The Synthesis, Characterization, and Catalytic Applications of Mesocellular Silica Foams

by
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M. Phil. Engineering
University of Cambridge, UK, 1996

B. S. E. Chemical Engineering
Princeton University, 1995

Submitted to the Department of Chemical Engineering in Partial Fulfillment of the Requirements for the Degree of

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Abstract

Despite recent progress in materials synthesis, there are few materials with narrow pore size distributions and well-defined pore structures in the size range of 100 - 500 Å. Materials with pores of 100 - 500 Å possess a potential combination of high surface areas and pore sizes accommodating of large molecules that could make them of great use in the catalysis and separation of complex molecules important to the fine chemicals and pharmaceuticals industries.

We have synthesized mesocellular silica foams (MCF) by using triblock copolymer (PEO-PPO-PEO, Pluronic) micelles to template the formation of silica from tetraethoxysilane precursors. The combination of the polymer amphiphile with a hydrophobic swelling agent (such as trimethylbenzene) resulted in larger pore sizes and more open pore structures than had previously been obtained with surfactant templates. The MCF materials have pore sizes of up to 350Å, void fractions of > 0.85 and surface areas of ~ 700 m²/g.

The basic properties of the swollen triblock copolymer micelles were investigated to provide a better understanding of their templating behavior. Small-angle neutron scattering (SANS) in conjunction with a thermodynamic model for swollen micelle formation were used to determine the size, shape and internal structure of the Pluronic micelles. Knowledge of the micelle structure and aggregation behavior was used to investigate the effects of changing polymer and oil types on the size of the swollen micelles and therefore to select the best systems for templating large pores in silica sol-gels.
Synthesis experiments revealed that when tetraethoxysilane was added to micellar solutions containing only small amounts of oil, SBA-15 materials consisting of cylindrical pores packed in hexagonal arrays were formed. At an oil-to-polymer mass ratio of ~ 0.2, MCF (consisting of spherical cells connected by windows) was produced. We determined that the silica structures form as a result of the silica-induced precipitation of a polymer/silica rich phase. We have found two key factors in determining the pore size and structure of Pluronic-templated silica materials that were not previously well understood. First, there must be sufficient silica present in solution to precipitate the polymer aggregates. Second, it is the equilibrium structure of the concentrated precipitate, not the original solution, that determines the pore structure of the final material.

To demonstrate the utility of the MCF materials, we have used MCF as a catalyst support for two different reactions: the Heck reaction and asymmetric hydrogenation. Palladium metal clusters were vapor-grafted onto MCF and several other large-pore silicas to generate active Heck catalysts. The activities of the “Pd-TMS” catalysts were equal to those of the best homogeneous organometallic catalysts reported in the literature. At 160°C, the activity of the MCF-supported catalyst was also better than that of catalysts supported on other mesoporous silicas. The high activity of the MCF-supported catalyst was attributed to its large pores and open pore structure, which reduced pore diffusion limitations on the reaction rate.

Asymmetric hydrogenation was chosen as a model reaction because the highly selective reaction required the use of organometallic catalysts, which could only be heterogenized in large pores. We developed a ‘strong ligand’ heterogenization method that allowed us to anchor asymmetric hydrogenation catalysts to silica surfaces without modifying the chiral ligands that impart enantioselectivity to the active metal center of the catalyst. The resulting heterogeneous asymmetric hydrogenation catalysts had the same selectivity as homogeneous catalysts, proving that immobilization within the large pores of MCF did not distort the active complexes. However, the slow reaction rate of the hydrogenation reaction meant that the reactions were kinetically, not transport, limited; therefore, the activity of MCF-supported catalyst was not significantly higher than that of complexes immobilized on commercially available large-pore silica gels.

Thesis Supervisor: Jackie Y. Ying, Professor of Chemical Engineering
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## CONTENTS

### Chapter 1 — Background and Motivation

1.1 Introduction  13

1.2 Synthesis of Silica with Controlled Pore Sizes  14
   1.2.1 Sol-Gel Processing of Porous Inorganic Materials  14
   1.2.2 Surfactant-Templated Mesoporous Materials  15
   1.2.3 Polymer-Templated Mesoporous Materials  19
   1.2.4 Colloidal Templating of Mesoporous and Macroporous Silicas  20

1.3 Mesoporous Silicas as Catalyst Supports  20
   1.3.1 Metal-Deposited Mesoporous Silica Catalysts  21
   1.3.2 Organometallic and Enzyme Immobilized Mesoporous Silica Catalysts  23

1.4 Research Motivation  27

1.5 References  29

### Chapter 2 — The Properties of Swollen Pluronic Micelles

2.1 Introduction  31

2.2 Experimental Procedures  33
   2.2.1 Dynamic Light Scattering  33
   2.2.2 Microemulsion Stability Measurements  34
   2.2.3 Neutron Scattering  34

2.3 Modeling  35
   2.3.1 Thermodynamic Model of Microemulsion Structure  35
   2.3.2 Neutron Scattering Model  40

2.4 Results and Discussion  43
   2.4.1 Model Confirmation Using SANS and DLS Studies  43
   2.4.2 Effects of Alcohol and Acid on Swollen Polymer Micelles  49
   2.4.3 Model Predictions  52
      2.4.3.1 Effect of Changing Polymer Type  52
      2.4.3.2 Effect of Changing Oil Type  55

2.5 Summary  57

2.6 References  59
Chapter 3 — The Synthesis and Characterization of Mesocellular Foams

3.1 Introduction 61

3.2 Experimental Procedures 62
  3.2.1 Material Synthesis 62
  3.2.2 Material Characterization 62

3.3 Results and Discussion 64
  3.3.1 The Synthesis of Mesocellular Silica Foams and the Effect of Oil Concentration 64
  3.3.2 Effect of Oil Type 69
  3.3.3 Effect of Polymer Type 71
  3.3.4 Effect of Silica Concentration 74
  3.3.5 Templating Mechanism 75

3.4 Summary 79

3.5 References 81

Chapter 4 — Pd on Mesoporous Silica Supports for Heterogeneous Heck Catalysis

4.1 Introduction 83

4.2 Experimental Procedures 85
  4.2.1 Catalyst Synthesis and Characterization 85
  4.2.2 Heck Reaction Studies 87

4.3 Results and Discussion 89
  4.3.1 Pd-TMS Catalyst Synthesis and Characterization 89
  4.3.2 Effects of Temperature and Pore Size on Heck Reaction Kinetics 92
  4.3.3 Catalyst Recovery and Reuse 98

4.4 Summary 101

4.5 References 103

Chapter 5 — Heterogeneous Asymmetric Hydrogenation

5.1 Introduction 104

5.2 Experimental Procedures 107
  5.2.1 Catalyst Synthesis and Characterization 107
  5.2.2 Catalytic Testing 109
5.3 Results and Discussion 111
  5.3.1 Homogeneous Acetonitrile Asymmetric Hydrogenation Catalysts 111
  5.3.2 Comparison of Three Strong Ligands for the Heterogenization of
      Ru-BINAP Catalysts to Silica Surfaces 112
  5.3.3 Comparison of the Homogeneous Isonitrile Catalyst to Isonitrile
      Catalysts Immobilized on Different Silica Supports 115
  5.3.4 Asymmetric Hydrogenation Mechanism 121
  5.3.5 Comparison of Isonitrile Catalysts to Other Heterogeneous and
      Homogeneous Asymmetric Hydrogenation Catalysts 129

5.4 Summary 130

5.5 References 132

Chapter 6 — Reccomendations for Future Work

6.1 Future Directions for Mesocellular Silica Foams 133

6.2 References 134

Chapter 7 — Conclusions 135
LIST OF FIGURES

p.16 1.1 Transmission electron micrograph of MCM-41
p.17 1.2 Schematic diagram of the liquid crystal templating mechanism proposed by Beck et al.
p.17 1.3 Surfactant templated silicate reaction progress from lamellar to hexagonal structure
p.18 1.4 Charge matching mechanism for the formation of mesoporous materials using ionic surfactant templates.
p.20 1.5 Transmission electron micrograph of ordered macroporous silica templated by closely packed latex spheres.
p.24 1.6 Schematic diagram showing the fixation of an amine-modified metalloporphyrin catalyst to the walls of mesoporous niobium-doped silica through amine-niobium interactions.
p.25 1.7 Glucoamylase activity and surface area as functions of pore diameter for controlled pore glasses.
p.26 1.8 Schematic diagrams indicating the effects of immobilized solutes on the diffusion of other solutes in the pore.

p.36 2.1 Swollen micelle structure.
p.40 2.2 Neutron scattering geometry used in all SANS experiments.
p.46 2.3 Neutron scattering data (symbols) and most accurate data fits (solid curves).
p.47 2.4 The micellar diameter determined from SANS experiments for samples containing TMBA and those containing DCB.
p.50 2.5 The volume fraction of micelles relative to the volume fraction at 0 ethanol content plotted against the ethanol:polymer mass ratio.
p.50 2.6 Micellar diameter determined from SANS experiments versus the volume of oil added per mole of polymer for samples with an ethanol:polymer mass ratio of 0, 1, and 2.
p.51 2.7 Effects of HCl on the hydrodynamic diameter of swollen P123 micelles as determined by dynamic light scattering.
p.53 2.8 Model results for the effects of changing polymer molecular weight and composition on the radius of the micellar core.
p.56 2.9 Model results for the effects of changing oil type on the radius of the micellar core.
p.63  3.1 Schematic representation of the polymer-templated mesoporous silica synthesis.

p.64  3.2 Transmission electron micrograph of SBA-15 synthesized using Pluronic P123 with no swelling agent added.

p.64  3.3 Small-angle X-ray scattering pattern of SBA-15.


p.66  3.5 Small-angle X-ray scattering patterns of mesoporous silicas templated by Pluronic P123 swollen with 1,3,5-trimethylbenzene.

p.66  3.6 Transmission electron micrographs of mesoporous silicas templated by Pluronic P123 swollen with 1,3,5-trimethylbenzene.

p.67  3.7 Nitrogen adsorption-desorption isotherms and pore size distributions of mesoporous silicas templated by Pluronic P123 swollen with 1,3,5-trimethylbenzene.

p.68  3.8 Pore size for mesoporous silica templated by P123 versus the amount of TMB swelling agent added.

p.70  3.9 Pore diameter for mesoporous silica templated by P123 with the addition of: 1,2-dichlorobenzene, 1,3,5-trimethylbenzene, benzene, cyclohexane, heptane.

p.71  3.10 Small angle X-ray scattering patterns for silica templated by P123 swollen heptane.

p.71  3.11 Small angle X-ray scattering patterns for silica templated by P123 swollen with benzene.

p.76  3.12 Pore size distributions for non-templated silica gel and P123-templated silica gel.

p.78  3.13 Schematic diagrams of the polymer-templated mesoporous silica synthesis mechanism.

p.86  4.1 Schematic of the condensation bridge used for vapor grafting Pd onto mesoporous silica supports.

p.91  4.2 XRD pattern of Pd-TMS13 displaying only broad humps corresponding to Pd.

p.92  4.3 Transmission electron micrographs of Pd-TMS13.


p.94  4.5 Temperature dependence of the Heck coupling of bromoaceto phenone with n-buty lacrylate over Pd-TMS13 (MCF supported).

p.94  4.6 The rate of Heck coupling reaction over Pd-TMS13 at 160°C, 140°C, 130°C, 125°C, and 120°C.

p.95  4.7 Temperature dependence of the Heck coupling reaction over Pd-TMS12 (SBA-15 supported) and Pd-TMS11 (MCM-41 supported).
p.96 4.8 Heck coupling activity of Pd-TMS13 catalysts without oxidation treatment and with oxidation treatment at 400°C.

p.97 4.9 Heck coupling reaction over Pd-TMS13 and Pd-TMS12. Bromoacetophenone-to-Pd molar ratio of 100,000.

p.98 4.10 X-ray diffraction patterns of Pd-TMS13 catalysts before reaction, and after reaction with no treatment, oxidation post-reaction treatment and reduction-oxidation-reduction post-reaction treatments.

p.98 4.11 STEM images and EDS elemental maps of Pd-TMS13 before reaction, and after reaction.


p.100 4.13 Heck coupling reaction over Pd-TMS13 catalysts run with a triethylamine:bromoacetophenone ratio of 1.1 and 2.2.

p.105 5.1 Three prior methods of immobilizing asymmetric hydrogenation catalysts.

p.107 5.2 The structure of a BINAP-Ru-acetonitrile catalyst.

p.110 5.3 Schematic diagram of high-pressure hydrogenation reactor.

p.111 5.4 Conversion of methylacetamidoacrylate over catalyst 1 at 60°C and 25°C.

p.114 5.5 The conversion of methylacetamidoacrylate over Ru-BINAP catalysts heterogenized using three different strong ligands.

p.117 5.6 MAA hydrogenation over homogeneous isonitrile catalyst, and heterogeneous isonitrile catalysts.

p.118 5.7 Conversion of dimethyl itaconate over catalyst 4 supported on MCF.

p.120 5.8 PA-FTIR spectra of isonitrile-Ru-BINAP based catalysts.

p.120 5.9 Conversion of MAA for sequential reaction runs with the same catalyst.

p.121 5.10 Conversion of dimethyl itaconate over catalyst 1.

p.125 5.11 Michaelis-Menten model fit to experimental data.

p.126 5.12 Reaction rate of DMI over homogeneous catalyst 1 compared to Michaelis-Menten model predictions and reaction rate of DMI over heterogeneous catalyst 4 compared to Michaelis-Menten model predictions.
LIST OF TABLES

p.44  2.1  Chemical Properties used in the Thermodynamic Model of Micellar Aggregation
p.45  2.2  Pluronic Micelle Characteristics as Determined by Model Calculations and SANS Experiments
p.54  2.3  Effects of Changing Pluronic Molecular Weight and Composition on Micelle Size
p.57  2.4  Solubility Limits for Various Oils in Water-Pluronic Solutions

p.69  3.1  Pore characteristics of polymer-templated silicas as determined by nitrogen adsorption experiments
p.73  3.2  Pore characteristics of mesoporous silicas templated by three different polymers.

p.75  3.3  Pore characteristics of polymer-templated and untemplated silica gels.

p.90  4.1  Characterization Data for Pd-TMS Heterogeneous Heck Catalysts

p.115  5.1  Pore characteristics and compositions of isonitrile-Ru-BINAP heterogeneous catalysts
p.127  5.2  Comparison of asymmetric hydrogenation catalyst activities
LIST OF SCHEMES

p.84  4.1  Heck reaction
p.85  4.2  Homogeneous palladacycle (Herrmann et al., 1995)
p.88  4.3  Heck coupling of bromoacetophenone and n-buylacrylate
p.88  4.4  Heck reaction mechanism1

p.106  5.1  BINAP-Ru-isonitrile synthesis
p.108  5.2  Heterogeneous asymmetric hydrogenation catalyst synthesis
p.110  5.3  Asymmetric hydrogenation reactions
p.113  5.4  Strong ligand synthesis
p.122  5.5  Catalyst activation
p.123  5.6  Hydrogenation reaction mechanism
CHAPTER 1
Background and Motivation

1.1 Introduction

Porous materials play an important role in improving the economic and environmental efficacy of numerous chemical processes. Porous materials are used as catalysts, catalyst supports and filters, and therefore provide for both efficient reaction and separation. The pore size and structure are crucial variables for the application of porous materials along with the chemical composition of the solid matrix of the material. Pore size and inter-connectivity govern the diffusion of molecules in the material and also determine the bulk properties of the material, such as crush strength.

While porous materials have been used in the chemical industry since its inception, there are increasing efforts to precisely control the size and shape of pores in inorganic materials. New understanding of molecular interactions and self-assembly processes has led to the synthesis of porous materials with pore dimensions on the angstrom and nanometer scales, possessing narrow pore size distributions, high surface areas (in excess of 1000 m²/g), and well-defined pore structures.

The International Union of Pure and Applied Chemistry (IUPAC) has divided porous inorganic solids into three main classifications. Materials that contain pores with diameters of less than 20 Å are considered ‘microporous’ materials, those with pore diameters in the range of 20 - 500 Å are defined as ‘mesoporous’ materials, and materials with pores greater than 500 Å in diameter are termed ‘macroporous’.

Despite the recent progress in materials synthesis, there are few materials with narrow pore size distributions and well-defined pore structures in the size range of 100 - 500 Å, i.e. the upper portion of the mesoporous regime. Materials with pores of 100 - 500 Å possess a potential combination of high surface areas and pore sizes accommodating of large molecules that could make them of great use in the catalysis and separation of complex molecules important to the fine chemicals and pharmaceuticals industries.

Amorphous silica has been an important material for the formation of mesoporous systems since its diverse variety of synthetic routes lends the material to flexible and
creative processing approaches, its basic molecular architecture leads to thermal and chemical stability, and its surface chemistry allows for facile modification to generate tailored catalytic and separation media.

1.2 Synthesis of Silica with Controlled Pore Sizes
In addition to the synthetic flexibility, thermal and chemical stability, and facile surface modification of amorphous silica, the material can be made with very large surface areas and controlled pore sizes. High surface area, porous silica is primarily fabricated through sol-gel processing and the pore size of the material can be controlled through the choice of drying environment and through the use of single molecule templating, surfactant aggregate templating, or polymer aggregate templating as described in the following sections. Non-templated and molecular-templated silicas possess pores of less than 10 nm, so researchers have utilized colloidal particles to template large pores in sol-gel derived silicas. The colloidal-templated materials tend to have relatively monodispersed pores of greater than 350 nm in diameter. Thus, there exists a gap in the pore diameter of mesoporous silicas that spans over an order of magnitude and prevents application of these materials to a number of important processes, such as the synthesis and separation of fine chemicals and pharmaceuticals.

1.2.1 Sol-Gel Processing of Porous Inorganic Materials
The most common starting point in the sol-gel process is the mixing of metal alkoxides in a hydrolyzing environment. Metal alkoxides are typically dissolved in an aqueous solution with co-solvents, such as alcohols, which are added to achieve the necessary concentration of the alkoxide. Gelation of the initial alkoxide solution occurs via a two-step process shown in Equations 1.1 - 1.3.

\[
\text{Hydrolysis} \\
\equiv \text{Si-OR} + \text{H}_2\text{O} \rightarrow \equiv \text{Si-OH} + \text{ROH} \tag{1.1}
\]

\[
\text{Condensation} \\
\equiv \text{Si-OH} + \text{HO-Si} \rightarrow \equiv \text{Si-O-Si} + \text{H}_2\text{O} \tag{1.2}
\]

\[
\equiv \text{Si-OH} + \text{RO-Si} \rightarrow \equiv \text{Si-O-Si} + \text{ROH} \tag{1.3}
\]
First, the metal alkoxide is hydrolyzed to a metal hydroxide, which then forms a metal oxide network by condensing either with another hydroxy group or with an alkoxy group. The hydrolysis of the alkoxide may be catalyzed by both acids and bases, but the condensation step generally occurs more slowly under acidic conditions. The gel is allowed to condense further during the aging step in order to increase crosslinking in the metal oxide network, and thereby increase the structural stability of the gel.

