface of the surfactant micelle.

5.4.1. Synthesis of HMS Like Silicas with TDA at varying Solvent Compositions

The grain size and textures of mesostructured silicas synthesized with primary amine surfactants are directly related to the homogeneity of the surfactant solution from which they precipitate.⁵ Long alkyl chain primary amines are significantly hydrophobic entities and have limited solubility in aqueous solutions. Adding ethanol or other solvents of lesser polarity to aqueous solutions suitably lowers the overall polarity of the solvent and aids in dissolving the amine surfactant into solution. Low polarity, high volume percent ethanol solvents yield homogeneous reaction mixtures from which large mesoporous monolithic particles (>500 nm diameter) with smooth surfaces precipitate. Highly polar solvents containing a lower volume percent of ethanol cause the neutral amine surfactant to exist as colloidal emulsions. The presence of emulsions
promotes the nucleation of small mesostructured silica grains (<250 nm) and intergrowth into larger sponge-like particles. These sponge-like particles have a high surface roughness and also aggregate in a way as to form a mass fractal cluster.⁵ Small angle X-ray diffraction (SAXS) can identify not only the average grain size, but can also determine the surface roughness and fractal nature of these materials. The difference between monolithic mesostructured silicas and sponge-like particle morphologies, however, can be easily observed in their gas adsorption behavior.

Figure 5.2 is a plot of the N₂ adsorption-desorption isotherms for the mesostructured silicas assembled from TDA surfactant in water-ethanol mixtures with increasing volume percent ethanol and decreasing solvent polarity. Each plot clearly indicates the presence of framework mesoporosity as seen by the abrupt uptake of N₂ at partial pressures between 0.2 and 0.6. The sample assembled from 10% (v:v) ethanol solution, however, differs substantially from the others in the high partial pressure region. This sample exhibits a significant uptake of N₂ at partial pressures above P/Po = 0.80. This gas uptake corresponds to the capillary condensation in pores formed between the intergrown mesostructured grains of the sponge-like particles, or intra-particle pores. Specifically, this uptake of N₂ is a signature of intra-particle textural porosity within a sponge-like particle morphology. As seen in HMS silicas, this typically occurs in samples synthesized from highly polar, non-homogeneous solutions.



Figure 5.2: N₂ adsorption-desorption isotherms for calcined mesoporous silicas assembled with TDA surfactant in aqueous solutions initially containing 10-70% volume % ethanol at 45 °C for 20 h and an l°/S° mole ratio of 5.0. The ethanol formed by the hydrolysis of TEOS was not included in defining the initial solvent composition. For example, curve labeled 10% is the isotherm for the product assembled from a solvent initially containing a 10% ethanol : 90% H₂O (v:v) solvent. The isotherms are offset vertically by 200 cm³/g, STP for clarity.

Silicas synthesized in solvent compositions with 30% volume ethanol, or greater, show little or no intra-particle textural porosity. The TDA surfactant is increasingly soluble in these decreasingly polar solvents associated with increasing ethanol content. As a result, mesostructured silicas with monolithic morphologies assembled with TDA surfactants nucleate from homogeneous solutions. This behavior is entirely analogous to HMS silicas synthesized with primary amines. Simply by decreasing the alcohol content of the synthesis mixture, heterogenous reaction mixtures of colloidal surfactant emulsions are generated, from which the synthesis of sponge-like silicas with intra-particle porosity can be assembled.

Each of the above samples displays a similar mesostructured framework, as revealed by powder X-ray diffraction (Figure 5.3), independent of grain size and textural porosity. The intense primary X-ray diffraction peak at low angle and a broad shoulder at higher angle is characteristic of the scattering from disordered wormhole-like pore structures. These patterns are similar to HMS wormhole structures assembled from long alkyl chain neutral primary amines as surfactants, wherein the correlation peak indicates the average pore to pore distance. There is virtually no difference in the position and shape of the correlation peaks for the samples assembled from 10%, 30% and 50% ethanol and only a slight shift to higher angle for the correlation peak for the sample made from 70% ethanol.



Figure 5.3: Powder x-ray diffraction patterns of calcined mesoporous silicas assembled with TDA surfactant in aqueous solutions initially containing 10-70% volume % ethanol at 45 °C for 20 h and an $1^{\circ}/S^{\circ}$ mole ratio of 5.0. The ethanol formed by the hydrolysis of TEOS was not included in defining the initial solvent composition. For example, curve labeled 10% is the isotherm for the product assembled from a solvent initially containing a 10% ethanol : 90% H₂O (v:v) solvent. The spectra are offset vertically by 3000 (cps) for clarity. Samples are offset 3000 (cps) for clarity.

Figure 5.4A-C are TEM images of the samples synthesized from 10% and 30% ethanol solutions. Figure 5.4 A&B are low and high magnification images respectively, from the 10% sample and illustrate the sponge-like texture of the silica. Figure 5.4A shows the clustering of the small grains with significant intergrowth and the arising intra-particle porosity. The disordered wormhole like pore structure is clearly seen in the higher magnification image (Figure 5.4B) along with pores of uniform diameter. Figure 5.4C&D show the TEM image of the large, monolithic particles synthesized from low polarity solvents. These images do not exhibit the textural porosity seen in Figure 5.4A&B. Based on TEM images, the particles size formed from 30% ethanol are larger than 400 nm in diameter. These results are duplicated for the examples synthesized under even higher ethanol content (not shown). Again, the high magnification image shows a disordered wormhole pore structure similar to that seen in Figure 5.4B.

As in the synthesis of HMS silicas with primary amine surfactants, the control of particle size and shape in the synthesis of mesoporous silicas from polyamine surfactant is directly related to the polarity and subsequent homogeneity of the surfactant solution. The existence of surfactant colloidal emulsions in highly polar solvents with low volume percent alcohols not only provide for the structure directing surfactant phase but also nucleates the growth of small grains analogous to seeding in classical crystal growth. On the other hand, homogeneous solutions generally yield large crystallite sizes.

Figure 5.4: TEM images of calcined mesoporous silicas assembled from: (A and B) a heterogeneous reaction mixture of TEOS and TDA surfactant in a solvent initially containing 10% ethanol (v:v) and (C and D) a homogeneous reaction mixture of TEOS and TDA surfactant in a solvent initially containing 30-70% ethanol (v:v).



5.4.2. Synthesis of HMS Like Silicas with TDA at Varying I^o/S^o Values

The synthesis of mesostructured silicas through a neutral assembly pathway relies on H-bonding between the polar surfactant and silica species present in solution. H-bonding between silica and surfactant species induces curvature to the surfactant array allowing for the cooperative assembly of stable wormhole-like pore structures. The curvature of the interface is directly dependent on the ratio of silica to surfactant (l^o/S^o) present.

Figures 5.5 and 5.6 are powder X-ray diffraction patterns of mesostructured silicas synthesize using TDA surfactants and ratios of TEOS to TDA (1° /S^o) of 3.0, 4.0 and 5.0. The as synthesized samples (Figure 5.5) all exhibit an intense primary scattering peak with a pore to pore correlation distance of approximately 4.8 nm. Samples synthesized at 1° /S^o ratios of 4.0 and 5.0 show broadened shoulders at higher angles indicating disordered wormhole pore structures similar to those seen in HMS synthesized from amine surfactants. The powder X-ray diffraction pattern for the sample with an 1° /S^o ratio of 3.0, however, shows a resolved peak at 2.4 nm. This peak indicates that there is a significant amount of lamellar character to the as synthesized material and that the observed X-ray diffraction peaks are actually the d₀₀₁ and d₀₀₂ peaks of a lamellar phase.