After aging, the gel still contains excess water not used in hydrolysis of the alkoxide, alcohol produced during hydrolysis, and other additives present in the starting mixture, so the gel must be dried either under atmospheric conditions or supercritically. During atmospheric drying, large capillary pressures develop in the gel due to evaporation of the liquid in the pores. The high capillary pressures often lead to pore collapse, which results in decreased surface area. Supercritical drying greatly reduces capillary pressures in the gel by eliminating the vapor-liquid interface, and thus, supercritically dried gels (termed aerogels) maintain a higher surface area and a more open pore structure than the conventionally dried gels (xerogels). However, the high temperatures and pressures necessary to reach supercritical CO₂ or H₂O conditions obviously make supercritical drying a more expensive process. After drying, gels are frequently calcined in excess of 500°C in order to burn off remnant organics and surface adsorbed species. Xerogels and aerogels possess a significant fraction of pores in the mesoporous regime, but are characterized by ill-defined pore morphologies and broad pore size distributions.

1.2.2 Surfactant-Templated Mesoporous Materials

As previously mentioned, the pore structure in inorganic polymeric gels frequently collapses during the drying and calcination steps, leading to reduced surface areas and pore volumes in the final material. One way to prevent pore collapse, other than supercritical drying, is to form voids in an otherwise dense inorganic matrix by incorporating an organic molecule into a fully condensed gel. The organic phase may then be removed to form pores. In this approach, the pore size and shape are governed by the templating molecule, while the pore volume and connectivity are determined by the volume fraction of the organic phase present in the gel.¹
Templating the formation of porous inorganic solids with individual molecules results in the formation of microporous zeolite materials, which have a crystalline silicate-based framework with a well-defined pore structure. An example of microporous silica synthesis is the sol-gel processing of silica by co-condensing tetraethoxysilane with 4,4'-bis(triethoxysilyl)biphenyl. When the organic template is burned out of the dense silica matrix, a continuous network of micropores is created. The resulting zeolitic structure contains pore openings < 1.5 nm that will allow only small molecules to enter and react, thus providing shape and size selectivity in separations and catalytic reactions.

A major breakthrough in the synthesis of well-defined mesoporous materials came in 1992 with the development of ‘supramolecular templating’, which involved the use of molecular aggregates, instead of individual molecules, as the framework-directing agents. Mobil researchers used micellar assemblies of surfactant molecules to template a new family of porous silicate and alumino-silicate materials designated M41S. The M41S family of materials possesses regularly spaced pores with diameters of 2 - 10 nm. Among the M41S materials are MCM-48, which possesses spherical pores arranged on a cubic lattice with the space group la3d, and the lamellar MCM-50 in which the silicate sheets remain intact even after surfactant removal due to small silica pillars connecting the layers. MCM-41, however, is the mesoporous material that has attracted the most attention. It consists of long cylindrical pores that form a two-dimensional hexagonal lattice as shown in Figure 1.1. The combination of open porosity and high surface area (in excess of 1400 m²/g) in a chemically inert silica material that is thermally stable up to 1000 K makes MCM-41 the ideal catalyst support for reactions that involve molecules too large to fit into the micropores of zeolites.

MCM-41 and the other M41S materials are synthesized by mixing quaternary ammonium surfactants such as hexadecyltrimethylammonium bromide with a silicon alkoxide in an aqueous solution. Both basic and acidic conditions have been successfully
used to catalyze the hydrolysis and condensation of alkoxide precursors to form the silica walls of the M41S materials. Increasing the reaction temperature (up to \( \sim 150^\circ C \)) has been found to decrease formation times and to increase the mechanical stability of MCM-41 due to more complete condensation of the silica precursors.\(^{10}\) Using surfactant molecules with chain lengths up to 18 carbons long results in MCM-41 structures with pores of \( \sim 4 \) nm in diameter. Molecules such as trimethylbenzene can be used to swell the region occupied by the hydrophobic surfactant tails, thereby producing pores with \(< 10 \) nm diameters.

Initially, two mechanisms were proposed for the formation of MCM-41. The Mobil researchers\(^{9}\) argued that the surfactant molecules first formed a liquid crystalline phase around which the silicate molecules condensed to produce the highly ordered mesoporous materials after surfactant removal (see Figure 1.2). Since it has been demonstrated that MCM-41 will form under conditions where the surfactant alone would not form a liquid crystalline phase (\( i.e. \) the surfactant aggregates into independent micelles), Chen et al.\(^{11}\) proposed that the silicate precursors partially condensed around individual surfactant micelles and then the micelles aggregated together. Finally, by condensation between silica molecules from neighboring micelles, the hexagonal MCM-41 mesostructure was formed. However, it was shown that MCM-41 could be obtained even when the surfactant concentration is below the critical micelle concentration.\(^{10}\) In fact, under many conditions the surfactant and partially condensed silicate would first form layered mesostructures and as the reaction proceeded, the layers eventually evolved into the hexagonally-packed cylinders of the MCM-41 structure (Figure 1.3).\(^{10}\)
Figure 1.4 Charge matching mechanism for the formation of mesoporous materials using ionic surfactant templates. (a) Electrostatic repulsion between similarly charged surfactant head groups leads to a large micelle surface area per surfactant head group. (b) Ions in solution screen neighboring head group charges from each other. (c) Screening results in smaller micelle surface areas per surfactant molecule and therefore less micelle surface curvature. The silicate-surfactant aggregates initially form lamellar structures. (d) As silica condenses, screening diminishes, surface curvature increases, and cylindrical silica-surfactant structures are formed.

To explain the results of Monnier et al., a “charge density matching” mechanism of surfactant templating was proposed, and is schematically depicted in Figure 1.4. Under the basic conditions of most MCM-41 synthesis procedures, the silicate monomers in solution are negatively charged, therefore the monovalent ammonium ions at the head of the surfactant molecules must be as closely packed as possible to generate a surface charge density that is equal to that of the silicate monomers. Lamellar structures have the smallest surface area per head group and so initially the surfactant/silicate complexes form layers. The repulsion between similarly charged silicate monomers is reduced at the organic/inorganic interface by the screening effect of nearby surfactant head groups, and so the silicate monomers preferentially condense at the surfactant surfaces. As condensation proceeds, the charge per monomer unit in the silicate layer decreases and the surfactant molecules rearrange into the hexagonally packed cylinders, which have a higher surface area per head group, in order to match the new surface charge density of the silicate wall. Further silicate condensation leads to the formation of the stable MCM-41 structure.

Charge density matching has been generalized to include other inorganic compounds and surfactant molecules. As in the synthesis of MCM-41, cationic surfactants (S+) will
self-assemble with anionic inorganics (\(I^–\)). Conversely, anionic surfactants (\(S^–\)) can serve as templates for cationic inorganic species (\(I^+\)). Surfactants and inorganics of the same charge can also self-assemble through the mediation of free ions present in solution (\(M^+, X^-\)) forming \(SM^{+}\) and \(S^+X^-\) complexes. The work of Tanev and Pinnavaia has further expanded the range of self-assembling systems to include neutral inorganic species (\(I^0\)) templated by neutral surfactants (\(S^0\)) through hydrogen-bonding interactions.\(^{14}\)

### 1.2.3 Polymer-Templated Mesoporous Materials

Pinnavaia and co-workers followed their initial work on neutral surfactant templating by investigating the effectiveness of surfactants with ethylene oxide oligomer head groups as templating molecules.\(^{15,16}\) Polyethylene oxide chains with up to 30 monomer units in length were linked to alkyl surfactant molecules and were successfully employed as templating molecules. The ordering of cylindrical pores in the “MSU” materials was not as well-defined as in ionically templated MCM-41 materials. In fact, some silicates were described as containing “wormhole motifs”, but pore sizes in excess of 5 nm were reported without the use of swelling agents. Bagshaw \textit{et al.} also used polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymers (\((\text{PEO})_{13}(\text{PPO})_{30}(\text{PEO})_{13}\)) as templating agents and obtained materials with pore diameters of nearly 6 nm and BET surface areas in excess of 1100 m\(^2\)/g.

Attard \textit{et al.} have also used ethylene oxide oligomer surfactants to template the formation of mesoporous phases.\(^7\) This work reported forming cubic, hexagonal, and lamellar porous silica phases by starting with surfactant/water mixtures that possessed the corresponding liquid crystalline phases. Experiments were also performed with low surfactant concentration solutions such that only independent micelles were formed. The low PEO surfactant concentration mixtures formed only fine precipitates with heterogeneous mesostructures. Attard \textit{et al.} have interpreted these results as indicating that neutral surfactant templating works on a different mechanism from ionic templating, and that in the neutral case, the liquid crystalline surfactant phase directly templates the condensation of the inorganic phase.

Despite the intensive research on surfactant-templated mesoporous materials and the recent investigations on macromolecular templates, the largest pore diameter reported in
any of these materials thus far is ~ 10 nm. The largest pores obtained without the use of swelling agents, which deleteriously effect pore uniformity and packing, is ~ 6 nm. Thus, while the synthesis of high surface area, well-defined nanoporous materials such as MCM-41 has significantly expanded the size range of molecules that may diffuse through the pores over that of zeolites, pore sizes have not yet reached the point as to be broadly useful with complex substrate molecules.

1.2.4 Colloidal Templating of Mesoporous and Macroporous Silicas
Stein and co-workers have successfully created well-defined macroporous materials using monodisperse spherical polymer colloids as templates. In this templating method, the colloidal spheres are first concentrated into a close-packed cake through filtration or centrifugation. Inorganic precursors then permeate the spaces between the close-packed spheres. Following a heat treatment to solidify the inorganic network, the polymer spheres are removed by calcination to expose a periodic three-dimensional array of open-pore structures with voids of 350 nm or greater (see Figure 1.5).

Figure 1.5 Transmission electron micrograph of ordered macroporous silica templated by closely packed latex spheres.

1.3 Mesoporous Silicas as Catalyst Supports
The unique physical properties of mesoporous silicas, such as MCM-41, have made these materials attractive candidates for catalytic applications. The high specific surface areas are conducive to high active site loadings and therefore provide for enhanced catalytic activity. The large pore size (relative to that of microporous zeolites) reduces the diffusional restriction of reactants and products, allowing for the use of mesoporous materials in catalytic reactions involving large substrate molecules. The large pore size of mesoporous materials also enables the immobilization of large active complexes onto the interior surface of the pores. However, a major restriction of MCM-41 materials is the
one-dimensional nature of the pore structures that lead to longer effective diffusion distances and lower catalyst effectiveness factors. Despite this fact, MCM-41 has been widely studied in catalysis research because of its facile preparation.

The first catalytic studies with mesoporous molecular sieves focused on metal-substituted MCM-41 materials whereby active sites were incorporated directly into the silica matrix during the condensation step of the material synthesis. The reactions studied were mostly oxidation and acid catalysis. Typical catalysts involved the substitution of titanium and aluminum into the silica matrix, creating valence defect active sites. The properties of these and other metal-substituted mesoporous catalysts have been reviewed in detail by Ying et al. In summary, the process of generating active sites during the condensation of the mesoporous material results in poor control of the active site number, location and type. Subsequent research investigated the efficacy of depositing active metal clusters onto the surface of MCM-41, after the mesoporous material had been synthesized and calcined. The deposition of heteroatoms onto the surface of mesoporous materials largely mimics current industrial practice for the dispersion of active materials onto conventional high surface area supports, and significant advancements in this field of research are summarized in the following section. Additionally, mesoporous molecular sieves have been used as supports for the immobilization of organometallic and enzyme catalysts. Immobilization of highly selective catalysts provides a bridge between homogeneous catalysts and the typically less selective heterogeneous catalysts. The current state of this growing area of research is discussed in section 1.3.2. Although extensive research efforts have been undertaken to explore the applications of mesoporous molecular sieves to bulk chemical catalysis, industrial use has been limited, so far.

1.3.1 Metal-Deposited Mesoporous Silica Catalysts

There are several well-established techniques for depositing catalytically active clusters onto inactive but high surface area porous supports. Perhaps the most common method is the incipient wetness impregnation technique. In this process, the active compound, typically a metal, is dissolved in a solvent as a salt or organic precursor. The precursor solution is mixed with the solid support to form a slurry, and the solution impregnates the pores of the support. The slurry is then dried such that the precursor is deposited on
the surface of the support and finally, the material is calcined to remove any residual solvent and the unwanted ligands of the precursor. The incipient wetness impregnation technique typically results in the dispersion of ~10-nm clusters of the active metal or oxide on the surface of the support. The impregnation method has been used to introduce active catalysts onto the surface of surfactant-templated mesoporous silica supports.

In an early catalytic application of mesoporous silicas, NiO and MoO₃ were supported on MCM-41 by the incipient wetness impregnation technique for use in gasoil hydrocracking processes. A loading of 15 wt% transition metal oxides was introduced onto the support but the surface area of the MCM-41 decreased only slightly. The NiMo-MCM-41 catalyst showed higher hydrodesulfurization and hydrodenitrogenation activities than NiMo supported on zeolite USY or on xerogel. The better performance of the NiMo-MCM-41 catalyst was attributed to its mesoporous structure that facilitated access to its high dispersion of active components.

Platinum-modified MCM-41 aluminosilicates with pore diameters of ~3 nm have been used as catalysts for the isomerization of n-hexane. Although platinum on SiO₂-Al₂O₃ xerogels yielded a slightly higher overall conversion of n-hexane, the Pt-MCM-41 catalyst showed significantly higher selectivity, possibly because the uniform pores of MCM-41 favored a particular conformation of the branched hydrocarbon.

In addition to altering the selectivity and activity of catalysts previously supported on zeolites or xerogels, supramolecular-templated silicas can also be used to support catalysts that could not be synthesized using supports with smaller pores. To generate strong heterogeneous acid catalyst sites, Kresge et al. deposited large heteropolymetallic acids, such as H₃PW₁₂O₄₀, into the pores of MCM-41 using the incipient wetness method. By using a support with high surface area and large pores, good acid site dispersion was achieved for the isomerization of n-butane. Isobutene was obtained with selectivity exceeding 80%, which was substantially higher than that achieved over a ZSM-5 zeolite catalyst. The change in selectivity between catalysts was again attributed to the differences in pore size between the mesoporous and zeolitic supports.
1.3.2 Organometallic and Enzyme Immobilized Mesoporous Silica Catalysts

Highly selective and complex catalysts are frequently developed as homogeneous catalysts for numerous reasons, first and foremost being that the detailed active site structures and reaction mechanisms are more easily studied through well-established solution techniques, such as nuclear magnetic resonance (NMR) spectroscopy, than by surface science techniques that are usually limited to ultrahigh vacuum environments. In-depth knowledge of organometallic and enzyme catalyst structures and pathways is important since the main reason these expensive catalysts are used is to synthesize high value added products to exacting purities. However, homogeneous catalysis has a number of deficiencies. First, the catalysts must be separated from the product mixture, and for large catalyst complexes, separation from non-volatile products is not always a trivial task. Second, once the catalysts are separated from the product, they must be recovered in a reusable form. This is frequently impossible due to the fragile nature of enzyme and organometallic active sites, thus leading to significant catalyst replacement expenses. Finally, many homogeneous catalysts deactivate due to the formation of stable dimeric compounds that do not rejoin the catalytic cycle.

The immobilization of active and selective catalysts onto a robust heterogeneous support would yield significant processing advantages. First, the catalysts could be easily separated from the reaction mixture via filtration. Without exposure to harsh separation conditions, the catalyst is much more likely to remain active for subsequent reaction cycles. Several groups have attempted to heterogenize organometallic or enzyme catalyst complexes onto mesoporous supports.

In order to create a heterogeneous epoxidation catalyst, Sutra and Brunel first treated MCM-41 with \((\text{CH}_3\text{O})_2\text{Si(\text{CH}_2)_3\text{Cl}}\), thus generating surface-bound 3-chloropropylsilane moieties. The surface chloro groups were then reacted with the amine group of 3-(3,5-di-tert-butylsalicylidenediaminopropyl)amine to produce surface-immobilized Schiff base ligands. The active metal center was introduced subsequently, in the form of a \([\text{Mn(II)}(\text{acetylacetone})_2]\) solution. After rinsing to remove excess metal, the surface-bound organometallic species were oxidized to yield the active Mn(III) complex. The immobilized Mn(III) complex showed good epoxidation activity with the advantage of being easily separable from the reaction mixture by centrifugation or filtration. Several other groups
have used similar synthesis procedures to construct catalytically active organometallic complexes on the surface of mesoporous supports. While this method of fixing homogeneous catalysts has the advantage of producing high catalyst loadings on the high surface area mesoporous supports, it has the disadvantage of not allowing for the usual purifications in between the organometallic synthesis steps and, therefore, the surface-bound catalysts include a significant fraction of impurities.

To resolve the impurity problem, Zhang and Ying have used an alternate method for fixing organometallic complexes onto the surface of supramolecular-templated mesoporous materials. They substituted the periphery of metalloporphyrins with several amine groups and purified the modified catalytic complex. The MCM-41 support was doped with niobium and the strong niobium-amine interactions were used to anchor the metalloporphyrin to the surface of the support as shown in Figure 1.6. These heterogenized metalloporphrin materials proved to be excellent catalysts for the hydroxylation of cyclohexane and for the epoxidation of cyclohexene, and the materials could be recovered and reused without loss of catalytic activity. Zhang and Ying did notice a significant effect of pore size on the activity of their catalysts and concluded that the large metalloporphyrin catalysts were obstructing the diffusion of reactants in the mesopores of the support.

From the discussion above, it can be seen that many groups have employed supramolecular-templated mesoporous materials as catalyst supports and have used the unique combination of pore size/volume, ordered pore structure, and high surface area provided by these materials to improve the selectivity and activity of their catalyst or even to synthesize catalysts that could not be made in a support with smaller pores. However, few researchers have attempted to quantify the effects that support pore size and surface

Figure 1.6 Schematic diagram showing the fixation of an amine-modified metalloporphyrin catalyst to the walls of mesoporous niobium-doped silica through amine-niobium interactions.
area have on the supramolecularly templated systems. A more detailed understanding of the relationship between pore size, surface area and catalyst activity for the mesoporous silica supports would allow one to take advantage of the flexibility in pore size tailoring provided by the supramolecular templating method, and to develop a material with pore sizes and surface areas specifically optimized for a given catalytic application.

Weetall has studied the loading and activity of enzymes immobilized on controlled pore glass supports with various pore diameters in order to quantify the relationship between pore size, surface area and catalyst activity in mesoporous materials. The results for immobilized glucoamylase activity and support surface area versus pore diameter are shown in Figure 1.7. Higher surface areas give greater immobilized catalyst loadings, and there is an inverse relationship between pore diameter and surface area, so the support with the smallest possible pore size should be used. However, if the pores are too small, they severely restrict reactant diffusion or exclude the enzyme entirely and, therefore, Weetall claims that there will always be an optimal pore diameter for a given immobilized catalyst. As seen in Figure 1.7, the optimal pore size for glucoamylase is ~ 30 nm.

The optimal pore diameter of 30 nm is far greater than the characteristic dimensions of glucoamylase, and so the ideal pore size is obviously determined by something other than complete exclusion of the enzyme from the pore. Hossain and Do have performed both theoretical and experimental investigations of pore diffusion in immobilized catalyst systems and have determined that the pore diameter that yields the highest catalyst loading is governed by "restricted pore diffusion". The prevailing explanations for restricted diffusion in pores of small diameter are the infinite mass transfer resistance of the pore wall and its effects on the surrounding fluid. Friedman and Kraemer first suggested that the reduced diffusivity in fine pores resulted from increased frictional drag.
on the solute as a result of the proximity of the solid walls. Renkin has developed the most widely used correlation between the solute diameter-to-pore diameter ratio ($\alpha$) and the effective diffusivity of the solute in the pore. He has found that solutes with dimensions as small as 5% of the pore diameter can exhibit significantly retarded diffusion. In the model of Hossain and Do, restricted pore diffusion also takes into account the effects of previously immobilized catalyst complexes on the diffusion of non-fixated molecules through the pore as shown in Figure 1.8. The previously immobilized complexes decrease the pore radius available for subsequent catalyst diffusion to a value of $R_{eff}$. Hossain and Do determined that restricted pore diffusion becomes important for enzyme diameter-to-pore diameter ratios greater than 0.07, and that this effect leads to non-uniform enzyme distributions in the pore and decreased overall enzyme loadings. The model and experiments by Hossain and Do also indicate an optimal pore diameter for achieving the greatest enzyme loading, which occurs at an $\alpha$ just below where restricted diffusion takes effect.

In addition to affecting catalyst loading, restricted diffusion also affects the transport of reactant molecules to the immobilized active sites and therefore the effective activity of the catalyst. The liquid-phase diffusivity of solutes through porous media with pore diameters on the order of the solute size has previously been investigated with regard to chromatographic and membrane filtration processes. Satterfield et al. have performed numerous studies on the diffusion and adsorption of molecular solutes in materials with pores of ~ 3 - 4 nm and have found that the restricted diffusion expression used by Renkin does not apply to pores in this regime perhaps due to the breakdown in the assumption of a solvent continuum within the pore. Brenner and co-workers have also addressed the problem of the diffusion of finite-sized solutes and of reactive point solutes.
in small pores.\textsuperscript{32-34} This research has generated a number of more general expressions for diffusion, reaction and adsorption in mesopores, and has shown that solute-to-pore size ratios of approximately 0.25 can reduce the effective diffusivity to less than one half of its unbounded value. The above investigations all point to the fact that the activity of catalytic complexes immobilized on mesoporous supports can be severely limited by the diffusion of the complex during fixation (which reduces the overall catalyst loading) and the diffusion of the solute through the pores during reaction.

\section{1.4 Research Motivation}
Currently there is a large gap between high surface area controlled pore size materials with pore diameters of $< 10$ nm and those with pore diameters $> 100$ nm. The pores of supramolecular-templated mesoporous silicas are limited to relatively small diameters by the size of the amphiphile aggregates and by their stability under synthesis conditions. The pore size of xerogels and aerogels can be varied over a wide range through careful adjustment of the condensation and drying conditions, but the pore size distribution of these materials tends to be much broader than that of the templated mesoporous silicas, rendering much of the gel surface area inaccessible to larger target molecules. The pore size of colloidal-templated silicas is limited only by the size of the particle templates, but the difficulty of synthesizing, compacting and impregnating very small particulate templates requires that such materials be applied only to very expensive devices or processes. Therefore, it is our aim to create mesoporous materials with high surface areas ($> 500$ m$^2$/g), narrow pore size distributions, and tunable pore diameters between 10 and 100 nm. Such mesoporous materials could fill an important niche as catalyst supports and separation media. The large pore sizes would allow for the fixation of complex organometallic or enzyme catalysts to the surface of the pores, while concurrently allowing sufficient room for the unhindered diffusion of bulky reactant and product molecules (such as those of importance in the fine chemical and pharmaceutical industries).

The immobilization of organometallic catalyst complexes onto mesoporous supports that would not adversely affect catalyst activity (either through mass transport limitations or through catalyst deformation in constricting pores) could surmount a major hurdle in fine chemical and pharmaceutical processing: contamination from residual homogeneous
catalyst. In the processing of high-purity chemicals, product separation costs frequently dwarf reactor and catalyst costs. When organometallic catalysts are used in organic syntheses, the catalyst is frequently one of the most difficult components to remove. Catalysts heterogenized on robust supports could be simply removed through an one-step filtration process, and this inexpensive and mild separation method would yield the advantage of recovering the catalyst in its active form. Therefore, in addition to synthesizing mesoporous materials with pores of 10 - 100 nm, we also endeavor to fixate catalysts to these materials, to determine the activity of these heterogeneous catalysts relative to conventional homogeneous catalysts, and to prove the separability and reusability of the novel catalytic materials.

In order to test various aspects of our catalyst supports, we have selected two exemplary reactions: the Heck reaction and asymmetric hydrogenation. Both reactions are employed in important industrial processes that currently utilize homogeneous catalysts, and both reactions are sufficiently flexible in terms of reactants used and products made to be of broad applicability.
1.5 References


22 Kresge, C. T.; Marler, D. O.; Rav, G. S.; Rose, B. H.; (Mobil Oil Corp.) USA Patent 5366945, **1994**.


CHAPTER 2
The Properties of Swollen Pluronic Micelles

2.1 Introduction
One of the more effective methods for increasing the pore size of mesoporous materials beyond those of alkyl-surfactant templated silicas is to use amphiphilic polymer templates, as mentioned in Section 1.3.2. In particular, polymer-templated syntheses utilizing poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers (alternatively known as Pluronics) have been successfully developed by Bagshaw et al. and Attard et al. to create well-defined mesoporous silica materials.\(^1\)\(^2\) The use of poly(alkylene oxide) amphiphiles introduces a number of new effects that are important to the phase behavior of these micellar systems and the silicate materials they template. First, the hydrophilic group is a long chain rather than a single polar group, so that hydration and entropy effects are very important in determining the shape of the hydrophilic block and the volume that it occupies. The specific nature of PEO and PPO interactions with water is also important. Both PEO and PPO are more soluble in water at low temperatures. PPO is relatively insoluble in water by 20°C, while PEO solutions do not form a second phase until \(\sim 90^\circ\text{C}\). While the characteristics noted above were not specifically used by Bagshaw et al. and Attard et al. to explain the phase differences between poly(alkylene oxide) templated and alkyl-surfactant templated materials, both groups noted that well-ordered mesophases did not form unless the aqueous polymer templating solution was initially in the liquid crystalline regime. Recent research by Zhao et al. has shown that Pluronic surfactants with a higher molecular weight and with different PEO-to-PPO ratios than those used by Attard et al. can template ordered silica mesostructures even when the concentration of polymer is well below the level necessary to form liquid crystals.\(^4\) The well-ordered mesoporous silica materials obtained by Zhao et al., called SBA-15, consist of hexagonal arrays of long cylindrical pores (symmetry group: \(p6mm\), also found in MCM-41) with pore diameters of 5 - 7 nm and surface areas in excess of 750 \(\text{m}^2/\text{g}\).

On the basis of the successful results obtained by Bagshaw et al.,\(^1\) Attard et al.\(^2\) and Zhao et al.,\(^4\) we have selected Pluronic triblock copolymers as the templating agents for our large-pore mesostructured materials synthesis. In addition to proof of concept, the Pluronics have two other important properties. First, the Pluronics are widely used
surfactants in industry and are therefore readily available, inexpensive, and well-studied. This is important since any porous materials to be used in catalytic and separations processes must not be prohibitively expensive, and also because the properties of the base polymer are established. Second, one of the main industrial uses for Pluronics with high PEO-to-PPO ratios is in oil-in-water emulsification. This allows the use of oil 'swelling agents' to expand the hydrophobic core of the polymer aggregate, and therefore the ability to increase the pore size and to change the mesophase of the final mesoporous material. We intend to use the combination of poly(alkylene oxide) amphiphiles and hydrophobic swelling agents to fabricate the ultralarge-pore mesostructured materials that would be beneficial for the separation and reaction of large molecules. In order to understand and rationally control the types of materials templated by swollen Pluronic micelles, it is necessary to understand the behavior of the swollen aggregates themselves. We have therefore endeavored to model and experimentally confirm the behavior of the swollen Pluronic micelles in order to select the most promising candidates for templating systems.

The use of PEO-PPO-PEO triblock copolymers as oil-in-water emulsifiers has led to their application in a wide variety of fields from water remediation to cosmetics and drug delivery, and has engendered several studies of the copolymer amphiphile's ability to solubilize hydrophobic compounds. Alexandridis and co-workers have noted the rich micellar phase behavior of Pluronic-oil-water mixtures. Numerous researchers have tested macroscopic properties of swollen micellar systems, such as their cloud point, rheological behavior, and stability in the presence of various co-solvents. Other experimentalists have performed detailed studies of the microscopic structure of PEO-PPO-PEO micelles in water using techniques such as dynamic and static light scattering, small angle X-ray scattering (SAXS), as well as small-angle neutron scattering (SANS). Theorists have also turned their attention to Pluronic micelles and oil-swollen micelles, developing models capable of predicting the bulk properties as well as the microscopic structures of the complex fluids. However, most experimental studies of oil-swollen Pluronic micelles, even those utilizing powerful scattering techniques such as SAXS and SANS, have taken simplified views of the oil-polymer aggregates by treating them as homogeneous hard spheres or cylinders, and have not attempted to confirm the detailed structural predictions of available models.
We have compared the results of neutron scattering experiments on Pluronic micelles swollen by different oils to the predictions of a thermodynamic model for Pluronic-oil aggregate formation first developed by Nagarajan and Ganesh.13 These experiments achieved three goals: they confirmed the accuracy of the model; they reduced the neutron scattering fit parameters to a reasonable number, thus simplifying interpretation of the data; and they resulted in a more detailed understanding of the major factors contributing to the formation and stability of these important self-assembled structures. Once the accuracy of the model was established, we used it to predict the size of micellar aggregates consisting of various types of polymers and oils, as well as different oil concentrations. The modeling results were then used to select templating systems for the synthesis of mesoporous silica materials discussed in Chapter 3.

2.2 Experimental Procedures

2.2.1 Dynamic Light Scattering
Dynamic (quasi-elastic) light scattering (DLS) experiments were conducted on the oil-swollen polymer aggregates at 35°C with a Lexel 95 Argon-ion laser and a Brookhaven high-precision photomultiplier at a scattering angle of 90°. Data were acquired with a Brookhaven 9000AT correlator. The periods for the acquisition of the autocorrelation function ranged from 0.1 μs to 0.5 s. Particle size distribution was obtained from nonnegatively constrained least-squares analysis of the data.21 The viscosity of the polymer-oil-water solutions was measured using a Glimont capillary flow viscometer. The refractive index of the solvent (water) was 1.38, while that of the micelles was assumed to be 1.48.

The polymer solutions used in the dynamic light scattering experiments were synthesized by first dissolving 0.012 mmol of polymer (e.g. 0.7 g of Pluronic P123) in 25 mL of deionized water. To the polymer-water solutions, amounts of oil ranging from 0 to 1.0 g were added. Several different oils were used in the DLS experiments, including heptane, 1,3,5-trimethylbenzene (TMB), and 1,2-dichlorobenzene (DCB). The oils used in these studies were chosen to represent a range of different chemical families (e.g. aliphatic
versus aromatic) and different Hildebrand solubility parameters. Hydrochloric acid was also added to the swollen micellar solutions in some experiments since this compound would be present during the synthesis of mesoporous silicas in order to catalyze the hydrolysis and condensation of the silica precursor.

### 2.2.2 Microemulsion Stability Measurements
The stability point of the swollen micellar systems was determined by visual observation of clouding and the formation of a second phase. Polymer solutions were made using the procedure described above for light scattering samples. Oils were then added to the solutions in 0.05 g increments and, after each oil addition, the solution was stirred for three hours and then allowed to equilibrate for 24 h. When a second phase was observed in the sample after the equilibration period, the solution was deemed unstable and no further oil was added. Where possible, the results of the visual stability measurements were compared to oil solubility measurements taken by the direct gas chromatography method.²²

### 2.2.3 Neutron Scattering
The small-angle neutron scattering experiments were performed at the National Institute of Standards and Technology, Gaithersburg, Maryland, on the 30-m SANS spectrometer, neutron guide NG3. We used neutrons of wavelength $\lambda = 6 \text{ Å}$ with $\Delta \lambda / \lambda = 15\%$ at sample-to-detector distances of 2 and 13 m. This instrument configuration allowed us to cover a range in the magnitude of the wave vector transfer $|q| = |k_j \cdot k_\delta| = \left(4\pi / \lambda \right) \sin \theta$ from 0.005 to 0.3 Å⁻¹. The neutron intensity was corrected for instrument dark-current, empty cell scattering and beam transmission in order to obtain an absolute neutron intensity. For all experiments, 1 mm-thick quartz cells were used. The samples were injected into the sample cells at room temperature and the cells were then placed in the instrument sample chamber and heated to 35°C. Samples were allowed to equilibrate for several hours before data were taken and the temperature was controlled within ± 0.5°C.
A typical microemulsion sample was made by first dissolving 0.1 g of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock co-polymer (Pluronic P123, EO$_{20}$-PO$_{70}$-EO$_{20}$, MW ~ 5800, BASF) in 10 g of distilled water. To the aqueous polymer solution, 0 - 0.1 g of 1,3,5-trimethylbenzene or 1,2-dichlorobenzene (Aldrich) was slowly added. The resulting microemulsion was stirred for several hours and then allowed to equilibrate at room temperature for at least 48 h.

Two samples were made for each oil concentration: one used a mixture of H$_2$O and D$_2$O in the solvent such that the neutron scattering length density (SLD) of the solvent matched that of the polymer (~ $5 \times 10^{-7}$ Å$^{-2}$), and one in which both the solvent and oil were mixed with deuterated compounds in order to increase the contrast between oil, polymer and solvent.

2.3 Modeling

2.3.1 Thermodynamic Model of Microemulsion Structure
The basic structure of a PEO-PPO-PEO triblock copolymer micelle consists of a well-hydrated corona of PEO and a core that contains PPO. Previous SANS studies by Goldmints et al.$^{18}$ and Liu et al.$^{17}$ have taken slightly different approaches to this ‘core-shell’ model. Although PPO and PEO chains are indistinguishable in neutron scattering due to their nearly identical neutron scattering length densities, the greater hydration of the PEO chains means that the corona and core regions of PEO-PPO-PEO micelles in water can be clearly identified. Determining the distributions of polymer within these regions, however, is less straightforward. Both Goldmints et al.$^{18}$ and Liu et al.$^{17}$ have obtained the most accurate fits to neutron scattering data when they included small amounts of water in the PPO core. Both groups used a homogeneous distribution of PPO and water in the micellar core with PPO volume fractions of 80 - 97%. The PEO corona, on the other hand, contains a significant amount of water, and some researchers have estimated that three water molecules are hydrogen-bonded to each ethylene oxide (EO) unit.$^{29}$ Other investigations indicated a total hydration of approximately 20 water molecules per EO unit due to mechanical entrapment.$^{24}$ Therefore, the total PEO volume fraction in the corona is 10 - 40%, assuming a homogeneous distribution of PEO according to Goldmints et al.$^{18}$ Liu et al., however, use a Gaussian distribution
to describe the concentration of PEO from the core interface into the solvent, and have obtained accurate fits to neutron scattering data using this model without the need for a micelle polydispersity fitting parameter.\textsuperscript{17}

To the described PEO-PPO-PEO micelles, we now desire to add an oil solubilized in the PPO core. Even if we make the simplifying assumptions that the PPO core contains no water, since it now contains oil, and that PPO and PEO are homogeneously distributed in the core and corona, respectively, we are still left with at least five fit parameters, including the micelle polydispersity parameter, as shown in Figure 2.1. We have therefore employed a thermodynamic model for the solubilization of hydrocarbons in triblock copolymers developed by Nagarajan and Ganesh to predict the microemulsion droplet size and composition, thus reducing the number of free parameters necessary to fit the SANS data.\textsuperscript{15,25} The model is based on the ‘pseudophase’ approximation for micelle aggregation in which the swollen micellar aggregates are assumed to be a separate ‘phase’ in thermodynamic equilibrium with singly dispersed polymer and oil molecules in aqueous solution. Prior theoretical work has shown that the formation of a pure oil core at the center of the aggregate is less thermodynamically stable than a micellar core consisting of thoroughly mixed polymer and oil,\textsuperscript{26} therefore, only aggregates of the latter type are considered in this model. Furthermore, intermicellar interactions are neglected.

\textbf{Figure 2.1} Swollen micelle structure: (a) location of components, and (b) important parameters: \( R \) is the core radius, \( D \) is the corona (or shell) thickness, \( \phi_{\text{PPO}} \) is the volume fraction of PPO in the core that is assumed to be constant, and \( \phi_{\text{PEO}} \) is the volume fraction of PEO in the corona that is also assumed to be constant. Note that, including a micelle polydispersity parameter, there are five variables necessary for describing this simplified swollen micelle model.
and so the model is only strictly applicable to dilute solutions of swollen micelles. The mole fraction, $X_{gi}$, of aggregates containing $g$ polymer molecules and $j$ oil molecules is

$$X_{gi} = X^g_i X^j_i \exp \left( - \frac{g}{kT} \Delta \mu^0_{gi} \right)$$  \hspace{1cm} (2.1)

$$\Delta \mu^0_{gi} = \frac{1}{g} \mu^0_{gi} - \mu^0_i - \frac{j}{g} \mu^0_{ij}$$  \hspace{1cm} (2.2)

where $X_i$ and $X_{ij}$ are the mole fractions of singly dispersed polymer and oil molecules, respectively. $\Delta \mu^0_{gi}$ is the change in chemical potential due to the addition of one polymer molecule to the aggregate, $\mu^0_i$ is the standard state chemical potential of a singly dispersed polymer molecule, and $\mu^0_{ij}$ is the chemical potential of the oil in water, $k$ is Boltzmann's constant, and $T$ is the absolute temperature.