The powder X-ray diffraction patterns of the calcined silicas (Figure 5.6) reveals that the $l^{\circ}/S^{\circ} = 3.0$ sample decreases in intensity upon calcination, whereas there is with little or no change seen for the $l^{\circ}/S^{\circ} = 4.0$ and 5.0 samples.



Figure 5.5: Powder x-ray diffraction patterns of as made mesoporous silicas assembled from TEOS and TDA surfactant at varying I°/S° ratios and 45 °C for 20 h. The composition of the reaction solvent was initially 30% ethanol : 70% H₂O (v:v). Patterns are labeled as to their I°/S° ratio. Samples are offset 1000 (cps) for clarity.



Figure 5.6: Powder x-ray diffraction patterns of calcined mesoporous silicas assembled from TEOS and TDA surfactant at varying I°/S° ratios and 45 °C for 20 h. The composition of the reaction solvent was initially 30% ethanol : 70% H₂O (v:v). Patterns are labeled as to their I°/S° ratio. Samples are offset 1000 (cps) for clarity.

The decrease in XRD intensity for the 3.0 sample suggests that the as-made structure is primarily lamellar and unstable to surfactant removal. This decrease in intensity results from a decrease in the number of pore to pore scattering centers as would be expected upon collapse of the lamellar structure upon removal of the surfactant. The X-ray pattern does, however, indicate that some mesopores remain intact within the material. The X-ray diffraction pattern for the $1^{\circ}/S^{\circ} = 4.0$ and 5.0 show these samples to be completely stable to the removal of surfactant and that the pore structures are those of a disorder wormhole mesophase.

Table 5.1: Textural properties of calcined molecular sieves assembled with TDA and $l^{o}/S^{o} = 3.0-5.0$

Sample	V _T ^b (cc/g)	V _f ^c (cc/g)	V _{tx} ^d (cc/g)	V _{tx} /V _f	Pore Diameter HK (nm)	BET SA (m²/g)
3.0	1.13	0.61	0.52	0.85	4.8	894
4.0	1.00	0.86	0.14	0.16	4.8	813
5.0	1.00	0.90	0.10	0.11	4.3	877

^aAll samples were prepared at surfactant concentration of 0.23 M TDA and calcined at 600 °C. ^bV_T, total pore volume obtained from the volume of N₂ adsorbed at 0.99 P/Po. ^CV_f, framework pore volume obtained from the volume of N₂ adsorbed at 0.60 P/Po. ^dV_{tx}, textural pore volume obtained from the difference (V_T-V_f).

Table 5.1 summarizes the adsorption characteristics of calcined silicas with $1^{\circ}/S^{\circ}$ ratios of 3.0, 4.0 and 5.0. As with HMS silicas synthesized with

monoamine surfactants, increasing the ratios of $1^{\circ}/S^{\circ}$ results in increases in the surface curvatures at the organic-inorganic interface and a decrease in pore size. $1^{\circ}/S^{\circ}$ values of 3.0 result in a lamellar mesophase that partially collapses upon calcination. $1^{\circ}/S^{\circ}$ values of 4.0 and 5.0 have sufficient silica present to induce adequate curvature to the interface resulting in stable wormhole pore materials. $1^{\circ}/S^{\circ}$ values of 5.0 yield materials with smaller pores than 4.0, again indicating the increasing surface curvature induced with increasing $1^{\circ}/S^{\circ}$ ratio.

The TEM images of calcined silicas with I°/S° ratios of 4.0 and 5.0 are similar to those seen earlier (Figure 5.4A&C). Both contain disordered wormhole-like pore structures of uniform pore diameter within monolithic particles larger than 400-500 nm in diameter as expected for mesostructures assembled from a solvent composition of 30% ethanol : 70% H₂O (v:v). The sample prepared at an I°/S° value of 3.0 yields somewhat different images as seen by TEM. Figure 5.7A-D shows two distinct particle morphologies present in the I°/S° 3.0 sample. Figure 5.7A shows particles with a high degree of two dimensional or sheet-like character. These particles resemble crumbled balls of paper. Evident in the higher magnification image (Figure 5.7B) is the lamellar character comprising these sheet-like materials, most of which have likely collapsed upon calcination as indicated by X-ray diffraction. Figure 5.7C shows the low magnification image of a non-distinct particle with a uniform wormhole-like pore structure similar to those seen for I°/S° values of 4.0 and 5.0. Higher magnification images (Figure 5.7D) of these particles clearly show the wormhole like pore structure.

Figure 5.7: TEM images of a calcined mesoporous silicas assembled from TEOS and TDA surfactant at an $1^{\circ}/S^{\circ}$ ratio of 3.0 at 45 °C for 20 h. The composition of the reaction solvent was initially 30% ethanol : 70% H₂O (v:v). (A and B) show one of two predominant particle morphologies, these with a high degree of two dimensional or sheet-like character resembling crumbled balls of paper. Also evident at high magnification (B) is the lamellar character comprising these sheet-like materials. (C and D) are low and high magnification images, respectively, of the second predominant particle morphology that is based on a uniform wormhole-like framework structure similar to those seen for samples assembled at $1^{\circ}/S^{\circ}$ values of 4.0 and 5.0.





The neutral assembly mechanism in the synthesis of mesostructured silicas synthesized with polyamines surfactants is comparable to that of primary amines. H-bonding interactions between surfactant array and silica species in solution increase the surface curvature of the interface allowing for the formation of wormhole pore structure from unstable lamellar phases. Presence of insufficient silica ($1^{\circ}/S^{\circ} \leq 3$) is unable to increase the surface curvature adequately to form non-lamellar structures. At $1^{\circ}/S^{\circ}$ values of 3.0, X-ray diffraction and TEM analysis lend evidence that lamellar structures form, though also evident to a limited degree are stable, wormhole-like pore structures. Increasing the $1^{\circ}/S^{\circ}$ ratio above 3 under mild conditions continually increases the surface curvature at the interface resulting in pores of diminishing diameter analogous to results for primary amines.

Tallow diamine surfactants behave similar to monoamine surfactant in the synthesis of HMS like molecular sieves at mild synthesis temperatures. Both the pore forming and particle forming interactions are analogous to those defined in the synthesis of HMS silicas using long alky chain primary amine surfactants. ^{5,13} Of significant interest is the behavior of these surfactants in the synthesis of silicas similar to MSU-G materials using reagent conditions specific to MSU-G synthesis at mild and hydrothermal assembly temperatures.

5.4.3. Synthesis of MSU-G Like Silicas with TDA at Increasing Assembly Temperatures

The silicas described in the following section were assembled at $1^{\circ}/S^{\circ}$ molar ratios typical of those used in the original synthesis of MSU-G silicas. However, a tallow diamine (TDA, $C_xH_{2x+1}NH(CH_2)_3NH_2$, x=14-18) surfactant was used in place of a pure Gemini $C_{12}NH(CH_2)_2NH_2$ surfactant at increasing synthesis temperatures.⁹ In these experiments, the $1^{\circ}/S^{\circ}$ ratio was 4.18, the initial solvent composition was 15% ethanol (v:v) and the assembly temperatures was 20-100 °C at a reaction time of 48 h.