To simplify calculations, it has been assumed that the aggregates are monodisperse, and so the characteristics of the swollen micelle at equilibrium may be obtained by minimizing the chemical potential with respect to the number of polymer and oil molecules in the aggregate,

$$\frac{\partial}{\partial g} \left( \Delta \mu^0_{gi} \right) \frac{1}{kT} = 0, \quad \frac{\partial}{\partial j} \left( \Delta \mu^0_{gi} \right) \frac{1}{kT} = 0$$  \hspace{1cm} (2.3)

According to the theory of Nagarajan and Ganesh,\textsuperscript{13,15} the change in chemical potential due to aggregation is determined by seven components,

$$\Delta \mu^0_{gi} = \langle \Delta \mu^0_{gi} \rangle_{\text{PPO, dil}} + \langle \Delta \mu^0_{gi} \rangle_{\text{PPO, def}} + \langle \Delta \mu^0_{gi} \rangle_{\text{PEO, dil}} + \langle \Delta \mu^0_{gi} \rangle_{\text{PEO, def}}$$

$$+ \langle \Delta \mu^0_{gi} \rangle_{\text{sc}} + \langle \Delta \mu^0_{gi} \rangle_{\text{sw}} + \langle \Delta \mu^0_{gi} \rangle_{\text{loop}}$$  \hspace{1cm} (2.4)

in which $\langle \Delta \mu^0_{gi} \rangle_{\text{PPO, dil}}$ is the change in chemical potential due to dilution of the PPO block with oil in the micelle core, $\langle \Delta \mu^0_{gi} \rangle_{\text{PPO, def}}$ is due to the deformation of the PPO
block in the core to meet the uniform concentration constraint, \( \langle \Delta \mu^0_{\text{PEO,def}} \rangle \) is due to the dilution of PEO with water in the micelle corona, \( \langle \Delta \mu^0_{\text{PEO}} \rangle \) is due to the deformation of PEO in the corona, \( \langle \Delta \mu^0_{\text{loc}} \rangle \) is due to the localization of the PPO-PEO junction at the core-corona interface, \( \langle \Delta \mu^0_{\text{int}} \rangle \) is the change in chemical potential caused by the formation of the core-corona interface at which oil and water come into contact, and \( \langle \Delta \mu^0_{\text{loop}} \rangle \) is due to the formation of a loop in the PPO block so that both PPO-PEO junctions of the triblock copolymer can be at the core surface. The expressions for each of these chemical potential terms have been derived in references 13 and 25, thus only the results are summarized below.

\[
\frac{\langle \Delta \mu^0_{\text{PEO,def}} \rangle}{kT} = N_{\text{PPO}} \left[ \frac{v_{\text{PPO}}}{v_j} \left( \frac{1 - \phi_{\text{PPO}}}{\phi_{\text{PPO}}} \right) \ln \left( 1 - \phi_{\text{PPO}} \right) + \frac{v_{\text{PPO}}}{v_j} \left( 1 - \phi_{\text{PPO}} \right) \chi_{\text{PPO,1}} \right] \\
- N_{\text{PPO}} \left[ \frac{v_{\text{PPO}}}{v_w} \left( \frac{1 - \phi_{\text{PPO}}}{\phi_{\text{PPO}}} \right) \ln \left( 1 - \phi_{\text{PPO}} \right) + \frac{v_{\text{PPO}}}{v_w} \left( 1 - \phi_{\text{PPO}} \right) \chi_{\text{PPO,W}} + \left( \frac{\sigma_{\text{PPO,W}L_{\text{PPO}}^2}}{kT} \right) \frac{6}{\alpha_{\text{PPO}} N_{\text{PPO}}^2} \right] 
\]  

(2.5)

where \( N_{\text{PPO}} \) is the number of propylene oxide segments in the block; \( v_{\text{PPO}}, v_j \) and \( v_w \) are the molecular volumes of a PO segment, oil and water, respectively; \( \phi_{\text{PPO}} \) and \( \phi_{\text{PPO,1}} \) are the volume fractions of PPO in the micelle core and in the singly dispersed state, respectively; \( \chi_{\text{PPO,1}} \) and \( \chi_{\text{PPO,W}} \) are the Flory-Huggins interaction parameters for PPO/oil and PPO/water, respectively; \( \sigma_{\text{PPO,W}} \) is the interfacial surface tension of PPO and water; \( L_{\text{PPO}} \) is the length of a propylene oxide segment; and \( \alpha_{\text{PPO}} = (6/\pi)^{1/3} N_{\text{PPO}}^{1/3} \) is the chain expansion parameter of PPO (i.e. the difference between the unperturbed end-to-end PPO chain length and the length of the swollen PPO chain). The first two terms of equation 2.5 account for the enthalpy and entropy of mixing PPO and oil in the micelle core. The third and fourth terms represent the enthalpy and entropy of the PPO chain in the singly dispersed state that the chain leaves in order to join the aggregate, and the final term accounts for the disappearance of the PPO-water interface present in the singly dispersed state.

The change in chemical potential due to deformation of the PPO block is given by,

\[
\frac{\langle \Delta \mu^0_{\text{PEO,def}} \rangle}{kT} = \left[ \frac{3p^2}{40} \right] \frac{R^2}{\langle N_{\text{PPO}} / 2 \rangle L_{\text{PPO}}} - \left[ \frac{3}{2} (\alpha_{\text{PPO}}^2 - 1) - \ln \alpha_{\text{PPO}}^3 \right] 
\]  

(2.6)
where $R$ is the radius of the micelle core and all other variables are defined as in equation 2.5. This expression represents the difference in the configurational free energy of a single PPO chain confined to the micelle core and that of the PPO chain in aqueous solution. The first term of equation 2.6 accounts for the non-uniform deformation of the PPO necessary to achieve the homogeneous concentration of the core assumed in the model, and the second term represents the deformation of a singly dispersed polymer chain.

\[
\frac{\langle \Delta \mu^0 \rangle_{\text{PEO,dis}}} {kT} = N_{\text{PEO}} \left[ \frac{v_{\text{PEO}}}{u_w} \phi_{\text{PEO}} \ln (1-\phi_{\text{PEO}}) + \frac{v_{\text{PEO}}}{u_w} (1-\phi_{\text{PEO}}) \chi_{\text{PEO},W} \right] \\
-N_{\text{PEO}} \left[ \frac{v_{\text{PEO}}}{u_w} \phi_{\text{PEO},1} \ln (1-\phi_{\text{PEO},1}) + \frac{v_{\text{PEO}}}{u_w} (1-\phi_{\text{PEO},1}) \chi_{\text{PEO},W} \right]
\]  

(2.7)

Equation 2.7 takes into account the change in hydration of the PEO blocks of the polymer upon entering the micelle corona (first two terms) from its singly dispersed state (last two terms).

\[
\frac{\langle \Delta \mu^0 \rangle_{\text{PEO,cor}}} {kT} = \left[ \frac{3L_{\text{PEO}} R} {\alpha / 2 \phi_{\text{PEO}} 1 + (D/R)} \right] - \left[ 3 (\alpha_{\text{PEO}}^2 - 1) - 2 \ln \alpha_{\text{PEO}}^2 \right]
\]  

(2.8)

in which $a$ is the area of the core surface occupied by each PEO block and $D$ is the thickness of the micelle corona. The first term in equation 2.8 denotes the free energy of deformation of the PEO blocks in the micelle corona, while the second term represents the corresponding free energy of the PEO blocks in the singly dispersed state.

\[
\frac{\langle \Delta \mu^0 \rangle_{\text{cor}}} {kT} = -2 \ln \left[ \frac{3L_{\text{PEO}}} {R (1 + D/R)^3} \right]
\]  

(2.9)

Equation 2.9 accounts for the entropic penalty paid by forming a micelle due to the localization of the PPO-PEO junction at the core-corona interface.
\[
\frac{\Delta \mu^0_g}{kT} = \frac{a}{kT} \left[ \sigma_{\text{PPO},W} \phi_{\text{PPO}} + \sigma_{\text{W},W} (1 - \phi_{\text{PPO}}) \right]
\] (2.10)

In equation 2.10, \( \sigma_{\text{PPO},W} \) and \( \sigma_{\text{W},W} \) are the surface tensions of PPO-water and oil-water, respectively. It is assumed that the volume fraction of PEO in the corona is very small, and therefore all oil and PPO at the core surface are exposed to water (leading to the \( \sigma_{\text{PPO},W} \) and \( \sigma_{\text{W},W} \) terms).

\[
\frac{\Delta \mu^0_g}{kT} \bigg|_{\text{loop}} = \frac{3}{2} \beta \ln(N_{\text{PPO}})
\] (2.11)

The final term in the model accounts for the backfolding in the central PPO block that is required so that both terminal PEO blocks can be in the corona. In this expression, \( \beta \) is an excluded volume parameter that is assumed to be unity.

2.3.2 Neutron Scattering Model

The neutron scattering configuration used for our experiments is shown in Figure 2.2. The neutron scattering intensity, \( I(q) \), is reported as the neutron scattering cross-section, \( \sigma \), per unit solid angle, \( \Omega \), divided by the total sample volume, \( V \).

![Neutron scattering geometry](image)

**Figure 2.2** Neutron scattering geometry used in all SANS experiments. \( I_0 \) is the intensity of the incident neutron beam, \( I_t \) is the intensity of the transmitted neutron beam, \( k_i \) is the incident neutron wave vector, \( k_s \) is the scattered neutron wave vector, \( \theta \) is the scattering angle, and \( \Omega \) is the detector solid angle.
\[ l(q) = \frac{1}{V} \frac{\partial \sigma}{\partial \Omega} = \frac{\partial \Sigma}{\partial \Omega} \quad (2.12) \]

The overall neutron scattering cross-section comprises two terms, the coherent \((\sigma_{coh})\) and incoherent \((\sigma_{inc})\) scattering, \(\sigma = \sigma_{coh} + \sigma_{inc}\). The change in the incoherent scattering of neutrons with unit solid angle is constant, therefore, \(\partial \sigma_{inc}/\partial \Omega = C_{inc}\) and

\[ l(q) = \frac{\partial \Sigma_{coh}}{\partial \Omega} + \frac{C_{inc}}{V} \quad (2.13) \]

The differential coherent scattering cross-section per unit volume for particulate samples can be expressed as the product of the number density of particles, an intraparticle form factor that accounts for the scattering from the atoms in a single micelle, \(P(q)\), and an interparticle structure factor, \(S(q)\), which accounts for the interactions between micelles,\(^{21}\)

\[ \frac{\partial \Sigma_{coh}}{\partial \Omega} = \frac{N_p}{V} P(q)S(q) \quad (2.14) \]

where \(N_p\) is the total number of particles. Since we are working with very dilute solutions of swollen micelles, \(\sim 1 - 3\) vol\%, we assume that interparticle interactions are negligible and therefore, \(S(q) \sim 1\). The intraparticle form factor may be expressed as the square of the Fourier transform of the neutron scattering length density spatial distribution.

\[ P(q) = |F(q)|^2 = \left| \int_{\text{particle}} \left[ \rho(r) - \rho_s \right] \exp(\mathbf{i}q \cdot \mathbf{r}) d^3r \right|^2 \quad (2.15) \]

where \(\rho(r)\) is the neutron scattering length density (SLD) at position \(r\), and \(\rho_s\) is the scattering length density of the solvent.
Since the thermodynamic model for microemulsion formation assumes that the volume fractions of PEO in the corona and PPO in the core are homogeneous, the neutron scattering length density is therefore assumed to be constant within the core and the corona, such that:

\[
\rho(r) = \begin{cases} 
\rho_1 = \rho_{\text{PPO}} \phi_{\text{PPO}} + \rho_{\text{oil}} (1 - \phi_{\text{PPO}}), & \text{for } 0 \leq r \leq R_1 \\
\rho_2 = \rho_{\text{PEO}} \phi_{\text{PEO}} + \rho_{\text{water}} (1 - \phi_{\text{PEO}}), & \text{for } R_1 \leq r \leq R_2
\end{cases}
\] (2.16)

in which \(\rho_1\) and \(\rho_2\) are the scattering length densities of the core and the corona, respectively, \(\rho_{\text{PPO}}, \rho_{\text{PEO}}, \rho_{\text{oil}}\) and \(\rho_{\text{water}}\) are the SLDs of PPO, PEO, oil, and water. As above, \(\phi_{\text{PPO}}\) is the volume fraction of PPO in the core and \(\phi_{\text{PEO}}\) is the volume fraction of PEO in the corona. \(R_1\) is the core radius and \(R_2\) is the corona radius \(\text{(i.e. } R_2 = R_1 + D, \text{ where } D\text{ is the thickness of the corona)}\).

Substituting equation 2.16 into equation 2.15, multiplying by the overall particle number density, and integrating, we obtain:

\[
I_{\text{coh}}(q) = \frac{N_p}{V} \left[ \frac{4\pi}{3} R_1^3 (\rho_1 - \rho_2) \frac{3 j_1(qR_1)}{qR_1} + \frac{4\pi}{3} R_2^3 (\rho_2 - \rho_3) \frac{3 j_1(qR_2)}{qR_2} \right]^2
\] (2.17)

where \(j_1\) is a spherical Bessel function given by,

\[
j_1(x) = \frac{\sin(x) - x \cos(x)}{x^2}
\] (2.18)

Thus, equation 2.17 expresses the relation between the neutron intensity and the wave vector transfer for a suspension of non-interacting particles with cores of radius \(R_1\) and uniform SLD of \(\rho_1\), and coronas of radius \(R_2\) and SLD of \(\rho_2\). In order to fit the neutron scattering data with the neutron scattering model, we used a non-linear least-squares fitting algorithm that was developed at NIST. The fitting parameters used in this algorithm are the volume fraction of particles, \(\phi\), which is used to determine \(N_p/V\), the average core radius, \(R\), the corona thickness, \(D\), the core SLD, \(\rho_1\), the corona SLD, \(\rho_2\), the solvent SLD, \(\rho_3\), the incoherent background, and the core dispersity, \(p\). The polydispersity
of the micelle cores was expressed using the normalized continuous Schultz distribution,
\( f(r) \),
\[ f(r) = (z + 1)^{z+1} x^x \exp \left[ -(z+1)x \right] / r \Gamma(z+1) \]  \hspace{1cm} (2.19)

in which \( \bar{r} \) is the mean core radius, \( x = r/\bar{r} \), and \( z = (1 - p^2) / p^2 \), where the polydispersity is defined as \( p = \sigma / \bar{r} \), and \( \sigma^2 \) is the variance of the distribution. Including a polydisperse core in the model alters the form factor such that the size-average form factor is given by,
\[ P(q) = \overline{F^2(q)} = \int f(r) F^2(qr) \, dr \]  \hspace{1cm} (2.20)

### 2.4 Results and Discussion

#### 2.4.1 Model Confirmation with SANS and DLS Studies

The overall SANS fitting procedure described in equations 2.12 - 2.20 utilizes eight fitting parameters; therefore, to ensure the physical significance of our data fits, we employed the thermodynamic model (equations 2.1 - 2.11) to predict \textit{a priori} as many variables as possible. Each of our samples was made with a fixed oil-to-polymer mass ratio, so in determining the minimum free energy state of our systems from the thermodynamic model, the number of oil molecules per molecule of polymer in the aggregate was fixed, and the aggregation number of the micelle and the corona thickness were varied until a minimum in the change in chemical potential was found. Table 2.1 summarizes the values of the model parameters used in this study. Once the optimum aggregation number and corona thickness for a given oil-to-polymer ratio were found, the core radius, volume fraction of PPO in the core (and hence core SLD), and the volume fraction of PEO in the corona (leading to the SLD of the corona) could all be determined. So of the eight parameters in the neutron scattering model, only the total volume fraction of particles, the core polydispersity, the incoherent scattering background, and the solvent SLD were not predicted by the thermodynamic model. The volume fraction of particles
Table 2.1 Chemical Properties used in the Thermodynamic Model of Micellar Aggregation

<table>
<thead>
<tr>
<th>Component, i</th>
<th>Molecular Volume, ( v ) (Å³)</th>
<th>Molecular Length, ( L=v^{1/3} ) (Å)</th>
<th>Component i-Water Interfacial Tension, ( \sigma_{iw} ) (J/Å²)</th>
<th>Solubility Parameter, ( \delta_i ) (MPa¹/²)</th>
<th>Polymer-Water Interaction Parameter, ( \chi_{iw} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>96.5</td>
<td>4.6</td>
<td>2.6 \times 10^{-22}</td>
<td>19.0</td>
<td>2.1</td>
</tr>
<tr>
<td>PEO</td>
<td>64.6</td>
<td>4.0</td>
<td>8.0 \times 10^{-23}</td>
<td>20.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Heptane</td>
<td>243.0</td>
<td>6.2</td>
<td>5.1 \times 10^{-22}</td>
<td>15.1</td>
<td>-</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>179.0</td>
<td>5.6</td>
<td>5.0 \times 10^{-22}</td>
<td>16.8</td>
<td>-</td>
</tr>
<tr>
<td>TMB</td>
<td>232.0</td>
<td>6.1</td>
<td>3.6 \times 10^{-22}</td>
<td>18.4</td>
<td>-</td>
</tr>
<tr>
<td>Benzene</td>
<td>146.0</td>
<td>5.2</td>
<td>3.4 \times 10^{-22}</td>
<td>18.8</td>
<td>-</td>
</tr>
<tr>
<td>DCB</td>
<td>187.0</td>
<td>5.7</td>
<td>3.2 \times 10^{-22}</td>
<td>20.9</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>30.0</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

and the SLD of the solvent are easily controlled during sample preparation. The total volume fraction of micelles is simply the total volume of polymer and oil added to the solution (accounting for the concentration of singly dispersed polymer and oil determined from the known solubilities of the compounds) divided by the total sample volume. The neutron scattering length density of the water solvent is well known and can be adjusted by mixing H₂O and D₂O. The incoherent scattering background is used to fit the \( C_{inc} \) term in equation 2.13 and contains no structural information; therefore, its presence as a fit parameter does not detract from the interpretation of the structural data. The incoherent scattering is fit to the constant neutron scattering intensity at high \( q \), and therefore the core polydispersity is the only remaining fit parameter.

The results of the thermodynamic model were applied to the neutron scattering model and these curves were used to fit the neutron scattering data, initially with the core polydispersity as the only fit parameter. These initial ‘model’ fits to the neutron scattering data gave excellent results and subsequently, the core diameter and corona thickness of the micelle were varied slightly to improve the accuracy of the fit and to obtain the ‘experimental’ micelle dimensions. This procedure was used to fit scattering data from samples with the contrast increased between oil and water through the addition of
deuterated compounds in order to enhance the "core-shell" structure of the swollen micelles. It was also used for samples in which the solvent had been contrast-matched to the polymer, in effect making the scattering from the corona negligible and reducing the "core-shell" structure of the micelles to that of a simple sphere consisting of a mixture of polymer and oil. The model predictions of important parameters and the results of the most accurate 'experimental' fits are summarized in Table 2.2.

**Table 2.2 Pluronic Micelle Characteristics as Determined by Model Calculations and SANS Experiments**

<table>
<thead>
<tr>
<th>Oil Type, Mass Ratio</th>
<th>$R_{\text{experiment}}$ (Å)</th>
<th>$R_{\text{model}}$ (Å)</th>
<th>$R_{\text{matched}}$ (Å)</th>
<th>$D_{\text{experiment}}$ (Å)</th>
<th>$D_{\text{model}}$ (Å)</th>
<th>Polydisp.</th>
<th>$q_{\text{PPO}}$</th>
<th>$q_{\text{PEO}}$</th>
<th>$g$</th>
<th>$a^d$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMB 0.10</td>
<td>70</td>
<td>71</td>
<td>60</td>
<td>20</td>
<td>25</td>
<td>0.15</td>
<td>0.66</td>
<td>0.25</td>
<td>190</td>
<td>333</td>
</tr>
<tr>
<td>TMB 0.20</td>
<td>76</td>
<td>77</td>
<td>67</td>
<td>20</td>
<td>22</td>
<td>0.15</td>
<td>0.75</td>
<td>0.25</td>
<td>211</td>
<td>351</td>
</tr>
<tr>
<td>TMB 0.34</td>
<td>89</td>
<td>85</td>
<td>73</td>
<td>20</td>
<td>22</td>
<td>0.15</td>
<td>0.64</td>
<td>0.25</td>
<td>247</td>
<td>371</td>
</tr>
<tr>
<td>TMB 0.53</td>
<td>100</td>
<td>95</td>
<td>93</td>
<td>18</td>
<td>22</td>
<td>0.15</td>
<td>0.53</td>
<td>0.24</td>
<td>287</td>
<td>399</td>
</tr>
<tr>
<td>TMB 1.05</td>
<td>100</td>
<td>115</td>
<td>95</td>
<td>18</td>
<td>20</td>
<td>0.18</td>
<td>0.37</td>
<td>0.23</td>
<td>347</td>
<td>481</td>
</tr>
<tr>
<td>DCB 0.22</td>
<td>65</td>
<td>69</td>
<td>68</td>
<td>20</td>
<td>22</td>
<td>0.15</td>
<td>0.86</td>
<td>0.26</td>
<td>177</td>
<td>340</td>
</tr>
<tr>
<td>DCB 0.55</td>
<td>82</td>
<td>84</td>
<td>85</td>
<td>20</td>
<td>22</td>
<td>0.15</td>
<td>0.64</td>
<td>0.24</td>
<td>232</td>
<td>380</td>
</tr>
<tr>
<td>DCB 1.06</td>
<td>110</td>
<td>98</td>
<td>103</td>
<td>18</td>
<td>21</td>
<td>0.17</td>
<td>0.47</td>
<td>0.23</td>
<td>277</td>
<td>436</td>
</tr>
</tbody>
</table>

a) $R_{\text{matched}}$ is the radius of the micelle core experimentally determined from samples in which the scattering length density of the water has been matched to that of the polymer, rendering the corona undetectable. b) Values for the volume fractions of PPO in the micelle core and PEO in the micelle corona were obtained from the thermodynamic model and used unchanged in the fitting of the SANS data. c) $g$ represents the polymer 'aggregation number', i.e. the total number of polymer molecules in one micelle. The polymer aggregation number was determined using the model. d) $a$ is the core surface area per polymer molecule. The values listed were obtained from the model.

The fits to both contrast-matched and contrast-enhanced samples using 1,3,5-trimethylbenzene and 1,2-dichlorobenzene as the swelling agents are shown in Figure 2.3. The accuracy of the fits to data from both contrast-matched samples (Figures 2.3(a) and 2.3(c)) and contrast-enhanced samples (Figure 2.3(b) and (d)) indicates that the approximations of a homogeneous mixture of oil and polymer in the core and of a homogeneous volume fraction of PEO in the corona are reasonable ones.
Figure 2.3 Neutron scattering data (symbols) and the most accurate data fits (solid curves) for (a) samples containing TMB in which the neutron scattering length density of the water has been matched to that of the polymer, with TMB-to-polymer mass ratios of (O) 0.34, (■) 0.20 and (x) 0.10; (b) samples containing TMB in which the contrast between water and polymer has been enhanced to clarify the 'core-shell' micelle structure, with TMB-to-polymer mass ratios of (O) 1.05, (■) 0.55 and (x) 0.20; (c) contrast-matched samples containing DCB, with DCB-to-polymer mass ratios of (O) 1.06, (■) 0.55 and (x) 0.22; (d) contrast-enhanced samples containing DCB, with DCB-to-polymer mass ratios of (O) 1.06, (■) 0.55 and (x) 0.22.
The accuracy of the thermodynamic model in predicting the micelle structure can be seen in Figure 2.4, in which the overall micellar diameter from the most accurate fits to the SANS data and the initial predictions from the model are plotted against the volume of oil added. Figure 2.4 and Table 2.2 show that the model provides a very good starting point for the data fit, predicting the micellar diameter to within 5% accuracy for oil-to-polymer mass ratios below 0.5. The thermodynamic model correctly predicts the monotonic increase in micellar diameter with increasing oil content, although the micelle diameter predicted by the model tends to increase slightly less rapidly with increasing oil content than is experimentally observed. Furthermore, dynamic light scattering (DLS) studies of the oil-swollen micellar solutions have been performed to provide an independent confirmation of the micelle polydispersities obtained from our fits to the neutron scattering data. DLS experiments showed that the polydispersities of our oil-polymer aggregates ranged from 10 to 19%, in good agreement with the neutron scattering polydispersities of 15 - 18% shown in Table 2.2. Thus, all of the structural fit parameters from the neutron scattering model have been either theoretically predicted or confirmed by an independent technique.

As seen in Table 2.2 for both TMB and DCB mass ratios of ~ 1.0, the model predictions become less accurate at high oil concentrations. This is expected for two reasons: first, polymer chains behave differently at high extensions, and second, oil-to-polymer ratios greater than 0.4 for TMB and 0.5 for DCB are above the microemulsion stability limit. The PPO blocks in the core become considerably extended as the core swells with oil. At the maximum oil:polymer ratio used in this study (TMB:P123 ~ 1), the experimentally determined core radius is 100 Å. It is assumed that the extended PPO block length is roughly equivalent to the core diameter since the PPO block must double over to ensure that both PEO blocks are in the corona. The contour length or end-to-end distance of the
fully extended PPO block ($N \cdot L$) is $\approx 160$ Å and that of the unperturbed PPO block ($N^{1/2} \cdot L$) is $\approx 38$ Å. Thus, the maximum observed extension is roughly $2/3$ of the maximum extension, and $\approx 3$ times the unperturbed distance. It is noted by Kuhn and Grün²⁵ and by James and Guth²⁶ that the simple model of a freely jointed Gaussian chain must be modified at extensions beyond approximately $1/2$ of the maximum. Furthermore, the PPO and PEO block deformation expressions given in equations 2.6 and 2.8 do not limit the length of the blocks to their contour length and are therefore highly suspect at large extensions.

While the treatment of polymer chains at high extensions is one source of error at high oil contents, the transcendence of the microemulsion stability limit or cloud point is undoubtedly another. Above the cloud point, P123 solutions containing an oil phase segregate into a Windsor type I microemulsion (i.e. an oil-rich phase and an aqueous phase containing microemulsion droplets). The thermodynamic model was not intended to accurately predict the structure of swollen micelles beyond the phase separation point, however, it can offer important insight into the factors leading to the formation of a separate oil-rich phase. It has been shown in previous theoretical work that the oil solubilized by Pluronic surfactants does not readily form a separate oil core, and therefore the Pluronic-oil aggregates are most accurately described as swollen micelles rather than microemulsion droplets.²⁸ This trait means that the assumption of a homogeneous polymer-oil mixture in the core of the micelle is reasonable up to the phase separation point, but it also means that the size of the micellar core is limited by the contour length of the hydrophobic PPO block. Stretching the PPO block to reach the center of the micelle and thus preventing the formation of a pure oil core significantly decreases the entropy of the aggregate and therefore destabilizes the micelle. One way to solubilize more oil without further stretching the PPO block is to form smaller but more numerous micelles. The formation of more micelles, however, increases the overall core surface area and hence increases the core surface area per polymer molecule, $a$. The increase in $a$ leads to increased oil-water interactions that also destabilize the swollen micelle and eventually lead to formation of a separate oil phase. As shown in Table 2.2, the model predicts that $a$ steadily increases with increasing oil content and that the cloud point seems to be reached at a surface area of 400 Å² per polymer molecule. The position of the microemulsion stability limit also explains why the neutron scattering data for samples with TMB:P123 of 0.53 and 1.05 shown in Figure 2.3(b) are nearly identical. The
swollen micelles apparently do not grow after the cloud point has been reached, with all of the additional oil going into the oil-rich phase.

The high solubilization capacity and selectivity of Pluronic surfactants for aromatic over aliphatic hydrocarbons has been noted. This preference for aromatics is likely due to stronger dipole/induced-dipole interactions between the permanent dipole of PPO and the more easily induced dipole of an aromatic (relative to an aliphatic) molecule. However, the greater polarity of 1,2-dichlorobenzene relative to 1,3,5-trimethylbenzene appears to have little effect on the volumetric solubility of the two compounds. As seen in Figure 2.4, the micelle diameters of DCB and TMB swollen samples are nearly identical at the same oil volumes. Small differences are noted in the aggregation number and surface area per polymer molecule for the DCB- and TMB-swollen samples. The DCB-swollen samples have lower aggregation numbers and higher surface areas per polymer molecules than the TMB-containing samples due to the more favorable interactions between DCB and water. A difference between DCB and TMB solutes is also present in the agreement between the core radii of contrast-matched samples ($R_{\text{matched}}$) and the radii of contrast-enhanced samples ($R_{\text{experiment}}$). For DCB-containing samples, the agreement between $R_{\text{matched}}$ and $R_{\text{experiment}}$ in Table 2.2 is good. In the case of TMB-containing samples, $R_{\text{matched}}$ is consistently ~ 10 Å lower than $R_{\text{experiment}}$. This may be an indication that the TMB is not perfectly homogeneously distributed in the core, and that the TMB concentration decreases close to the core-corona interface, again indicative of the poorer interactions of TMB and water compared to those between DCB and water.

2.4.2 The Effects of Alcohol and Acid on Swollen Polymer Micelles

In addition to studying the structure of the swollen micelles, we also investigated the effects of alcohols and acids on the size and structure of the swollen micelles. In the first set of experiments, small amounts of ethanol were added to a solution of polymer in water. The addition of ethanol to the polymer solution immediately decreased the volume fraction of micelles in the solution, as seen in Figure 2.5, indicating that very small amounts of ethanol act to increase the solubility of the singly dispersed polymer and hence reduce the micelle volume fraction. However, when the size of the pure polymer micelles is compared with ethanol content, as in Figure 2.6, there is very little change in micellar diameter for the range of ethanol concentrations studied.
Figure 2.5 The volume fraction of micelles relative to the volume fraction at 0 ethanol content (θ_{M0}) plotted against the ethanol:polymer mass ratio for (▲) TMB;polymer = 0.5, (■) DCB;polymer = 0.5, and (x) pure polymer. The relative volume fraction of micelles was determined from the absolute neutron scattering intensity at q = 0, \( \sqrt{I(0)/I_0(0)} = \theta_{M} / \theta_{M0} \).

Figure 2.6 Micellar diameter determined from SANS experiments versus the volume of oil added per mole of polymer for samples with an ethanol:polymer mass ratio of (x) 0, (■) 1 and (▲) 2. (a) TMB and (b) DCB were employed as the solute. Note that there is negligible change in the micellar diameter with changing ethanol concentration for samples that contain no oil.
Neutron scattering data were also collected for micellar solutions containing TMB or DCB to which various amounts of ethanol had been added (see Figures 2.5 and 2.6). The data in Figure 2.5 indicate that ethanol has a very different effect on oil-swollen micelles than it does on pure polymer micelles. Instead of decreasing the total volume fraction of micelles in the solution, as was seen for the pure polymer micelles, ethanol appears to increase the total volume fraction of oil-swollen micelles. From Figure 2.6(a) it can be seen that ethanol has very little effect on the size of the swollen micelles until phase segregation occurs at an oil-to-polymer mass ratio of ~ 0.4 (oil volume/mole polymer ~ 6000 Å³).

After phase separation, the presence of ethanol appears to allow slightly larger micelles to form in the aqueous phase of type I microemulsion. As mentioned previously, one cause of swollen micelle destabilization is an increase in the surface area per polymer molecule with increasing oil content, which allows for a greater number of unfavorable oil-water interactions. Addition of ethanol to the solution decreases the oil-water surface tension and allows stable swollen micelles to form with slightly lower polymer surface concentrations. The effects of ethanol on the structure of DCB-swollen micelles were slight. It should be noted, however, that none of the DCB-containing samples to which ethanol was added were significantly beyond the phase segregation limit.

Dynamic light scattering studies have been performed on swollen micellar solutions to which HCl had been added. These experiments are significant since HCl will be present in the mesoporous silica templating solutions in order to catalyze the hydrolysis and condensation of the silica precursors. Figure 2.7 shows a plot of the micellar diameter of various swollen P123 systems with different HCl contents. The micellar diameter increases with HCl concentration due to the effect of ionic strength on the solubility of PEO in water. PEO is less soluble in solutions containing a high concentration of Cl⁻ ions,
and the change in PEO solubility affects the hydrophilic-lipophilic balance in the polymer leading to large polymer aggregates with high aggregation numbers.

2.4.3 Model Predictions
The accuracy of the thermodynamic model for polymer-oil aggregation was clearly established using SANS and DLS experiments on the P123/TMB or P123/DCB systems. The fact that the model predicted the values of the neutron scattering variables to within 5 - 10% of their optimal values and that the only unconstrained fit parameter for the neutron scattering data was the polydispersity of the micelles, the value of which was confirmed to be reasonable by comparison to DLS data, gave us confidence that the model could be successfully used to predict the size and structure of other polymer-oil systems. The model was therefore used to predict the effects of varying the size of the PPO hydrophobic segments in the Pluronic triblock copolymers and to determine the effects of changing the length of the PEO end-blocks. The model was also used to estimate the effect of changing the oil type on the size of the micelles.

2.4.3.1 Effect of Changing Polymer Type
There are two main variables that define the Pluronic triblock copolymers, the polymer molecular weight and the PEO-to-PPO ratio. Using the thermodynamic model proposed by Nagarajan and Ganesh, we have investigated the effects of polymer molecular weight and composition on the size and structure of swollen Pluronic micelles. In the modeling of all polymer variations, 1,3,5-trimethylbenzene was used as the swelling agent and the oil-to-polymer mass ratio was held constant at 0.2. First, in order to predict the effects of changing the Pluronic molecular weight, we fixed the composition of the triblock copolymer to be 30 wt% PEO, which is the same composition used in the base-case modeling and neutron scattering studies discussed in Section 2.4.1, and the same as that used in the mesoporous silica synthesis experiments of Zhao et al. The size of the polymer used in the model was varied from ~ 3400 to 8400 g/mol, resulting in a variation of the central block from 40 to 100 propylene oxide units in length. Second, to investigate the effects of changing the PEO-to-PPO ratio, the length of the central PPO
block was held constant in the model at 70 propylene oxide units, and the length of the PEO end chains was varied from 5 to 50 ethylene oxide units each.

The model results from changing the amphiphilic triblock copolymer structure are summarized in Figure 2.8 and Table 2.3. The model results show that for Pluronic micelles swollen with TMB, increasing the molecular weight of the polymer, and thereby increasing the length of the central PPO block, increases the size of the micellar core in a nearly monotonic fashion (Figure 2.8). The increase in core size with increasing polymer molecular weight is expected for two reasons: a longer PPO chain may be extended further without incurring significant entropic penalties, and for polymers of similar composition, a higher molecular weight polymer is less soluble in water, leading to higher aggregation numbers (see Table 2.3) and therefore larger core volumes. Figure 2.8 also shows that for Pluronics with the same PPO block length, higher PEO content leads to micelles with smaller cores. This effect of PEO content is primarily due to the increased solubility of polymer containing large amount of PEO. Since polymers with high PEO fractions can more effectively screen unfavorable PPO-water interactions even in a singly dispersed state, micelles with low aggregation numbers, \( g \), become more stable and therefore the core size decreases.

![Figure 2.8](image)

*Figure 2.8* Model results for the effects of changing polymer molecular weight and composition on the radius of the micellar core. The core radius increases as the molecular weight of the polymer increases (\( \Delta \)), at a fixed composition of 30 wt% PEO and a TMB:polymer mole ratio of 12:1. The core radius decreases as the fraction of PEO in the polymer increases (\( \square \)), at a fixed PPO block length of 70 propylene oxide units and a TMB:polymer mole ratio of 12:1.
Table 2.3 Effects of Changing Pluronic Molecular Weight and Composition on Micellar Size

<table>
<thead>
<tr>
<th>$N_{PEO}^a)$</th>
<th>$M_{PPO}^b)$</th>
<th>$R_{model}$ (Å)</th>
<th>$D_{model}$ (Å)</th>
<th>$\varphi_{PPO}^c)$</th>
<th>$\varphi_{PEO}^d)$</th>
<th>$g^e)$</th>
<th>$a^f$ (Å²)</th>
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<td>80</td>
<td>22</td>
<td>0.71</td>
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<td>225</td>
<td>358</td>
</tr>
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<tr>
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<td>47</td>
<td>0.71</td>
<td>0.17</td>
<td>135</td>
<td>424</td>
</tr>
</tbody>
</table>

a) Total number of ethylene oxide units in the polymer. b) Number of propylene oxide units in the polymer. c) Volume fraction of PPO in the micellar core. d) Volume fraction of PEO in the micelle corona. e) Polymer 'aggregation number', i.e. the total number of polymer molecules in one micelle. f) Core surface area per polymer molecule.

From modeling the effects of polymer variation on micellar size, it appears that a polymer with the largest possible PPO block length and the smallest possible PEO fraction would yield micelles with the largest hydrophobic core size (for a constant amount of swelling agent), and therefore should template the largest pores in condensed silica structures. There are limitations to these trends that are not addressed by the model, however, since a polymer that is too large with too low of a PEO content will not be sufficiently soluble in water or may not possess the necessary surface activity to solubilize significant amounts of oil. For example, a high molecular weight Pluronic with ~ 10 wt% PEO is much less soluble in water than one with 30 wt% PEO, and in an oil-water mixture it tends to form reverse micelles swollen by water in a separate oil phase. Thus, to create stable oil-in-water microemulsions with the largest core diameter possible, Pluronics with PEO contents of ~ 30 wt% and large PPO blocks should be used. The Pluronic with the largest PPO block (~ 70 PO units) and 30 wt% PEO is P123.
2.4.3.2 Effect of Changing Oil Type

The thermodynamic model for polymer aggregation was used to study the effects of changing oil type on the structure of the swollen micelles. The types of oil investigated were chosen to represent a variety of different interactions between oil and polymer as well as oil and water. The strength of the oil’s interactions with the polymer is expressed in the Flory-Huggins interaction parameter, $\chi_{\text{PPO-oil}}$. The Flory-Huggins interaction parameter provides an estimate of the enthalpy of mixing between the oil (the “solvent”) and the PPO core of the micelle (the “solute”),

$$\Delta H_{\text{PPO-oil}}^{\text{mix}} = RT \chi_{\text{PPO-oil}} \phi_{\text{PPO}} n_{\text{oil}}$$  \hspace{1cm} (2.21)

in which $\phi_{\text{PPO}}$ is the volume fraction of polymer and $n_{\text{oil}}$ is the number of moles of oil. The interaction parameter may be calculated from the Hildebrand solubility parameters of the oil, $\delta_{\text{oil}}$, and the polymer, $\delta_{\text{PPO}}$.

$$\chi_{\text{PPO-oil}} = \frac{v (\delta_{\text{oil}} - \delta_{\text{PPO}})^2}{RT}$$  \hspace{1cm} (2.22)

where $v$ is the molar volume of the oil, which is assumed to be the same as the molar segmental volume of the polymer. Thus, compounds with similar solubility parameter values will have small positive enthalpies of mixing, indicating more favorable interactions than those between compounds whose solubility parameters are substantially different.