Powder X-ray diffraction patterns (not shown) of the as-made and calcined samples synthesized at 20 °C and 45 °C are similar to patterns in Figure 5.3 indicating the presence of disordered uniform wormhole-like mesopores. Figure 5.8 is the N₂ adsorption-desorption isotherm for the calcined samples synthesized at 20 °C and 45 °C. Both samples show uptake of N₂ due to capillary condensation within the framework confined mesopores between 0.4-0.5 P/Po signifying uniform pores of ~4.4 nm in diameter (Figure 5.8 (inset)). The samples also show significant adsorption at high relative pressures indicating textural porosity. The 45 °C sample has a larger textural pore volume and also larger textural pores. The BJH model indicates the pore sizes of the textural pores are 13.5 and 23.7 nm for the 20 °C and 45 °C samples, respectively.

The particles appear to have a sponge-like morphology in the TEM images similar to images seen earlier (Figure 5.4A) for silicas with high textural porosity. Also evident in the images are the wormhole framework pores of



Figure 5.8: N₂ adsorption-desorption isotherms for calcined mesoporous MSU-G like silicas assembled from TEOS and TDA surfactant at 20 °C and 45 °C for 48 h. The composition of the reaction solvent was initially 15% ethanol : 85% H₂O (v:v). Both sample have high textural mesoporosity as indicated by the hysteresis loop at partial pressures >0.80. The isotherms are offset vertically by 100 cm³/g, STP for clarity. (Inset) Horvath and Kawazoe framework pore size distribution plot.

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uniform diameter similar to HMS silicas. Thus, assembly temperatures of 20 °C and 45 °C fail to provide a vesicular MSU-G like phase.

The properties of these silicas synthesized at mild temperatures are very similar to those of HMS silicas. They are comparable in their disordered pores structure, the uniform pore sizes, high framework and textural pore volumes present along with their TEM images. Therefore, the defining characteristics between HMS and MSU-G silicas are their synthesis temperature and the unique vesicle morphology of MSU-G silicas.

MSU-G like silicas, however, can be synthesized at 100 °C with TDA surfactants. They appear similar, but not identical to MSU-G silicas synthesized from pure Gemini surfactants⁹, as judged from the adsorption isotherms and their TEM images. The wide-angle X-ray diffraction patterns (not shown) reveal a very broad peak at 7.5 nm. In contrast, pure Gemini MSU-G silicas show extremely sharp well-resolved d_{001} peaks.

The N₂ adsorption isotherms (Figure 5.9) show highly texturally porous materials. The sample is plotted on two scales to highlight both the textural porosity (large scale) and the framework porosity (small scale). Total pore volume for each material approaches that of 2.48 mL/g with approximately 2.09 mL/g as textural pore volume and 0.39 mL/g of framework pore volume. The framework pore volume is similar to that seen in MSU-G materials. The framework pores are larger than seen in MSU-G due to the longer alkyl chain on the surfactant molecule. The capillary condensation step seen in the isotherm is less sharp than MSU-G and may be a result of the range of the alkyl chain

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Figure 5.9: N₂ adsorption-desorption isotherms for a calcined mesoporous MSU-G like silica assembled from TEOS and TDA surfactant at 100 °C for 48 h. The composition of the reaction solvent was initially 15% ethanol : 85% H₂O (v:v). The isotherms are plotted on two scales for clarity. A. Large scale highlighting the high textural porosity and, B. Highlighting the framework porosity of the material (Inset) Horvath and Kawazoe framework pore size distribution plot.

lengths present. Horvath-Kawazoe modeling of the adsorption branch of the isotherm indicates framework pore sizes of approximately 5.4 nm in diameter. MSU-G materials usually possess high textural porosity, yet the extreme volume exhibited by this sample is unique. BJH modeling of the adsorption branch shows a pore sizes similar to samples synthesized at mild temperatures. Though the framework pore size distribution is relatively narrow, the textural pore size distribution is much broader and centered at 46.2 nm.

TEM images of the high temperature samples (Figure 5.10A&B) show sponge-like particles that possess framework porosity. The sponge-like silicas are made of large aggregates of small grains intergrown with a significant amount of void space within the aggregate. There does appear to be significant evidence for vesicle or vesicle-like particles similar to MSU-G, though these particles are much smaller than normal MSU-G. Overall, the materials resemble aerogels in their textural porosity, yet they also posess substantial framework porosity.

As in MSU-G silicas, synthesis at 100 °C results in high cross-linking in the amorphous silica wall. $Q^4/(Q^3+Q^2)$ ratios for the as-made material is 6, comparable to typical MSU-G silicas. Again, the presence of multiple amine functional units at the head group of the surfactant results in sufficient H-bonding interactions at the interface between surfactant micelles and silica species to form mesostructured silicas, even under hydrothermal conditions. More over, the hydrothermal synthesis conditions drive the silica condensation to higher levels than synthesis at lower temperatures. Therefore, the $Q^4/(Q^3+Q^2)$ values are

Figure 5.10: TEM images of a calcined mesoporous MSU-G like silicas assembled from TEOS and TDA surfactant at 100 °C for 48 h. The composition of the reaction solvent was initially 15% ethanol : 85% H₂O (v:v). A. Low magnification image showing very small particle, highly aggregated silicas with a high degree of textural porosity. B. High magnification image showing framework pores and psuedo-vesicle particle morphology.



v 0 te h bo Su bo as dis Su Cur Cha deq silic Para the

significantly higher than can be achieved at mild temperatures through neutral assembly or through hydrothermal synthesis conditions with electrostatic assembly where charge balancing will limit the total degree of condensation.

5.5. Conclusion

Commercially available diamine surfactants of the type $RNH(CH_2)_3NH_2$ where R is a straight alkyl chain with 14-18 carbon atoms ($C_{14-18}H_{29-37}$), are not only suitable for the synthesis of silicas similar to HMS materials at mild temperature but also for the synthesis of vesicular MSU-G like silicas under hydrothermal synthesis conditions.

The driving force in the assembly of these mesostructured silicas is the Hbonding interaction at the interface between silica species and polyamine surfactant micelles. The surface curvature of the interface and the degree of Hbonding can be controlled through either variation of the I⁰/S^o ratio or the assembly temperatures, resulting in the formation of mesostructures with distinctly different surface curvatures. Increasing H-bonding interactions at the surfactant head group through increased I⁰/S^o ratios result in increasing curvatures of the micelle. Increasing surface curvatures are manifested in a change in mesophase formation from lamellar to wormhole and also in pores of decreasing diameter. These properties are analogous to those seen in HMS silicas synthesized with dodecylamine (DDA) surfactants.

The control of the particle sizes of these mesostructured silicas, again parallels properties identified in HMS silicas synthesized with DDA. Decreasing the polarity of the solvent synthesis mixture with the addition of increasing

volumes of a low polar solvent such as ethanol into highly polar H₂O results in complete dissolution of the diamine (TDA) surfactant forming a homogeneous solution from which large monolithic mesostructured materials precipitate. The TDA surfactant is not completely soluble in highly polar, high H₂O solvent systems and result in colloidal aggregates of surfactant in solution. Sponge-like mesostructured silicas with high textural porosity are precipitated from heterogeneous solution.

Lastly, the presence of multiple amine functional units at the head group of the surfactant molecule allows for increasing synthesis temperatures in the assembly of stable mesostructured silicas. Elevated temperatures decrease the H-bonding between amine surfactants and the silicate wall, resulting in the formation of an interface with less surface curvature tending toward lamellar. Yet even under hydrothermal conditions, adequate H-bonding occurs between the TDA head group and the silica wall to form a mesostructure with sufficient curvature to be stable. The decrease in curvature of the mesophase does appear in the lamellar, or vesicular type silicas formed. These silicas have framework properties similar to MSU-G materials, especially in the high degree of their silica crosslinking. In addition, these silicas have intra-particle textural pore volumes even larger than seen in typical HMS or MSU-G synthesis. The framework mesopore volume, high textural pore volume, and the high silica crosslinking should make these molecular sieves highly desirable as catalysts for condensed phase reactions requiring improved access and stability.

5.6. References

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⁸ Powder X-ray diffraction patterns of these α, ω -diamine surfactants in aqueous solutions indicate formation of lamellar mesophases. Though vesicular phases also yield lamellar X-ray patterns, there is no additional evidence to support the formation of vesicular surfactant phases in the absence of TEOS.

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¹³ Chapter 2

Chapter 6

Neutral Assembly of Mesostructured Silicas from Alkylamine Surfactants and Water Soluble Silicates

6.1. Abstract

Stable mesoporous molecular sieve silicas with 2.7 and 4.8 nm pore diameters, high framework pore volumes (up to 0.92 cc/g) and high textural pore volumes (0.40 cc/g) are synthesized from neutral alkylamine surfactants and water soluble silicate sources under slightly alkaline (pH=8-9) conditions. Dodecylamine surfactants or polyamine surfactants with head groups of two or three nitrogen centers with propylene spacers yield mesostructures with disordered wormhole framework topologies, whereas polyamine surfactants with larger head goups (four propylamine repeat units) yield hexagonal frameworks with a small intergrown domain size and relatively high intra-particle textural porosity. Polyamine surfactants allow use of mineral acids (HCI) to efficiently neutralize the base content of the silicate source. Sodium silicate solutions with a range of SiO₂/Na₂O ratios (2.1 - 3.3) are suitable precursors to these mesostructured silicas.

6.2. Introduction

A vast amount of attention has been given to supramolecular assembly of mesoporous (pore diameters of 2-50 nm) oxides with uniform pore sizes since Mobil researchers first disclosed in 1992¹ the synthesis of a new family of mesoporous aluminosilicate molecular sieves designated as M41S. The synthesis of these novel materials uses assemblies of guaternary ammonium surfactant molecules, or micelles, as structure directors in the assembly of stable molecular sieve silicas whose pore structures mimic liquid crystalline phases common in aqueous surfactant solutions.² Upon the removal of the organic component, these high surface area molecular sieves contain accessible pore volumes with uniform pore diameters. To date, the synthesis of mesoporous molecular sieves can be classified into several general pathways according to their organic-inorganic interfacial interactions. Electrostatic charge matching^{1,3,4}, H-bonding^{5,6,7,8}, and dative bonding interactions^{9,10}, at the organic micelle-inorganic interface have all been successfully utilized in the formation of mesostructured inorganic oxides. Until recently, however, the assembly of mesostructured materials relied on the use of either a costly organic reagent, such as the quaternary ammonium salts used in electrostatic pathways, on expensive molecular inorganic precursors. such as the or tetraethylorthosilicate (TEOS) used in H-bonding and dative bonding pathways.

Guth and coworkers first reported the synthesis of mesostructured silica by precipitation from a solution combining an inexpensive polyethylene oxide

(PEO) based surfactant, Triton-X 100, with low cost sodium silicate^{11,12}. The disordered wormhole pore structure, however, was not stable to complete surfactant removal at calcinations temperatures as high as 600 °C. Pinnavaia recently reported the first synthesis of stable mesostructured silicas using nonionic polyethylene oxide (PEO) surfactants and sodium silicate solutions as the inorganic precursors.¹³ Their methodology requires neutralization of the hydroxide content of the silicate with an organic acid while in the presence of the structure directing surfactant assemblies. This allows for the assembly of the structure at near neutral pH conditions and results in an oxidic framework whose pore topology can be either a disordered wormhole¹³ framework analogous to conventional N°I° assembled MSU-X⁶ mesostructures and designated MSU-X'. ordered crystalline phases similar to materials assembled through electrostatic pathways and designated MSU-H¹⁴, or large pore foam-like materials designated MSU-F¹⁴. The pore topology is dependent on the surfactant, auxiliary reagents and temperature used in the synthesis.

Mesoporous HMS silicas with a small, intergrown domains and spongelike particle textures are synthesized with long alkyl chain amines as the structure directing surfactant. These highly textured materials have found promising applications as heterogeneous catalysts^{15,16,17} and as supports for the immobilization of reagents¹⁸ due to the improved framework access associated with the sponge-like particle texture. Presently, silicas with these textural

properties have only been synthesized from costly molecular silica precursors such as TEOS. Replacing molecular silica precursors with sodium silicate should make highly textured mesostructures even more attractive for a variety of applications.

The present work examines the use of neutral amine surfactants with differing head group sizes as structure directing surfactants for the assembly of mesostructured silica from low cost, water-soluble silica sources. The combined use of inexpensive primary amine or commercially available tallow polyamine surfactants (Figure 6.1) along with water-soluble silicate sources offers an efficient, low cost route to mesostructured silicas, which we have designated MSU-SA for silicate amine assembly.



Figure 6.1: Tallow amine surfactants received from Tomah³ Products, Inc. x = 0 to 3. R is a straight alkyl chain with 14-18 carbon atoms (C₁₄₋₁₈H₂₉₋₃₇). X=0, tallow amine (TA); X=1, tallow diamine (TDA), X=2, Tallow Triamine (TTA), X=3, Tallow Tetraamine (TTeA).

Sodium silicate solutions with four different SiO₂/Na₂O ratios ranging from 2.1 - 3.3 were investigated as inorganic precursors in this unique method of mesostructure assembly. These silicate solutions provide silicate sources of

different initial silicate ion size²⁵ and distribution for neutralization and subsequent interaction with the amine surfactant in the mesostructure assembly. The H-bonding interaction between the silicate and the polyamine surfactant is essential in the assembly of MSU-SA silicas. The initial size of this silicate ion may directly affect H-bonding at the silica-micelle interface and, subsequently, the interfacial surface curvature and the resulting physiochemical properties of the mesostructure. Additionally, H-bonding at an interface with increased surface curvature may afford hexagonal or cubic structures analogous to those formed through electrostatic assembly procedures.^{3,4,19}

The formation of the reactive silica species results from neutralizing the hydroxide content in the silicate solution with equal molar equivalents of acid. With this general method, silicate solutions with a wide range of hydroxide concentrations can efficiently be used as inorganic precursors to the neutral assembly of MSU-SA materials.

6.3. Experimental

6.3.1. Reagents

The amines used in this study are labeled DDA for dodecylamine along with TA, TDA, TTA, and TTeA (Figure 1) to denote the Tallow Amine, Tallow Diamine, Tallow Triamine, and Tallow Tetraamine, respectively. DDA (Aldrich) is used as received. The tallow amines (Tomah³ Products Inc) are used without

further purification though they are impure as to their alkyl length and polyamine number.

The sodium silicate solutions were provided by PQ Corporation and Aldrich Chemicals. The silicate solutions were used as received. These solutions had SiO_2 : Na₂O molar values of ~2.1 to 3.3.