To obtain more detailed information about the nature of the interactions between compounds, Hansen has developed a three-dimensional solubility parameter that separately accounts for the contributions to the overall solubility parameter from dispersion (van der Waals or London) forces ($\delta_d$), hydrogen-bonding forces ($\delta_h$), and permanent dipole interactions ($\delta_p$). The overall solubility parameter is expressed as,

$$\delta^2 = \delta_d^2 + \delta_h^2 + \delta_p^2$$  \hspace{1cm} (2.23)

and using the three-dimensional Hansen solubility parameter, the Flory-Huggins interaction parameter is given by,

$$\chi_{\text{PPO-oil}} = \frac{v \left[ (\delta_{d,oil} - \delta_{d,PPO})^2 + (\delta_{h,oil} - \delta_{h,PPO})^2 + (\delta_{p,oil} - \delta_{p,PPO})^2 \right]}{RT}$$  \hspace{1cm} (2.24)
So, according to Hansen, the strength of each type of interaction (dispersive, hydrogen bonding, and dipolar) must be matched between the solute and the solvent to obtain good solubility. Since PPO possesses a permanent dipole and may act as a hydrogen bond acceptor as well as participating in dispersion interactions, we have selected three different types of oils for our modeling studies: those with weak dispersion interactions and no permanent dipole (cyclohexane), those with significant dispersion interactions and no permanent dipole (TMB, benzene), and that with strong dispersion interactions and a permanent dipole (1,2-dichlorobenzene). Shown in Figure 2.9 is a plot of the micellar core radius obtained from the thermodynamic model versus the volume of oil added per molecule of P123. Figure 2.9 shows that oils that have less favorable interactions with PPO tend to form larger micelles; however, it is the oil's interactions with water that truly determine the micellar size in this model, and the strength of the oil-water interactions happen to correlate to the strength of the oil-PPO interaction for the oils investigated. Large aggregates form in systems swollen by oils with high oil-water interfacial tensions in order to minimize the oil-water interfacial surface area, while those with more stable core-corona interfaces are driven by entropy to form smaller aggregates.

![Figure 2.9](image)

**Figure 2.9** Model results for the effects of changing oil type on the radius of the micellar core. The properties of micelles swollen by five different oils have been investigated: heptane (□), cyclohexane (●), 1,3,5-trimethylbenzene (△), benzene (○), and 1,2-dichlorobenzene (×).
It appears that using oils with less favorable interactions with water would produce the best systems for templating large pores, but again trade-offs exist. The correlation between oil-water interactions and oil-polymer interactions shows that oils that cause larger aggregates to form, also destabilize the micelles through unfavorable PPO-oil interactions. Table 2.4 gives the experimentally determined solubility limits for various oils. From Table 2.4, one can see that even though heptane may result in the formation of larger micelles per volume of oil added, only a small amount of this oil can be solubilized; therefore, to obtain larger micelles it is better to use an oil with a higher solubility that still has a reasonably high oil-water interfacial tension, such as TMB.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Solubility Limit (g oil / g PPO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>0.15</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.36</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>0.54</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.58</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>0.58</td>
</tr>
</tbody>
</table>

**Table 2.4 Solubility Limits for Various Oils in Water-Pluronic Solutions**

2.5 Summary
There have been numerous studies exploring the structure of pure Pluronic micelles through the use of small-angle neutron scattering and there have been several theoretical attempts to describe the internal structure of Pluronic micelles swollen with oil; however, most of the theoretical models have been confirmed by comparing their predictions to experiments involving macroscopically observed phenomena, such as phase separation, while the models themselves can provide more rich and detailed information. We have compared the structural predictions of a thermodynamic model for the formation of Pluronic-oil aggregates, developed by Nagarajan and Ganesh,\textsuperscript{13} to our SANS data. The thermodynamic model accurately predicts the volume fraction of oil inside the micellar core and the volume fraction of water in the micellar corona. It also estimates the sizes of the core and corona to within 15% of the experimental values. The success of the thermodynamic model in predicting the internal structure of the swollen micelles is especially important given the large number of parameters that would
otherwise be required to fit the SANS data for this complex system. The good agreement between theory and experiment found in this work gives us a reliable structure for the swollen micelles. Knowledge of this structure has been used to investigate the effects of changing polymer and oil types on the size of the swollen micelles and therefore to select the best systems for templating large pores in silica sol-gels.

From modeling the effects of changing polymer molecular weight and composition on the size of the swollen micelles, it was determined that polymers with high overall molecular weights but low PEO contents would yield the largest micelles. However, if the PEO content is below 20 - 30 wt%, the system will undergo phase separation. Modeling of various swelling agents indicated that oils with high oil-water interfacial surface tensions would yield micelles with the largest diameters, however, such oils tend to interact poorly with PPO and are not sufficiently soluble in the micellar cores to produce aggregates of the desired size. Favorable oil-PPO interactions leading to high oil solubilities are therefore the most important factor for obtaining large swollen micelles for the templating of ulralarge-pore mesostructured silica materials.

The investigation of swollen micelles also included a study of the effects of ethanol and HCl on these systems. These studies are significant since silicon alkoxides will be used as the silica source in the templating solution, and HCl will be necessary to catalyze the hydrolysis and condensation of the alkoxides, and alcohol will be released during hydrolysis. It was found that ethanol had little effect on the structure of the swollen micelles below the phase segregation limit, but that ethanol did appear to increase oil solubility, resulting in larger micelles above the phase segregation point. The presence of HCl in the micellar solution tended to increase the size of the oil-polymer aggregates due to the decreasing solubility of PEO with increasing solution ionic strength, which leads to an effectively more hydrophobic polymer that forms micelles with higher aggregation numbers.
2.6 References


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CHAPTER 3
The Synthesis and Characterization of Mesocellular Foams

3.1 Introduction
The initial success of using PEO-PPO-PEO triblock copolymers (Pluronic) to template mesostructured silicas with large pore sizes (5 - 7 nm in diameter)\textsuperscript{1,2,3} provides an excellent starting point for synthesizing materials with even larger pore diameters; however, much is not well understood about the formation mechanism of polymer-templated mesoporous silicas, so rational methods for increasing the pore size and manipulating the pore geometry have not been established. In particular, the work of Zhao et al.\textsuperscript{3} utilized low concentrations of Pluronic polymers to template silica mesostructures (SBA-15 materials) reminiscent of polymer liquid-crystalline phases that form at high concentrations, and yet no explanation of this transformation was provided. In Chapter 2, we verified that polymer solutions of the concentrations used by Zhao et al.\textsuperscript{3} form suspensions of well-dispersed spherical polymer micelles, but the silica mesostructures templated by these solutions consist of hexagonally packed arrays of cylindrical pores. Dynamic light scattering (DLS) and small-angle neutron scattering (SANS) studies of the polymer micelle solutions discussed in Chapter 2 have shown that while HCl and ethanol present in the synthesis solutions can alter the size of the micelles, they do not, by themselves, change the shape of the polymer aggregates. Various oils have been added to the polymer solutions in order to swell micellar cores and thus increase the pore size of the final silica material, but again, no transformation in the shape of the polymer micelles was detected upon addition of the oil.

In this Chapter, we investigate the effects of polymer type, oil type and concentration, as well as silica concentration on the pore size and structure of templated mesoporous silicas. We have found that the addition of aromatic swelling agents to Pluronic solutions leads to the formation of a novel mesocellular silica foam (MCF) material. MCF consists of spherical cavities with diameters of 220 - 350 Å interconnected to neighboring cells by ‘windows’ of ~ 80 - 150 Å. We have also used our experimental data to develop a coherent synthesis mechanism capable of explaining the transitions from well-dispersed spherical polymer micelles to hexagonally packed cylinders of polymer in a silica matrix,
and from these cylindrical composites to mesocellular foams upon the addition of oil. The formation of other Pluronic-silica composite structures is also discussed in the context of our synthesis mechanism.

3.2 Experimental Procedures

3.2.1 Material Synthesis
In the following syntheses, all materials were used as received from the vendors without further purification. Distilled water was used in all cases. Samples were prepared by first dissolving poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer in 1.6 M HCl at 35°C. Three different Pluronics were used, all supplied by BASF: P123 (MW = 5800, EO20PO70EO20), F127 (MW = 13500, EO100PO70EO100), P84 (MW = 3800, EO12PO45EO12). The acid was added to catalyze the hydrolysis and condensation of the silicon alkoxides to form silica. In a typical synthesis, 2 g of polymer (~0.4 mmol) was added to 85 g of the acidic solution. Amounts of oil ranging from 0 to 2 g were then added to the polymer solution, and the mixture was stirred for at least 1 h. Several different oils were used in the synthesis, including 1,3,5-trimethylbenzene, 1,2-dichlorobenzene, benzene, cyclohexane and heptane, all obtained from Aldrich. Tetraethylorthosilicate (TEOS, Aldrich, 4.25 g, 21 mmol) was added as the silica source. After stirring for 24 h at 35°C and aging for 48 h at 100°C, the solids were collected by filtration, rinsed with water and ethanol, and then dried in air. The resulting powder was calcined at 550°C for 6 h to remove residual polymer and to complete silica condensation, thus producing the mesoporous silica material. A schematic diagram of the material synthesis is provided in Figure 3.1.

3.2.2 Material Characterization
The calcined mesoporous silica materials have been characterized by nitrogen adsorption analysis, small-angle X-ray scattering (SAXS), dynamic light scattering, and transmission electron microscopy (TEM). Nitrogen adsorption experiments were performed on a Micromeritics ASAP 2010 instrument. From the nitrogen sorption measurements, the
surface area of the materials was determined using the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined using the approach of Broekhoff and de Boer in conjunction with Hill's approximation for the thickness of the adsorbed nitrogen layer.\textsuperscript{5} This technique is discussed more fully in Section 3.3.1. A Siemens SAXS instrument (sample-to-detector distance = 60 cm, non-monochromated Cu source operating at 40 kV and 30 mA) was used for structural analysis. For TEM studies, a JEOL JEM-200CX microscope (W filament, 200 kV) was employed.

**Polymer:** Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide), MW = 5,800

**Silica Source:** Tetraethoxysilane (TEOS)

**Oil:** 1,3,5-Trimethylbenzene

**Mesoporous Silica Synthesis Procedure**

- Polymer
- Water + HCl
- Oil
- TEOS
- condense at 100°C for 48 h
- filter, dry, calcine at 550°C for 6 h
- Final Mesoporous Material

**Figure 3.1** Schematic representation of the polymer-templated mesoporous silica synthesis. The Pluronic polymer (e.g. P123) is first dissolved in water with 1.6 M HCl. Oil (such as 1,3,5-trimethylbenzene) is then added to the solution. The silica precursor (tetraethoxysilane) is added with vigorous stirring. The mixture is aged at 35°C for 24 h and subsequently the temperature is raised to 100°C for an additional 48 h. After aging, the material is filtered and washed with water and ethanol, allowed to dry in air for 24 h, and finally calcined at 550°C for 6 h.
3.3 Results and Discussion

3.3.1 The Synthesis of Mesocellular Silica Foams and the Effect of Oil Concentration

Initially, the synthesis of SBA-15 materials was reproduced to yield mesoporous materials with cylindrical pores packed in hexagonal arrays, as shown in Figure 3.2. The SAXS pattern of SBA-15 is shown in Figure 3.3, and the presence of higher order scattering peaks at d-spacings of 1/\sqrt{3} (110) and 1/2 (200) of the primary (100) peak d-spacing confirmed the p6mm symmetry of SBA-15. The nitrogen adsorption-desorption isotherms for SBA-15 are shown in Figure 3.4. The SBA-15 material was ~ 800 m²/g in surface area, with a pore volume of 1 cm³/g and a median pore diameter of 6 - 7 nm. For the determination of the median pore diameter from nitrogen adsorption data, we used the algorithm developed by Lukens et al., who described the shape of the liquid (nitrogen) meniscus in the pores according to the method of Broekhoff and de Boer, but used the more computationally tractable description of the adsorbed nitrogen layer thickness proposed by Hill and coworkers. Lukens et al. have dubbed their approach the BdB-FHH method of pore size analysis. In the pore size analysis of SBA-15 using the BdB-FHH method, the pores were assumed to be cylindrical and to have uniform diameter, which provided an accurate description of the material based on the TEM in Figure 3.2. However, the slight
Figure 3.4 Nitrogen adsorption-desorption isotherms for SBA-15. The pore sizes were determined from each sorption branch using the BdB-FHH method, assuming a cylindrical pore geometry.

hysteresis between the adsorption and desorption isotherms shown in Figure 3.4 indicated some non-uniformities in the cylindrical pores, which might lead to bottle-necks that prevent the escape of nitrogen from the pores, resulting in the lower desorption pressures. Despite the minor non-uniformities in the pores, the 6 - 7 nm pore size determined by the BdB-FHH method correlated well with the pore dimensions measured using TEM.

1,3,5-trimethylbenzene (TMB) was added to the base SBA-15 synthesis solution as a swelling agent. The effects of changing oil type are discussed in Section 3.3.2, and the effects of using different Pluronic polymers is addressed in Section 3.3.3. Unless otherwise noted, the amount of oil added to the templating solution is stated as the oil-to-polymer mass ratio.

When the trimethylbenzene-to-polymer mass ratio was less than 0.2, the P123-TMB aqueous solution templated slightly swollen SBA-15 structures with pore diameters ranging from 6 nm (for TMB:P123 = 0) to 11 nm (for TMB:P123 = 0.2). The presence of \( p6mm \) symmetry in the swollen SBA-15 materials was confirmed by SAXS, which revealed three scattering peaks with the same \( d \)-spacing relationships as for unswollen SBA-15 and MCM-41. The SAXS pattern for a sample with TMB:P123 = 0.1 is shown in Figure 3.5(a).

The increase in the \( d \)-spacing of the (100) X-ray scattering peak with increasing oil content indicated the swelling effects of TMB on the final mesoporous silica, but the change in diameter of the actual cylindrical pores was monitored using TEM and \( N_2 \) adsorption analyses. The transmission electron micrograph and nitrogen adsorption-desorption isotherms of a sample made with an oil-to-polymer ratio of 0.1 are shown in Figure 3.6(a) and Figure 3.7(a), respectively. Both the TEM and the \( N_2 \) sorption data display slight shifts to larger pore sizes relative to the unswollen SBA-15 sample shown in Figures 3.2 and 3.4.
Figure 3.5 SAXS patterns of mesoporous silicas templated by Pluronic P123 swollen with 1,3,5-trimethylbenzene. The TMB:polymer mass ratios used in the synthesis of the three different samples are (a) 0.1, (b) 0.2 and (c) 0.5.

Figure 3.6 Transmission electron micrographs of mesoporous silicas templated by Pluronic P123 swollen with 1,3,5-trimethylbenzene. The TMB:polymer mass ratios used in the synthesis of the three different samples are (a) 0.1, (b) 0.2 and (c) 0.5.
Figure 3.7 Nitrogen adsorption-desorption isotherms (a, c, e) and pore size distributions (b, d, f) of mesoporous silicas templated by Pluronic P123 swollen with 1,3,5-trimethylbenzene. The TMB:polymer mass ratios used in the synthesis of the three different samples are (a, b) 0.1, (c, d) 0.2, and (e, f) 0.5.
The TEM image in Figure 3.6(b) shows a change in pore morphology for samples with oil:polymer ratios of 0.2 - 0.3. The walls of the cylindrical pores begin to buckle with approximately the same periodicity as the pore diameter, forming spherical nodes down the length of the pore. TEM micrographs show that materials synthesized with oil:polymer ratios greater than 0.3 no longer exhibit the hexagonally packed cylindrical pores of SBA-15. The mesoporous silica synthesized with an oil-to-polymer ratio of 0.5 (Figure 3.6(c)) had a morphology consisting of large (~ 30 nm) cavities or 'cells', surrounded by silica struts, and interconnected by 'windows' of ~ 8 - 15 nm in diameter.

In addition to the change in pore morphology, there was a significant increase in the pore size of the mesoporous material at an oil:polymer ratio of ~ 0.2 (see Figure 3.8). The pore diameters reported in Figure 3.8 have been determined by nitrogen adsorption and have been verified with TEM. To determine the pore size of the silica materials from the nitrogen adsorption data, we have used two different models. In the low oil concentration regime, the pores have been modeled as long straight cylinders as discussed above. For oil-to-polymer ratios above 0.2, the hysteresis in the nitrogen adsorption-desorption isotherms is significantly larger, as shown in Figures 3.7(c) and (e). Based on the electron microscopy results and the presence of significant hysteresis in the N\textsubscript{2} sorption isotherms, we have used a modification of the Broekhoff-de Boer (BdB-FHH) model for the higher oil concentration regime, which treats the pores as spherical cells with small openings or windows between cells.\textsuperscript{6} In the modified model of the N\textsubscript{2} sorption data, we derived cell sizes from the adsorption branches of the isotherms, while the desorption branches gave the window sizes. The other data obtained from the nitrogen sorption experiments, including specific surface area, pore volume, and pore size, are summarized in Table 3.1. Notably, the specific pore volume nearly doubled upon the transition to more spherical pores, going from 1.10 cm\textsuperscript{3}/g at TMB:P123 = 0.18 to 1.96 cm\textsuperscript{3}/g at TMB:P123 = 0.21.
Table 3.1 Pore Characteristics of Polymer-Templated Silicas as Determined by Nitrogen Adsorption Experiments

<table>
<thead>
<tr>
<th>TMB:P123 Mass Ratio</th>
<th>Pore Diameter(^a) (Å)</th>
<th>Surface Area(^b) (m(^2)/g)</th>
<th>Pore Volume (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>67</td>
<td>965</td>
<td>1.03</td>
</tr>
<tr>
<td>0.10</td>
<td>89</td>
<td>942</td>
<td>0.98</td>
</tr>
<tr>
<td>0.18</td>
<td>115</td>
<td>788</td>
<td>1.10</td>
</tr>
<tr>
<td>0.21</td>
<td>220</td>
<td>781</td>
<td>1.96</td>
</tr>
<tr>
<td>0.25</td>
<td>230</td>
<td>844</td>
<td>1.99</td>
</tr>
<tr>
<td>0.30</td>
<td>255</td>
<td>792</td>
<td>1.87</td>
</tr>
<tr>
<td>0.38</td>
<td>275</td>
<td>783</td>
<td>2.03</td>
</tr>
<tr>
<td>0.41</td>
<td>285</td>
<td>775</td>
<td>2.10</td>
</tr>
<tr>
<td>0.50</td>
<td>310</td>
<td>648</td>
<td>2.22</td>
</tr>
</tbody>
</table>

a) Pore diameter determined from nitrogen adsorption isotherms using the BdB-FHH method described in the text. For TMB:P123 < 0.2, a cylindrical pore geometry was assumed, for TMB:P123 > 0.2, spherical pores were assumed. b) Surface area was determined from nitrogen adsorption data using the BET method.