6.3.2. Synthesis of MSU-SA Silicas from DDA and Sodium Silicate

Sodium silicate (2.8 g, 27% SiO₂, 14% NaOH; 13 mmole SiO₂, 10 mmol NaOH) is added to 5.0 mL of H₂O with stirring. DDA (0.58 g, 3.2 mmol) is dissolved in either 2.5 mL or 10 mL of 1.0 M acetic acid (CH₃CO₂H) to yield H⁺/OH⁻ ratios of 0.25 and 1.0, respectively. H₂O (35 mL) is added to the surfactant to yield a clear solution at room temperature. The silicate solution is added drop-wise to the acidified amine solution with vigorous stirring. The reaction vessel containing the white gel is sealed and shaken at 220 rpm in a water bath at 45 °C for 20 hours. The product is filtered and washed with copious amounts of H₂O and allowed to air dry at room temperature for 24 hours. The reaction stoichiometries are as follows:

1 SiO₂ : 0.25 DDA : 0.78 NaOH : 0.195 or 0.78 CH₃CO₂H : 220 H₂O

6.3.3. Synthesis of MSU-SA Silicas from Polyamine Surfactants and Sodium Silicate

Polyamine surfactants (~2.52 mmole, Table 1) are dissolved in 5 mL of EtOH. One equivalent of 1.0 M HCl (Table 1) is added to the surfactant solution to neutralize the sodium hydroxide content of the sodium silicate used in each

reaction mixture. H_2O (35 mL) is added to the surfactant to yield a clear solution at room temperature. Sodium silicate (12.6 mmole SiO₂, Table 1) is added to 5 mL of H_2O . The silicate solution is added drop-wise to the acidified surfactant solution with vigorous stirring. The reaction vessel containing the white gel is sealed and shaken at 220 rpm in a water bath at 45 °C for 20 hours. The product is filtered and washed with copious amounts of H_2O and allowed to air dry at room temperature for 24 hours.

	S°	l°			H⁺
Surfactant ^a	Mass Surfactant (g) (~2.52 mmole)	Brand Silicate	SiO ₂ /Na ₂ O ^d	12.6 mmol ^e SiO ₂ (g)	HCI ^f (mmol)
ТА	0.61	27%SiO ₂ ^b	2.57	2.80	10.0
TDA	0.75	D™ ^c	2.06	2.56	12.2
TTA	0.89	RU™ ^c	2.51	2.24	10.0
TTeA	1.04	K™ c	3.02	2.35	8.3
		N™ ^c	3.29	2.66	7.7

Table 6.1: Quantities of reagents used in MSU-SA synthesis.

a. Tallow amines are labeled TA, TDA, TTA, and TTeA to denote the Tallow Amine, Tallow Diamine, Tallow Triamine, and Tallow Tetraamine respectively. b. 27% SiO₂, 14% NaOH silicate from Aldrich. c. P.Q. Corporation silicates by brand. d. Corresponding SiO₂/Na₂O ratios of silicate solutions. e. Mass of each silicate used to give 12.6 mmol of SiO₂. f. mmole of 1.0 M HCl added to neutralize Na₂O.
Surfactant is removed from all samples by calcination in air at 600 °C for 4 hours because there is no desire to recover the small amounts of surfactant used. However, complete removal of the neutral surfactant can be accomplished via a simple solvent extraction in hot EtOH.

6.3.4. Physical Measurements

Wide-angle powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Rotaflex Diffractometer with Cu K_{α} radiation (λ = 0.154 nm). Counts were accumulated every 0.02 degrees (20) at a scan speed of 1 degree (20)/min.

 N_2 adsorption-desorption isotherms were obtained at -196 °C on a Micromeritics ASAP 2010 Sorptometer using static adsorption procedures. Samples were outgassed at 150 °C and 10⁻⁶ Torr for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear part of the BET plot according to IUPAC²⁰ recommendations. The Horvath and Kawazoe model estimated pore size distributions from the adsorption branch of the isotherm.²¹

TEM images were obtained on a JEOL 100CX microscope with a CeB₆ filament and an accelerating voltage of 120 KV, a beam diameter of approximately 5 μ m and an objective lens aperture of 20 μ m. Sample grids were prepared via sonication of powdered sample in EtOH for 20 min and evaporating 1 drop of the suspension onto a carbon coated, holey film supported on a 3 mm, 300 mesh copper grid.

²⁹Si MAS NMR spectrums were recorded on a Varian 400 VRX solid-state NMR Spectrometer at 79.5 MHz under single-pulse mode with a 7-mm Zirconia

rotor, a spinning frequency of 4 kHz, and a pulse delay of 800 seconds. The chemical shifts where referenced to TMS (tetramethylsilane).

6.4. Results and Discussion

6.4.1. Synthesis of MSU-SA Silicas with DDA and Sodium Silicate

The assembly of mesostructured HMS⁵ and MSU-X⁶ silicas utilizes Hbonding between molecular silica precursors and the organic surfactant phase. In the case of HMS, the H-bonding interaction between the silicic acid derivative derived from TEOS hydrolysis and the head groups of the amine surfactant result in the formation of a wormhole pore structure from a surfactant solution containing an initially lamellar liquid crystal phase²². The transformation from lamellar surfactant to wormhole mesostructures occurs due to a lowering of the surfactant packing parameter, g, brought about by an increase in the effective head group area, a_o, of the surfactant upon H-bonding to the silica species resulting in an interface with increased surface curvature and wormhole like pore structures.²³ For H-bonding to occur between the water-soluble silica species and the amine head groups, the pH of the system must be sufficiently low (<10) as to diminish the negative charge of silicate, thereby increasing the number of silanols while reducing the number of charge compensating ions present at the interface. To explore this hypothesis, the primary amine surfactant solution was acidified to neutralize 25% and 100% of the hydroxide ions present in the sodium silicate solution.



Figure 6.2: XRD patterns of as-made and calcined MSU- SA silica molecular sieves formed from sodium silicate and dodecylamine (DDA) at 45 $^{\circ}$ C and the indicated ratios of H⁺/OH⁻. (----) as-made samples, (-----) calcined samples. Patterns are offset 1000 (cps) for clarity.

Figure 6.2 shows the powder X-ray diffraction patterns of the as-made and calcined MSU-SA silicas formed at H^+/OH^- ratios of 0.25 and 1.00. The product formed from the low acid content reaction mixture (ie. the high pH reaction mixture) shows X-ray patterns for the as-made material indicating the formation of a lamellar phase with three indexible (*001*) peaks and a basal spacing of 4.4 nm. This lamellar phase, however, is unstable to the removal of the surfactant and collapsed upon calcination as is seen in the X-ray diffraction of the calcined product.

At H⁺/OH⁻ ratio of 1.00, the pH of the reaction mixture has decreased to a approximately 8.0-8.5. With the hydroxide content of the silicate neutralized, the residual mildly alkaline pH results from the presence of basic amines in solution. For the mesostructure formed at this ratio, however, the X-ray diffraction pattern does not indicate a lamellar pattern. Instead, the pattern has only a primary peak at 3.5 nm and a significant shoulder at higher angle 20. This pattern is similar to HMS silicas synthesized with TEOS as the silica source and is indicative of a disordered wormhole pore structure.¹⁵ The primary peak position is related to the pore-pore correlation distance in the disordered sample. Upon calcination of the sample, the powder X-ray diffraction pattern exhibits an increase in the intensity of the primary peak in comparison to the as made sample. The increase in intensity confirms that the integrity of the silica framework is uncompromised upon calcination.



Figure 6.3: N₂ adsorption-desorption isotherms for the calcined MSU-SA silica molecular sieves formed with sodium silicate and DDA at pH= 8.0-8.5, 45 °C and equal molar amounts of acetic acid and OH⁻. (Inset) Horvath-Kawazoe pore size distribution plot modeled from the adsorption branch of the N₂ isotherm.

Figure 6.4: TEM images of a calcined MSU-SA silicas prepared from sodium silicate and DDA at 45 °C and a 1.0 : 1.0 ratio of acetic acid and NaOH. A. Low magnification image showing the intergrown small domains leading to a sponge-like particle texture, B. High magnification image of the wormhole framework structure along with the lamellar remnants of the initial surfactant phase.

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Figure 6.4:



Figure 6.3 shows the N₂ adsorption-desorption isotherm for the calcined MSU-SA sample assembled from sodium silicate and DDA containing equal parts acid to hydroxide. The sharp uptake of N₂ between P/Po of 0.2-0.3 indicates capillary condensation of N₂ within the framework-confined mesopores. The Horvath and Kawazoe plot (Figure 6.3, inset) indicates a very uniform pore diameter centered at 2.7 nm. Also evident is the significant volume of N₂ adsorbed at high partial pressures (>0.90). This latter trait denotes capillary condensation of N₂ between grains of a sponge-like silica and is a signature of intra-particle, or textural porosity. The BET surface area for this mesostructure is 952 m²/g with a framework pore volume of 0.55 cc/g.

The origin of the high textural porosity of MSU-SA silicas synthesized with DDA as deduced from the N₂ adsorption isotherm is clearly evident in the TEM images (Figure 6.4) in which the small grains, on the order of a few hundred nm, intergrow into much larger sponge-like particles with significant mesoporous void space within the interior of the particle (Figure 6.4A). Figure 6.4B shows that the wormhole pore structure propagates throughout the small grains. There are, however, remnants of a lamellar mesophase still evident in the material resulting from the initial surfactant array.²² The existence of these lamellar remnants combined with X-ray diffraction of the various samples yields valuable insight into the assembly mechanism of these MSU-SA silicas.

As the X-ray and N_2 adsorption data show, the addition of one equivalent of acid to neutralize the hydroxide content of the silicate source results in the

highest quality mesostructured silicas. Under these conditions the pH of the reaction mixture is mildly alkaline (pH values \geq 8.0 - 8.5) and the resulting reactive silica species is able to H-bond to the surfactant array to form a wormhole framework pore structure with stable silica walls. The interaction of the silica at the micelle interface results in the formation of a tubular, highly curved, micelle from the lamellar organic array. At acid additions less than one equivalent per equivalent of NaOH, the silica is formed at a higher pH (> 12) and a significant negative charge on the silica prevents H-bonding from occurring. Counter ions are needed to compensate the negative charge on the silicate wall, thus limiting H-bonding between the silica and the lamellar organic array. This results in a lamellar mesostructure and the collapse of the structure upon removal of surfactant.

Under the current assembly conditions, the choice of the neutralizing acid is significant. Substituting the acetic acid with equal parts of a mineral acid such as HCI to neutralize the hydroxide content of the silica results in the formation of lamellar mesostructures with powder X-ray diffraction patterns similar to those seen in Figure 6.2 for the 0.25 as-made silica. These silicas are not stable to the removal of the surfactant and collapse upon calcination. Thus acetate anions somehow participate in the assembly process. In the course of the formation of the wormhole framework structures from lamellar surfactant mesophases and sodium silicate solutions, the surface curvature of the primary amine surfactant micelle is not solely dependent on the amount of H-bonding silica at the micelle interface. In fact, sufficient curvature to the organic phase is accomplished only

through the use of a polar organic reagent (ie. carboxylate anion) to modify the surface of the primary amine micelle. The polar acetate ions resulting from the acetic acid neutralization of the silicate base apparently occupy positions at the interface of the organic micelle, thus increasing the overall effective head group area for the surfactant. This results in the increased surface curvature of the micelle which forms the wormhole mesostructure. Mineral acids, on the other hand, do not modify the silica - surfactant interface and an unstable lamellar mesophase is formed.

6.4.2. Synthesis of MSU-SA Silicas from Polyamine Surfactants and Sodium Silicate

In an effort to avoid the use of organic acids in the synthesis of stable silicas from water-soluble silicates, we employed the use of amine surfactants with head groups ranging in size from one to four amines with propylene spacers between nitrogen atoms (Figure 6.1). Increasing the effective head group area, a_o, with increasing polyamine number will decrease the value of the surfactant packing parameter, g. The decrease in surfactant packing parameter should result in an increased surface curvature of the organic phase upon interaction with the silicate and the formation of stable mesoporous structures. The direct increase in the head group size of the surfactant should, therefore, allow for the substitution of acetic or other organic acids, with inexpensive and readily available mineral acids, in this case, HCI.

Figure 6.5 is an X-ray Powder diffraction pattern of the calcined MSU-SA silicas formed using Tallow Amine (TA), Tallow Diamine (TDA), Tallow Triamine

(TTA), and Tallow Tetraamine (TTeA), respectively, as structure directors. The TA sample does not show any resolvable correlation peak, but only broad scattering intensity at low angle (20) indicating that unstable mesostructured silica was formed. In fact, the as-made sample displayed an X-ray diffraction pattern (not shown) indicating the formation of a lamellar mesophase similar to the as-made mesophase obtained with DDA. Each of the TDA, TTA, and TTeA samples, however, exhibit a well-resolved correlation peak. Both the TDA and TTA patterns show an unresolved shoulder at 3-4 degrees (20). X-ray diffraction patterns of this type are typical for porous materials with disordered wormholelike pore structures^{5,15}. The diffraction peak arises due to the scattering from the uniform correlation distance between pores of comparable diameter and spacing. The similarity of each pattern indicates an analogous pore structure for both of these calcined samples. The pattern for the TTeA sample does show some likeness to TDA and TTA, however, the scattering intensity at higher angle 20 is better resolved than the shoulders of the previous patterns. The X-ray diffraction pattern of the TTeA sample resembles that of mesostructured hexagonal KIT-1 mesophase²⁴. This type of pattern indicates either a disordered hexagonal pore structure, or a small domain hexagonal pore structure.

The calcined TA sample shows only moderate framework mesoporosity by N_2 adsorption as seen in Figure 6.6. The sample does exhibit significant textural porosity and a desorption hysteresis similar to those seen in clay systems, indicating the possible presence of plate-like particles. This type of particle morphology is common in lamellar mesostructured materials and is expected in



Figure 6.5: Powder x-ray diffraction patterns of calcined MSU-SA silicas assembled using tallow polyamine surfactants TA, TDA, TTA, and TTeA to denote the Tallow Amine, Tallow Diamine, Tallow Triamine, and Tallow Tetraamine respectively. Each sample was prepared at 45 °C from sodium silicate containing 27% SiO₂ from Aldrich. HCI was used to neutralize the NaOH content of the sodium silicate. Samples are offset 5000 (cps) for clarity.