SAXS data indicated a large shift in the $d$-spacing of the primary scattering peak in the transition region of TMB:P123 = 0.2 - 0.3, supporting the TEM and nitrogen adsorption data. However, the SAXS pattern of a sample synthesized with an oil:polymer ratio of 0.21 could still be indexed to the $p6mm$ space group characteristic of the SBA-15 material (Figure 3.5(b)). At an oil:polymer ratio of 0.5, the SAXS pattern (Figure 3.5(c)) did not match the $p6mm$ space group, and could instead be simulated by scattering due to randomly packed spheres.\(^7\) Characterization data indicated a new MCF ‘phase’ of mesoporous material consisting of spherical cavities 22 - 35 nm in diameter that were interconnected in three dimensions by windows of ~ 8 - 15 nm. This morphology yielded a highly open structure, as evidenced by the large pore volumes (in excess of ~ 2 cm\(^3\)/g or ~ 85% porosity).

3.3.2 Effect of Oil Type

The oils that were modeled as swelling agents in Section 2.4.3.2 were also used in mesocellular foam synthesis experiments. Figure 3.9 plots the $N_2$ adsorption pore size of the templated silica material against the volume of swelling agent added per mole of
P123 polymer. The results show a distinct division between aromatic and aliphatic swelling agents in that the aromatic swelling agents yield larger pore sizes. As noted in Table 2.4, aromatics have a higher solubility in Pluronic micelles than aliphatics. In contrast, only small amounts of heptane and cyclohexane were solubilized in the cores of the P123 micelles that little swelling of the templates occurred with the addition of these aliphatic oils.

Another significant difference between the silica materials templated by Pluronics swollen with aromatics and those swollen with aliphatics is the pore structure of the material. When heptane and cyclohexane were used as swelling agents, the resulting mesoporous silicas maintain a slightly swollen SBA-15 structure and did not undergo transition to the mesocellular foam ‘phase’. This effect is demonstrated in Figure 3.10, which shows the SAXS patterns of silica materials made with three different heptane concentrations. The higher order scattering peaks indicative of $p6mm$ symmetry are clearly visible, and the (100) peak shifts to only slightly lower angles (higher $d$-spacings) as the oil content increases. The mesopore structural development of silica materials made with aromatic swelling agents has been shown in Figures 3.5 and 3.11 for the cases of 1,3,5-trimethylbenzene and benzene, respectively. The SAXS patterns for the benzene-swollen samples show a clear change in samples with oil-to-polymer ratios of 0.12 and 0.25, corresponding to the transition between SBA-15 and MCF. This set of data also shows another trend in the MCF materials: the ordering of the material decreases as the oil content in the template increases. Silica materials synthesized with aromatic contents above the solubility limit also showed broad pore size distributions. The formation of a separate oil phase in these synthesis solutions means that the stable microemulsion droplets did not significantly increase in size as more oil was added. Rather, the incorporation of large emulsion droplets into the condensing silica material led to an ill-defined pore structure.
3.3.3 Effect of Polymer Type

The previous two sections have shown that the concentration of swelling agent can have a dramatic effect on the structure of the templated silica by inducing the SBA-15-to-MCF transition, and that the type of oil will also impact the structure of the resulting silica materials since only oils that are highly soluble in PPO, such as aromatics, will produce the mesocellular foam phase. The modeling results of Section 2.4.3.1 indicated that the type of polymer also had a significant impact on the silica structure templated by swollen micelles. As discussed in Chapter 2, the triblock copolymer must have sufficient hydrophilic (PEO) content to solubilize the oil in water, so we have investigated three different Pluronics for use as silica templates: P84 (40 wt% PEO, MW ~ 3800), P123 (30 wt% PEO, MW ~ 5800), and F127 (70 wt% PEO, MW ~ 13500). All three polymers have greater than 30 wt% PEO, and therefore, should act as good solubilizing agents for the oils. P84 has a shorter PPO block than P123, ~ 40 propylene oxide units as opposed to 70, but has only a slightly higher PEO content. F127, on the other hand, has approximately the same PPO block length as P123, but the PEO blocks on either end are five times longer (100 ethylene oxide units) than P123 (20 ethylene oxide units).
In the synthesis of silica mesostructures from the three different polymers, the same polymer-to-water mass ratio was used in all cases (see Section 3.2.1). Thus, the molar concentration of P84 was slightly higher, and that of F127 was slightly lower than in the P123 base case, but the dry volume of polymer added was approximately the same in all samples. The concentrations of HCl and TEOS were the same as in the P123 base case described in Section 3.2.1. Two different swelling agents (1,3,5-trimethylbenzene and 1,2-dichlorobenzene) were used at two different concentrations each (oil-to-polymer mass ratios of 0.25 and 0.5) for all three polymers investigated.

The characterization data for calcined silica materials templated by Pluronic P123 micelles swollen with either TMB or DCB at oil:polymer ratios of 0.25 and 0.5 were discussed in Section 3.3.1 and 3.3.2. At these oil concentrations, P123 micelles templated MCF with pore diameters in excess of 20 nm and pore volumes greater than 2 cm³/g. When P123 was used as the template, a white precipitate formed at the bottom of the reaction vessel after ~ 3 h of aging at 35°C. Little change in the precipitate was visually observed after the second aging procedure of 100°C for 48 h. Materials removed from the reaction vessel and filtered after the first aging step showed SAXS patterns similar to that of the final calcined foams, except the peak intensity was lower (indicating lower X-ray scattering contrast as expected from pores that contain polymer and from silica walls that were not fully condensed) and the d-spacing was larger than that of the calcined samples. Samples filtered after aging for 24 h at 35°C and 48 h at 100°C but not calcined also showed lower X-ray contrast and larger d-spacings than the calcined samples. The decrease in d-spacing upon calcination indicated that there was some further condensation and partial shrinkage of the silica framework during heat treatment at 550°C, although subsequent heating to 600°C showed no further decrease in pore size.

Silica materials templated by swollen P84 micelles began to precipitate during the initial 35°C aging period and showed no visible change after aging at 100°C for 48 h, as was observed for P123-templated materials. However, the pore sizes of the P84-templated materials were significantly smaller than those obtained using P123. Mesoporous silica templated by P84 with no oil added showed SBA-15 structure and a pore size of 45 Å, as opposed to 67 Å for SBA-15 templated by P123 (Table 3.2). The smaller pore size of the P84-templated materials was expected since the molecular weight of P84 is ~ 65% that of P123. The most significant differences between the P84 and P123 templates were
Table 3.2 Pore Characteristics of Mesoporous Silicas Templated by Three Different Polymers

<table>
<thead>
<tr>
<th>Polymer Type, Oil Type</th>
<th>Oil:Polymer Mass Ratio</th>
<th>Pore Diameter(a) (Å)</th>
<th>Surface Area(b) (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P84</td>
<td>0.00</td>
<td>45</td>
<td>967</td>
<td>0.85</td>
</tr>
<tr>
<td>P84, TMB</td>
<td>0.25</td>
<td>51</td>
<td>844</td>
<td>1.02</td>
</tr>
<tr>
<td>P84, DCB</td>
<td>0.50</td>
<td>88</td>
<td>858</td>
<td>1.25</td>
</tr>
<tr>
<td>P84, DCB</td>
<td>0.25</td>
<td>50</td>
<td>862</td>
<td>1.10</td>
</tr>
<tr>
<td>P84, DCB</td>
<td>0.50</td>
<td>71</td>
<td>861</td>
<td>1.20</td>
</tr>
<tr>
<td>P123</td>
<td>0.00</td>
<td>67</td>
<td>955</td>
<td>1.03</td>
</tr>
<tr>
<td>P123, TMB</td>
<td>0.25</td>
<td>230</td>
<td>844</td>
<td>1.99</td>
</tr>
<tr>
<td>P123, TMB</td>
<td>0.50</td>
<td>310</td>
<td>648</td>
<td>2.22</td>
</tr>
<tr>
<td>P123, DCB</td>
<td>0.25</td>
<td>225</td>
<td>748</td>
<td>2.09</td>
</tr>
<tr>
<td>P123, DCB</td>
<td>0.50</td>
<td>265</td>
<td>704</td>
<td>1.91</td>
</tr>
<tr>
<td>F127</td>
<td>0.00</td>
<td>64</td>
<td>885</td>
<td>0.74</td>
</tr>
<tr>
<td>F127, TMB</td>
<td>0.25</td>
<td>90</td>
<td>812</td>
<td>1.43</td>
</tr>
<tr>
<td>F127, TMB</td>
<td>0.50</td>
<td>152</td>
<td>770</td>
<td>1.49</td>
</tr>
<tr>
<td>F127, DCB</td>
<td>0.25</td>
<td>249</td>
<td>765</td>
<td>1.52</td>
</tr>
<tr>
<td>F127, DCB</td>
<td>0.50</td>
<td>174</td>
<td>838</td>
<td>1.40</td>
</tr>
</tbody>
</table>

a) Pore volume determined from nitrogen adsorption isotherms using the BdB-FHH method described in the text. For Oil:P123 < 0.2, a cylindrical pore geometry was assumed, for Oil:P123 > 0.2, spherical pores were assumed.

b) Surface area was determined from nitrogen adsorption data using the BET method.

Noted when swelling agents were used. Due to the shorter PPO blocks in P84 and the higher molar concentration of P84 used in the templating solutions, we would expect a higher number of smaller polymer-oil aggregates to form in the P84 solutions compared to the P123 solutions. The differences in pore size between silica obtained from swollen P84 solutions and those obtained from swollen P123 solutions were greater than expected, however, because the P84-templated silicas did not form MCF structures. Instead, the silicas obtained from swollen P84 micelles possessed p6mm symmetry and had pore sizes of only 50 Å and 71 Å for DCB:P84 ratios of 0.25 and 0.50, respectively.

Synthesis solutions containing Pluronic F127 showed completely different behavior from those containing either P84 or P123. Solutions containing F127 remained clear, viscous liquids for the full 24-h aging period at 35°C. When heated to 100°C, the entire volume of the solutions gelled. After calcination, the gels yielded hard glassy silica materials, as opposed to the white powders obtained when P84 or P123 were used as templates. F127-templated samples synthesized without the addition of a swelling agent possessed
pore sizes of ~ 65 Å, and a broader pore size distribution than P84- and P123-templated materials. The similarity in the pore sizes of silicas condensed in the presence of P123 and F127, which have the same PPO block length but different PEO block lengths, suggests that the silica network penetrates deep into the PEO corona, and that the pore size of the materials is therefore primarily determined by the size of the hydrophobic micellar core. Recent investigations into SBA-15 materials have indicated that the PEO blocks trapped in the condensed silica walls of the mesostructured materials generate micropores in the walls once the material has been calcined. Calcined gels synthesized with DCB:F127 = 0.25 and 0.5 possessed pores greater than 170 Å in diameter, but the pore sizes in F127-templated materials were unpredictable, with broad pore size distributions. None of the samples templated by F127 displayed ordered mesostructures in SAXS experiments.

3.3.4 Effect of Silica Concentration
To investigate the effect of silica concentration, two series of samples were prepared with varying amounts of tetraethoxysilane. Samples in the first series consisted of 84.2 g of 1.6 M HCl in water to which 2.0, 4.2 (base case), 6.0 and 10.0 g of TEOS were added. Samples in the second series had similar compositions to those in the first series, except the base case amount of 2.0 g of P123 was added to the second group of solutions.

Samples in the first series served as a control to determine the properties of silica gels made under the same conditions as the SBA-15 and MCF materials only with no templates present. All of the synthesis solutions that contained no polymer remained clear liquids after the 24-h aging period at 35°C. Upon aging for 48 h at 100°C, the solution with the lowest initial concentration of TEOS (2.0 g) and the base case TEOS concentration (4.2 g) had begun to gel, although both remained highly viscous fluids and some flow could be induced merely by tilting the reaction vessels. The two solutions containing higher silica concentrations formed clear, solid gels after aging at 100°C. In contrast, the P123-containing solution with the lowest TEOS content formed a cloudy white gel after 24 h at 35°C; and when heated to 100°C, the sample formed solid white chunks that did not occupy the entire solution volume. As mentioned in the previous sections, the base case P123-containing samples (4.2 g of TEOS) formed a white powdery precipitate at 35°C and little change was noted after aging at 100°C. The two P123-
Table 3.3 Pore Characteristics of Untemplated and Polymer-Templated Silica Gels

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Amount of TEOS$^a$ (g)</th>
<th>Pore Diameter$^b$ (Å)</th>
<th>Surface Area$^c$ (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.0</td>
<td>106</td>
<td>517</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>105</td>
<td>527</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>89</td>
<td>551</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>70</td>
<td>613</td>
<td>0.82</td>
</tr>
<tr>
<td>P123</td>
<td>2.0</td>
<td>85</td>
<td>813</td>
<td>1.5</td>
</tr>
<tr>
<td>P123</td>
<td>4.2</td>
<td>67</td>
<td>965</td>
<td>1.03</td>
</tr>
<tr>
<td>P123</td>
<td>6.0</td>
<td>71</td>
<td>750</td>
<td>1.05</td>
</tr>
<tr>
<td>P123</td>
<td>10.0</td>
<td>59</td>
<td>705</td>
<td>0.90</td>
</tr>
</tbody>
</table>

a) Amount of TEOS added per 85 g of 1.6M HCl solution.
b) Pore volume determined from nitrogen adsorption isotherms using the BdB-FHH method described in the text.
c) Surface area was determined from nitrogen adsorption data using the BET method.

containing samples with higher TEOS concentrations also formed white precipitates at 35°C, but after aging at 100°C, the precipitated phase formed a compact glassy gel at the bottom of the reaction vessel with only a small amount of the white powder remaining. These experiments demonstrate that the Pluronic templates not only create voids in silica gels, but also profoundly influence the manner in which the silica condenses.

Characterization data for the calcined untemplated and templated silica gels synthesized with varying TEOS content are reported in Table 3.3. The pore sizes and surface areas of the untemplated silicas are lower than those of P123-templated materials. The pore size distribution in the pure silica gel is also significantly broader than that in the P123-templated silica, as shown in Figure 3.12.

3.3.5 Templating Mechanism

Pluronic P123 solutions in the concentration range that we have investigated contain spherical micelles as has been demonstrated in Chapter 2. The addition of chloride ions and hydrophobic swelling agents has been shown to induce sphere-to-rod micellar trans-
formations in systems containing surfactants with aliphatic tail groups.\textsuperscript{9,10,11} However, SANS and DLS experiments on P123 solutions with added oils (up to oil:polymer mass ratios of 1.0) and HCl (up to 3.0 M) revealed no such transformations prior to the addition of a silica source. Upon addition of tetraethoxyxilane to P123-HCl-water solutions, a white precipitate was formed. Previously, researchers investigated the condensation of silica gels in the presence of PEO and found that similar precipitates formed.\textsuperscript{12,13,14} The calcined silica materials templated by pure PEO possessed large irregular cavities on the order of microns in size formed by the aggregation of PEO within the precipitated phase. SAXS, nuclear magnetic resonance (NMR) and calorimetry have been used to investigate the interaction between silica and PEO.\textsuperscript{12,15,16} It was found that protonated silica oligomers formed in acidic environments would hydrogen bond to the oxygens in PEO, and during the creation of these bonds, the water solvating the PEO is displaced. The PEO-silica complex is insoluble in water and so a phase rich in polymer and silica precipitates. Silica hydroxides condense slowly at low pH,\textsuperscript{17} and thus the molecules in the precipitated phase remain mobile, allowing the PEO to change conformation and minimize its energy within the highly concentrated phase. In our case, where PEO-PPO-PEO triblock copolymers were used, the polymer-silica complexes precipitated as with the pure PEO polymers, but once the phase rich in polymer-silica was formed, the triblock copolymers would microsegregate into a hexagonal liquid crystalline phase consisting of PPO cylindrical cores surrounded by a matrix of PEO and silica. The silica in the matrix then slowly condensed to form SBA-15, as illustrated in Figure 3.13(a).

The transition from SBA-15 to MCF occurred with the addition of a sufficient amount of oil to the synthesis solution. The transition to MCF was characterized by a large increase in pore diameter, but the slow evolution of the SAXS patterns from \textit{p6mm} symmetry to
scattering from packed spheres belied a more gradual change. Transitions in aggregate shape from rods to spheres upon addition of a critical amount of certain oils have been predicted theoretically\textsuperscript{18} and observed experimentally.\textsuperscript{19,20,21} According to Nagarajan and Ruckenstein,\textsuperscript{18} the solubilization-induced cylinder-to-sphere transition is a consequence of the smaller interfacial free energy and surfactant tail deformation free energy in a sphere. The importance of the oil-water interfacial free energy and the deformation of the surfactant tail gradually increase as more oil is added, with only small free energy differences separating the spherical and cylindrical aggregate free energies, and so the transition progresses with the addition of more oil.\textsuperscript{18} The transition from SBA-15 to MCF is therefore caused by a solubilization-induced rod-to-sphere transition in the precipitate phase rich in polymer-silica; this transition is required to reduce the oil-water interface and relieve the surfactant tail deformation in the aggregates.

Synthesis solutions containing F127, on the other hand, never formed a silica-polymer-rich precipitate (see Figure 3.13(b)). Due to the high PEO content of F127, there was a lower silica-to-PEO ratio than in the P84 and P123 synthesis solutions. Therefore, the number of EO units dehydrated through interactions with silica oligomers is not sufficient to precipitate the polymer. The F127 micelles, which contained some silica in the micellar corona, remained in solution until gelation occurred at 100°C. The temperature-induced gelation of Pluronic solutions has been previously observed.\textsuperscript{22,23,24} Although the cause of gelation in aqueous polymer solutions is not well understood, it is known that the gelation temperature decreases with increasing polymer molecular weight, with increasing salt concentration, and with the addition of lipophilic compounds. Thus, the presence of HCl and oil in the reaction mixture promoted gelation, and the silica condensed within the gel to solidify the structure and make it thermally irreversible. The matrix of the gel, however, consisted mostly of water and PEO, and so when the material was calcined, the silica walls of the samples would collapse as the polymer and water were removed, leaving materials with irregularly shaped pores and small pore volumes.
Figure 3.13 Schematic diagrams of the polymer-templated mesoporous silica synthesis mechanism. Scheme (a) shows the P123 templating mechanism in which a silica-P123-rich phase precipitates and forms a highly-ordered mesoporous silica material. Scheme (b) shows the F127 templating mechanism in which the entire solution gels, leading to the formation of disordered porous silica materials.
3.4 Summary

In an effort to understand the synthesis mechanism of polymer-templated mesostructured silica materials and to expand the range of pore sizes and structures that can be obtained using this technique, we have investigated the role of polymer size and composition, and oil type and concentration in determining the properties of templated silicas.