Figure 6.6: N₂ adsorption-desorption isotherms for calcined MSU-SA silicas assembled using tallow polyamine surfactants TA, TDA, TTA, and TTeA to denote the Tallow Amine, Tallow Diamine, Tallow Triamine, and Tallow Tetraamine respectively. Each sample was prepared at 45 °C from sodium silicate containing 27% SiO₂ from Aldrich. HCI was used to neutralize the NaOH content of the sodium silicate. The isotherms are offset vertically by 100 cm³/g, STP for clarity.

this case due to the formation of an unstable lamellar mesophase. Each of the polyamine samples does show N_2 adsorption characteristic of uniform diameter framework mesopores, along with adsorption at high partial pressures indicating intra-particle textural pores (Figure 6.6). The polyamine samples each have comparable pore volumes, surface areas and pore diameters (c.f. Table 6.2).

Sample	D- spacing (nm)	BET SA (m²/g)	V⊤ ^b (mL/g)	V _f ^c (mL/g)	V _{tx} ^d (mL/g)	Pore Diameter (nm)
<u>S°</u>						
ТА	N/A	580	1.38	0.44	0.94	4.7
TDA	4.9	915	1.21	0.90	0.31	4.8
TTA	4.9	863	1.19	0.79	0.40	4.7
TTeA	4.7	932	1.23	0.86	0.37	4.7

Table 6.2: Physiochemical properties of calcined MSU-SA molecular sieves^a.

^aAll MSU-SA materials were prepared at 45 °C. ^bV_T, Total pore volume obtained from the volume of N₂ adsorbed at 0.99 P/Po. ^cV_f, Framework pore volume obtained from the volume of N₂ adsorbed at 0.60 P/Po. ^dV_{tx}, Textural pore volume obtained from the difference (V_t - V_f).

Figure 6.7 shows a TEM image of the calcined sample assembled from TDA. Evident in the micrograph is the existence of uniform framework pores with a wormhole pore structure (Figure 6.7B). These framework pores exist in small grain (\leq 300 nm), highly intergrown sponge-like particles similar to HMS silicas¹⁵(Figure 6.7A). Textural porosity arises from voids between grains created upon intergrowth of these small wormhole domains and lamellar stacking

Figure 6.7: TEM images of calcined MSU-SA silicas assembled using tallow polyamine surfactant, TDA (Tallow Diamine). Each sample was prepared at 45 °C from sodium silicate containing 27% SiO₂ from Aldrich. HCI was used to neutralize the NaOH content of the sodium silicate. A. Low magnification micrograph, B. High magnification micrograph. Wormhole pore structures were observed throughout for both TDA and TTA samples.





Figure 6.8: TEM images of calcined MSU-SA silicas assembled using tallow polyamine surfactants TTeA (Tallow Tetraamine). Each sample was prepared at 45 °C from sodium silicate containing 27% SiO₂ from Aldrich. HCl was used to neutralize the NaOH content of the sodium silicate. A. Low magnification micrograph, B. High magnification micrograph. Hexagonally ordered pore structure observable within small (\leq 50 nm) domains throughout sample. (Inset) Selected area electron diffraction pattern (SAED) of cluster pictured in Figure 6.8A.





of wormhole arrays into a sponge-like particle and is independent of the framework porosity. The TTA sample shows similar topology.

The TTeA sample, however, shows a different pore structure. This sample has a local hexagonal symmetry of pores with small domain sizes (Figure 6.8). The grain size remains on the order of ~300 nm and these grains intergrow into large sponge-like clusters (Figure 6.8A) analogous to the textured particles of other polyamine samples. A higher magnification image of the sample (Figure 6.8B) better illustrates the local hexagonal order and small domain size of the material. Evident in an electron diffraction pattern of the cluster seen in Figure 6.8A (Figure 6.8B, inset) are multiple diffraction spots arising from scattering from a number of small hexagonally ordered domains. Mesopores oriented parallel to the grid and orthogonal to the viewing axis contribute to the two intense spots of the electron diffraction pattern.

Table 6.2 summarizes the physiochemical properties of the calcined mesoporous MSU-SA silicas synthesized with tallow amine surfactants. Each of the polyamine samples exhibits similar properties corresponding to highly porous and stable structured silicas. Conversely, the primary amine sample shows only low framework pore volume. In the presence of HCI, the primary amine, TA, micelle does not have sufficient surface curvature to form stable mesostructured silica and lamellar structures form. Increasing the effective head group area of the amine surfactant by using polyamines decreases the packing parameter and increases the surface curvature of the surfactant assembly. The micelle modifying acetate ions resulting from the acetic acid neutralization of the silicate

base are no longer needed for a similar increase in surface curvature of the micelle. The large head group of the polyamines allows for larger effective head group area, a_o, and subsequently, a decreased surfactant packing parameter, g, and increased micelle surface curvature. As the effective head group area increases with the use of TDA and TTA surfactants, wormhole micelles form in the presence of silicate and neutralizing acid resulting in a stable wormhole pore structure. An even larger head group such as on TTeA increases the surface curvature to the point that a hexagonal pore structure is formed. The increased surface curvature of the TTeA micelle results in a more rigid micelle that is able to pack into an ordered hexagonal array. The flexible wormhole micelles of the smaller head group surfactants TDA and TTA are less likely to pack into ordered arrays under these conditions. Regardless of the pore topology, the particle morphology retains its small, intergrown grains and the consequential high, intraparticle textural porosity.

Of note is the change in pore topology from a lamellar to wormhole and finally to a hexagonal structure by simply increasing the head group size with an increasing polyamine repeat of the structure directing surfactant. We believe this change in mesophase is analogous to the lamellar to cubic (la3d) to hexagonal trend seen in electrostatic assembly¹⁹ with increasing surface curvature. The difficulty in analyzing the wormhole pore structure seen in the current structures along with those of HMS⁵ and MSU-X⁶ silicas lies in its disorder. These results provide further evidence that the wormhole structure does contain significant 3-dimensional character similar to cubic morphologies.

6.4.3. Synthesis of MSU-SA Silicas from Polyamine Surfactants and Sodium Silicate Solutions of Differing SiO₂/Na₂O Ratios

Next we investigate the ability to use silicates with varying SiO₂/Na₂O ratios as precursors to the formation of mesoporous MSU-SA silicas. Figure 6.9 shows the X-ray powder diffraction patterns of calcined MSU-SA materials synthesized with silicate sources of different SiO₂/Na₂O mole ratios in the presence of a Tallow-Diamine surfactant (TDA). SiO₂ / Na₂O molar ratios are 2.07 (Brand D, P.Q.Corp.), 2.51 (RU), 3.02 (K); and 3.29 (N). Changing the SiO₂/Na₂O ratio of the silicate source has little to no effect on the position and intensity of the primary correlation peak. Each of the samples exhibits a correlation peak at low angle (20) accompanied by an intense shoulder at higher angles. Again, X-ray diffraction patterns of this type are typical for porous materials with disordered wormhole-like pore structures^{5,15}. The diffraction peak arising due to scattering from the uniform correlation distance between pores of comparable diameter and spacing. The similarity of each pattern indicates an analogous pore structure for each of the calcined samples independent of solution ion content or SiO_2/Na_2O ratio in the synthesis gel.

 N_2 adsorption-desorption isotherms (c.f. Figure 6.10) for the calcined samples with different SiO₂/Na₂O ratios show type IV isotherms for each. N_2 uptake corresponding to capillary condensation with in the framework confined mesopores occurs at approximately the same partial pressure for each sample indicating equivalent framework pore diameters (~4.8 nm) as is evident from the Horvath and Kawazoe pore size distribution plot (Figure 6.10, inset). Also



Figure 6.9: Powder x-ray diffraction patterns of calcined MSU-SA silicas assembled using Tallow Diamine (TDA) surfactant with P.Q. Corporation silicates; Brand D ($2.06 \text{ SiO}_2/\text{Na}_2\text{O}$), RU (2.51), K (3.02) and N (3.29). Each sample was prepared at 45 °C. HCI was used to neutralize the NaOH content of the sodium silicate. Samples are offset 2000 (cps) for clarity.



Figure 6.10: N₂ adsorption-desorption isotherms for calcined MSU-SA silicas assembled using Tallow Diamine (TDA) surfactant with P.Q. Corporation silicates; Brand D ($2.06 \text{ SiO}_2/\text{Na}_2\text{O}$), RU (2.51), K (3.02) and N (3.29). Each sample was prepared at 45 °C. HCI was used to neutralize the NaOH content of the sodium silicate. The isotherms are offset vertically by 100 cm³/g, STP for clarity. (Inset) HK pore size distribution plot highlighting equivalent pore size for each calcined sample.

evident from the N₂ adsorption isotherms is the existence of textural porosity in all samples by the uptake of N₂ at high partial pressures, >0.80 P/Po. Table 6.3 summarizes the physiochemical properties of each of the calcined silicas. Each sample shows comparable pore to pore correlation distances, BET surface areas, pore volumes, pore diameters and pore wall thickness.

Sample	D- spacing (nm)	BET SA (m²/g)	V⊤ ^b (mL/g)	V _f ° (mL/g)	V _{tx} ^d (mL/g)	Pore Diameter (nm)
SiO ₂ /Na ₂ O						
2.07	4.8	949	1.27	0.92	0.35	4.8
2.51	4.9	915	1.21	0.90	0.31	4.8
3.02	4.7	793	1.05	0.77	0.28	4.7
3.29	4.8	877	1.19	0.85	0.34	4.8

Table 6.3: Physiochemical properties of calcined MSU-SA molecular sieves^a.

^aAll MSU-SA materials were prepared at at 45 °C. ^bV_T, Total pore volume obtained from the volume of N₂ adsorbed at 0.99 P/Po. ^cV_f, Framework pore volume obtained from the volume of N₂ adsorbed at 0.60 P/Po. ^dV_{tx}, Textural pore volume obtained from the difference (V_t - V_f).

TEM images of the calcined sample from all silicate sources are similar to the micrographs seen in Figure 6.7. Again, evident in the samples is the existence of uniform framework pores with a wormhole pore structure. These framework pores also exist in small grained (<300 nm), highly aggregated particles similar to HMS silicas¹⁵. Textural porosity arises from voids between

grains created upon the intergrowth of small domains and is independent of the framework porosity.

The general method provided here for the synthesis of mesostructured silicas requires only the neutralization of the hydroxide content of the silicate source in the presence of the amine structure director resulting in a slightly alkaline solution (pH ~ 8.0 - 8.5). Sodium silicate solutions with SiO₂/Na₂O ratios of <2 possess generally monomeric silica species.²⁵ Increasing the SiO₂/Na₂O ratios above 2 results in solutions with higher populations of polymeric silicate species. Additionally, the increasing ion content of the reaction mixture with decreasing SiO₂/Na₂O ratio may well play a limiting roll in the H-bonding assembly of these materials. The commercially available silicate solutions used in this work span solutions of high sodium content (SiO₂/Na₂O = 2.1) to those with much lower sodium contents (SiO₂/Na₂O = 3.3). The comparable pore structures, porosity and particle texture obtained for each of the different samples indicate that highly porous silicas can be synthesized independent of the SiO₂/Na₂O ratio and the ion content of the synthesis gel. Low sodium content silicates (SiO₂/Na₂O = 3.3) are suitable for mesostructure assembly, though the silica present is invariably of high polymeric number and size compared to sodium silicates containing high amounts of sodium hydroxide.²⁵ On the other hand, the highly ionic solutions resulting from the acid neutralization of sodium silicate with high sodium content (SiO₂/Na₂O = 2.1) are equally suitable for the assembly of mesostructured silicas.

6.5. Conclusion

There has been a significant volume of research into supramolecular assembly of mesostructured materials since it was first reported¹. Much of the research focuses on the ability to synthesize structures with unique properties. HMS silicas, with their small particle nature and high textural porosity, offer unique properties for adsorption, sieving and especially catalysis. High textural porosity is an attractive property of catalysts and catalytic supports due to the increased access for reagents to reactive sites within the framework pores that these textural pores provide. The increased access results in higher catalytic activity in condensed phase alkylation reactions¹⁵ along with increased cracking of cumene²⁶ and decreased coke formation in gas phase reactions compared with identical processes with large, monolithic mesoporous catalysts.²⁷ Efforts to synthesize these unique mesoporous HMS silicas rely on cooperative assembly using the H-bonding between neutral amine surfactants and molecular silica species. One weakness of HMS synthesis has been the required use of costly molecular silica species (TEOS) in the assembly of these molecular sieves.

Primary amine surfactants and soluble silicate sources, however, can be efficiently utilized in the formation of stable mesoporous materials with wormhole framework pore structures. Simply by neutralizing the hydroxide content of the sodium silicate source with the use of an organic acid, such as acetic acid, in the presence of the structure directing surfactant allows for sufficient H-bonding at the interface between surfactant and silicate species. The acetate ion present in

the solution actively participates in the mesostructure formation. Insufficient acid content or the use of mineral acid results in the formation of an unstable lamellar mesostructure due to the averaged small head group area of the amine. The presence of these organic ions, which due to their polar nature are likely to reside in the palisade region or at the interface of the micelle, along with H-bonding between silica and surfactant successfully increases the average effective head group area of the surfactant leading to a increase in surface curvature producing the resulting stable wormhole pore structure.

Where as primary amines require the use of organic acids in the neutralization of the base content of the water soluble silicate species in the synthesis of MSU-SA silicas. Tallow polyamines do not require organic acids or the surfactant modifying anion in the synthesis of MSU-SA silicas due to the larger head group area of these molecules. Mineral acids such as HCI can be successfully employed as the neutralizing acid in the mesostructure synthesis.

Tallow polyamine surfactants have increased head group areas, a_o, compared to primary amines due to the multiple polar propylamine repeat units on the alkyl chain. This increased head group surface area, a_o, results in increased curvature of the surfactant micelle assembly due to a lowering of the surfactant packing parameter, g. Therefore, surface modifying organic species are not needed to synthesis stable mesostructured silicas. Increasing the polar amine head group size by using larger polyamine units influences a change in the pore mesophase formation from disordered wormhole to quasi-ordered hexagonally packed pores.

The general procedure provided here for the supramolecular assembly of MSU-SA silicas provides a novel route to the assembly of molecular sieve silicas with properties that parallel those of HMS silicas in their pore size uniformity, volume, and, more importantly, in their high textural porosity. Use of inexpensive and readily available tallow polyamines surfactants allows for the substitution of equally inexpensive water soluble silica sources for the previously used, and costly, TEOS in the assembly of MSU-SA silicas. Additionally, silicate sources of a wide range of SiO₂/Na₂O ratios are suitable inorganic precursors to the assembly of stable mesostructured silicas.

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