The key to the synthesis mechanism of Pluronic-templated silica structures is an understanding of the transition between well-dispersed spherical micelles and ordered cylindrical silica-polymer nanocomposites that takes place upon the addition of TEOS to SBA-15 synthesis solutions. By observing the precipitation of a polymer-silica-rich phase during SBA-15 synthesis and by noting the previously discovered interactions between silica oligomers and PEO that reduce the polymer solubility in water, we determined that the SBA-15 structure formed as a result of the silica-induced precipitation of a concentrated polymer phase with a composition similar to that of the H₁ liquid crystalline phase in pure polymer solutions. The fact that the silica condenses slowly under the acidic conditions of our experiments means that the polymer had time to adopt its equilibrium conformation in the newly formed polymer-silica-rich phase before the material solidified. Thus, we have found two key factors in determining the pore size and structure of Pluronic-templated silica materials that were not previously well understood. First, there must be sufficient silica present in solution to precipitate the polymer aggregates. If the PEO-to-silica ratio is too high, not enough EO sites will be bound to silica and the polymer will remain in solution. Second, because the silica condenses slowly under acidic conditions, it is the equilibrium structure of the concentrated precipitate, not the original solution, that determines the pore structure of the final material.

We have found that when aromatic swelling agents, such as benzene, trimethylbenzene and 1,2-dichlorobenzene, were added to a system templated with PEO-PPO-PEO, the hexagonally packed SBA-15 pore structure was maintained only for very low oil concentrations. Upon increasing the oil:polymer ratio, a new mesocellular foam phase was obtained. The MCF phase possesses a system of interconnected pores with diameters of 220 - 350 Å. We describe the synthesis conditions of these materials, and propose a mechanism for the phase transition of SBA-15 with p6mm symmetry and pore sizes of 40 - 120 Å to MCF with well-defined spherical pores of 220 - 330 Å.
The transition between the hexagonally structured SBA-15 and the mesocellular foam occurred at a oil:polymer mass ratio of 0.2 - 0.3. The transition to the MCF phase was characterized by a sharp increase in the pore size, while a hexagonal structure (p6mm) was still observed in the SAXS pattern. Transmission electron micrographs revealed buckling in the walls of the cylindrical pores for oil:polymer ratio of ~ 0.2. The increased hysteresis in the N₂ adsorption-desorption isotherms also indicated a change in pore morphology. We propose that the change in pore morphology, without an accompanying mesophase change in SAXS pattern, was due to the formation of a noded structure in the cylindrical pores while the pores maintained their hexagonal packing. As the oil concentration increased, the nodes would separate into spherical micelles, which aggregated to form the mesocellular foam material. The mesostructure change from cylindrical-to-spherical geometry was driven by the need to decrease micellar surface-to-volume ratio as more oil was added to the solution with a fixed amount of polymer. This led to a decrease in the oil-water interfacial free energy as well as the PPO block deformation free energy in the aggregate core.

The molecular weight and composition of Pluronic triblock copolymers that will form the MCF structure was limited by two competing effects: the minimum fraction of PEO in the polymer necessary to solubilize oil in water, and the maximum size and PEO content of the polymer beyond which the system will form a silica-polymer composite gel. Through an understanding of the synthesis chemistry, we have derived a new mesostructured silica phase, MCF, with large pore sizes and high pore volumes, and have developed a synthesis mechanism for Pluronic-templated materials capable of describing the silica structures obtained under a wide range of synthesis conditions.
3.5 References


CHAPTER 4
Pd on Mesoporous Silica Supports for Heterogeneous Heck Catalysis

4.1 Introduction
The fine chemical and pharmaceutical industries make extensive use of catalytic reactions to synthesize complex molecules to demanding purities. The high value added to fine chemicals and pharmaceuticals allows for the application of expensive catalysts, and many current catalysts used in these industries are intricate homogeneous organometallic compounds. While the expense of the catalysts used in fine chemical and pharmaceutical synthesis is considerable, it is not as significant as the cost of downstream separation/purification processes. The separation of non-volatile organometallic catalysts can be particularly difficult given that many fine chemical and pharmaceutical products are large, non-volatile molecules themselves, and therefore high-temperature distillations or liquid-liquid separations with subsequent solvent distillation must be used. Furthermore, metal impurities are strictly regulated in many products and so the separation of the catalyst must be complete. Following such extreme separation procedures, the organometallic catalysts are seldom active in their recovered state and cannot be used in subsequent reactions. In addition to expense, the separation steps add to the development and processing times—extremely detrimental in industries where time-to-market is of paramount importance.

The development of heterogeneous catalysts with activities and selectivities equal or superior to those of the homogeneous catalysts currently used in the fine chemical and pharmaceutical industries could improve production in several ways. Heterogeneous catalysts on robust supports could be easily separated from reaction mixtures using filtration in batch processes or could be used in continuous reactors. Ideally, the filtered catalyst could be reused in subsequent reactions thus saving on catalyst costs, but independent of catalyst reuse, the application of heterogeneous catalyst would eliminate the expensive and time-consuming separation steps necessary to remove homogeneous catalyst from the product stream, thereby improving product margins and time-to-market.
An effective heterogeneous catalyst support material must be stable under reaction conditions and must provide a large surface area for reasonable active site densities, while not imposing mass transfer limitations on reaction rates. Mesoporous silicas would appear to be an ideal support candidate given the stability of silica in a wide range of solvents at the moderate temperatures under which most fine chemical and pharmaceutical reactions take place (≤ 250°C), and the high surface areas that can be obtained. While current mesoporous silicas, such as MCM-41, have been modified as catalysts, their small pore diameters (typically 2 - 4 nm) limit their applicability to fine chemical catalysis. Even relatively small fine chemical and pharmaceutical products, such as candoxatril, can be 2 nm in size. So the use of MCM-41 catalyst supports would impose severe transport limitations on the reactions that produce these molecules. The larger pore dimensions of SBA-15 and MCF should make these materials better suited for application as fine chemical and pharmaceutical catalyst supports.

We have selected the Heck reaction to provide a case study for the development of an easily recoverable heterogeneous catalyst for an industrially important reaction in which homogeneous catalysts are typically used, and to test the effects of the support’s pore structure on reaction kinetics. The Heck reaction is a carbon-carbon coupling reaction involving the palladium catalyzed olefination of aryl and vinyl halides\textsuperscript{1,2} (see Scheme 4.1). It has been touted as one of the most important uses of transition metals in organic synthesis.\textsuperscript{3} The Heck reaction is used to produce a wide range of industrially important molecules,\textsuperscript{4,5} but the most active current catalysts for this reaction are homogeneous phosphapalladacycles\textsuperscript{4} (see Scheme 4.2) or unstable suspensions of colloidal palladium.\textsuperscript{4}

\begin{center}
\textbf{Scheme 4.1} Heck reaction
\end{center}
These catalysts are difficult to separate from reaction products. They also suffer from rapid deactivation by Pd agglomeration at temperatures above 130°C where they are initially most active, leading to limited catalyst lifetime and overall turnover numbers (TON = moles of product formed per mole of catalyst).³

We have sublimed a volatile organometallic compound through the pores of mesoporous silica supports to form a uniform layer of adsorbed material. The adsorbed organometallic complex is then reduced to form a highly dispersed metal layer on the silica support. The catalysts retain the excellent catalytic activity and selectivity associated with the homogeneous organometallic complexes, without the diffusion limitations imposed by many traditional porous supports. The heterogeneous catalysts further provide superior stability and ease of separation compared to homogeneous catalysts, making them highly attractive for applications in fine chemicals and pharmaceuticals synthesis.

### 4.2 Experimental Procedures

#### 4.2.1 Catalyst Synthesis and Characterization

The active Heck catalyst was formed by the vapor deposition of a volatile organo-palladium complex onto the walls of mesoporous silica materials, followed by reduction with H₂ according to the procedure used by Mehnert et al.⁷ First, the silica support material (~ 0.5 g) was degassed at 150°C and 10⁻² Torr for 24 hours. A layer of glass wool was placed on top of a glass frit fixed to the bottom of a short glass tube. In a glove box, the degassed silica material was placed on top of the glass wool and another piece of glass wool was used to secure the top of the column of silica powder. A round-bottom
flask containing the volatile organo-palladium complex ([Pd(η-C₅H₅)(η³-C₃H₅)], ~ 0.25 g, 1.2 mmol) was attached to the short glass tube below the frit. The entire assembly was then connected to a condensation bridge and the end containing the organo-Pd complex was submerged in an 85°C oil bath, and the condensation end of the tube was submerged in liquid N₂, as shown in Figure 4.1. The pressure in the condensation bridge was reduced to 10⁻² Torr and the palladium complex was sublimed through the column of mesoporous silica. The procedure continued until the column of silica had turned a uniform grey color. The Pd-grafted silica was then removed from the condensation bridge and placed in ¼" fritted glass tube. The tube was wrapped in heating tape and the powder was heated to 350°C under a constant flow of 7% H₂ in argon to give a uniform black powder. The Pd-modified mesoporous silica materials synthesized by this ‘vapor-grafting’ procedure are designated Pd-TMS materials (Pd-TMS11 when MCM-41 was used as the support, Pd-TMS12 when SBA-15 was employed as the support, and Pd-TMS13 when the Pd was supported on MCF).

![Diagram of condensation bridge](image)

**Figure 4.1** Schematic of the condensation bridge used for vapor grafting Pd onto mesoporous silica supports.
The Pd vapor-rafted silica materials were characterized by nitrogen adsorption analysis, small-angle X-ray scattering (SAXS), powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and inductively coupled plasma (ICP) elemental analysis. Nitrogen adsorption experiments were performed on a Micromeritics ASAP 2010 instrument. From the nitrogen sorption measurements, the surface areas of the materials were determined using the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined using the BdB-FHH method discussed in Chapter 3. A Siemens SAXS instrument (sample-to-detector distance = 60 cm, non-monochromated Cu source operating at 40 kV and 30 mA) was used for structural analysis of the mesoporous silica supports, and powder XRD data were collected on a Siemens D5000 θ-θ diffractometer with Ni-filtered Cu Kα radiation (40 kV and 30 mA) to determine the phase of the Pd. The crystallite sizes of the palladium clusters were determined from the full width at half maximum height of the Pd XRD peaks using Scherrer’s method. For TEM studies, a JEOL JEM-200CX microscope (W filament, 200 kV) was employed, and the size and dispersion of the Pd clusters were confirmed by HRTEM using a JEOL H2000 microscope (field-emission gun electron source operating at 2000 kV). STEM studies to map the elemental distribution in catalysts before and after reaction were performed on a JEOL STEM2000. Bulk elemental analysis of the catalyst materials to determine the overall palladium loading was carried out by the ICP technique at Quantitative Technologies Inc, Whitehouse, NJ.

4.2.2 Heck Reaction Studies

The Heck coupling of the aryl halide, 4-bromoacetophenone, to the olefin, n-butylacrylate, was used as a model reaction to test the reactivity of our heterogeneous catalysts (see Scheme 4.3). For a typical reaction, a 250 mL three-neck flask was fitted with a thermometer and a condensation column. The third neck was closed with a glass stopper and used as a charging port. Approximately 98 mL (1 mol) of N,N-dimethylacetamide (Aldrich) was added as the reaction solvent and 14 mL (0.06 mol) of dodecane (Aldrich) was used as an inert internal standard for gas chromatographic analysis. In the Heck reaction, the aryl halide and the olefin are coupled by the abstraction of the halide and an olefinic hydrogen by palladium (see Scheme 4.4). In order to return the catalyst to its active state, the hydrogen and halide must be removed from the palladium, which is
Scheme 4.3 Heck coupling of bromoacetophenone and n-butylacrylate

Scheme 4.4 Heck reaction mechanism\(^1\)
accomplished through the use of a basic co-reactant. The base used in our reaction studies was triethylamine (Aldrich, 15.5 mL, 0.12 mol). In the reaction mixture, 17.5 mL (0.12 mol) of n-butylacrylate (Aldrich) and 20 g (0.1 mol) of 4-bromoacetophenone (Aldrich) were added. The solution was then heated to the reaction temperature (120 - 160°C) by placing the flask in an oil bath of the desired temperature. After the reaction temperature had been reached, the catalyst (0.020 g of Pd-TMS with ~ 10 wt% Pd, 0.02 mmol Pd) was added. The limiting reagent in the reaction mixture was 4-bromoacetophenone, and the aryl halide-to-Pd ratio (i.e. the maximum turnover number for the reactions) was fixed at 5000, unless otherwise noted, typically by varying the amount of catalyst added to the base reaction mixture.

The progress of the reaction was monitored by taking 0.5 mL samples at regular time intervals. The samples were diluted with ~ 1 mL of ethanol to quench the reaction and were then filtered through Celite (Aldrich) to remove the catalyst particles. The samples were analyzed by gas chromatography (HP 5890, using an HP1 column). After completion of the reaction, the mixture was quenched with water (500 mL), and the organic products were extracted with diethyl ether (Aldrich, 3 x 250 mL). The organic phases were combined and concentrated in a rotary evaporator under reduced pressure. The cis/trans isomers of the coupling product were then separated by column chromatography using silica gel and a solvent mixture of 1:1 pentane and diethyl ether. The catalyst was filtered from the aqueous phase and was rinsed several times with water and diethyl ether (Aldrich) to remove residual salts and organics. The recovered catalyst was then dried at 150°C for several hours.

4.3 Results and Discussion

4.3.1 Pd-TMS Catalyst Synthesis and Characterization

Three different mesoporous silica materials were used as supports for Pd-TMS Heck catalysts: MCM-41, SBA-15, and mesocellular foam (MCF). The MCM-41 support was synthesized using the method of Beck et al. and the SBA-15 and MCF materials were synthesized using the procedures described in Chapter 3. The characterization data for the unmodified supports are reported in Table 4.1. Palladium was vapor-grafted onto each of the supports, and then the materials were reduced to form supported Pd metal.
Table 4.1 Characterization Data for Pd-TMS Heterogeneous Heck Catalysts

<table>
<thead>
<tr>
<th>Support Material</th>
<th>Pd-TMS11</th>
<th>Pd-TMS12</th>
<th>Pd-TMS13</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>1375</td>
<td>820</td>
<td>793</td>
</tr>
<tr>
<td>SBA-15</td>
<td>880</td>
<td>654</td>
<td>628</td>
</tr>
<tr>
<td>MCF</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

BET Surface Area (m²/g)

<table>
<thead>
<tr>
<th></th>
<th>before Pd-grafting</th>
<th>after Pd-grafting</th>
</tr>
</thead>
<tbody>
<tr>
<td>before Pd-grafting</td>
<td>24</td>
<td>65</td>
</tr>
<tr>
<td>after Pd-grafting</td>
<td>22</td>
<td>51</td>
</tr>
</tbody>
</table>

Pore Size (Å)

<table>
<thead>
<tr>
<th></th>
<th>before Pd-grafting</th>
<th>after Pd-grafting</th>
</tr>
</thead>
<tbody>
<tr>
<td>before Pd-grafting</td>
<td>310 (cell)/88 (window)</td>
<td>298 (cell)/80 (window)</td>
</tr>
<tr>
<td>after Pd-grafting</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Void Fraction

<table>
<thead>
<tr>
<th></th>
<th>before Pd-grafting</th>
<th>after Pd-grafting</th>
</tr>
</thead>
<tbody>
<tr>
<td>before Pd-grafting</td>
<td>0.68</td>
<td>0.74</td>
</tr>
<tr>
<td>after Pd-grafting</td>
<td>0.60</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Pd Content (wt%)

|                  | 21.7 | 8.5 | 11.0 |

Pd Surface Area (m²/g Pd)

|                  | 145  | 130 | 150  |

Catalysts as described in Section 4.2.1. Previous studies by Mehnert et al.7 established that Pd deposited on silica and alumina supports using traditional incipient-wetness impregnation techniques were poorly dispersed and showed little activity for the Heck reaction. The vapor grafting approach was therefore employed to ensure a uniform distribution of palladium precursor within the pores of the mesostructured supports, and to thereby increase the dispersion of the final Pd active metal component. As noted in the initial vapor-grafting protocol established by Mehnert et al., the success of the vapor deposition process depends on the properties of the volatile organometallic compound and on the reaction conditions. For example, the silica support material must be kept at the same elevated temperature as the organo-palladium complex in the flask below to prevent the bulk condensation of the compound in the pores and the subsequent formation of large metal clusters upon reduction.
Following the reduction of the grafted Pd complex, nitrogen adsorption experiments were performed on the Pd-TMS catalysts to determine if the supports’ BET surface areas or pore sizes had been altered by the vapor-grafting process. The data in Table 4.1 showed only slight decreases in the pore sizes and void fractions of the supports upon Pd deposition. The MCF support showed a particularly small fractional change in its void fraction upon Pd deposition, indicating that there were not a significant number of Pd clusters blocking the pores of this support in comparison to MCM-41 and SBA-15. In addition to nitrogen adsorption experiments, CO chemisorption analysis was performed on the catalysts to determine the surface area of palladium on the support (see Table 4.1). Elemental analysis of the catalysts (via ICP) indicated the total weight percent of palladium on the supports. Table 4.1 showed that the total palladium loadings were ~10 wt% for both polymer-templated mesoporous materials (i.e. SBA-15 and MCF), but the metal loading was significantly higher (22 wt%) for the MCM-41-supported catalyst. This was expected since MCM-41 has a higher surface area and should therefore adsorb more of the sublimed organo-palladium complex.

From the palladium loading and dispersion data, an approximate palladium cluster size can be determined by assuming a spherical crystallite morphology. For our catalysts, the calculated palladium crystallite diameters are 3 - 4 nm. Powder XRD was used to confirm the presence of palladium metal on the mesoporous supports and to verify the metal crystallite size. The XRD pattern of Pd-TMS13 in Figure 4.2 shows only broad humps corresponding to Pd diffraction, despite the presence of over 10 wt% Pd. The width of the peak can be correlated to the crystallite size using the algorithm developed by Scherer. The palladium peaks from the vapor-grafted catalysts are too broad to obtain reliable peak widths, indicating crystallites below 5 nm.

*Figure 4.2 XRD pattern of Pd-TMS13 displaying only broad humps corresponding to Pd.*
HRTEM was used to directly observe the nanometer-sized palladium clusters produced by the vapor grafting process. Figure 4.3 shows a HRTEM image of Pd-TMS13; a high population of 1 - 5 nm palladium clusters is clearly visible. In Figure 4.3(b) the lattice fringes of one of the crystallites can be observed and the spacing of the lattice fringes (~ 1.5 Å) matches that of metallic Pd. From the above characterization data, it can be seen that the vapor grafting process yields heterogeneous catalysts consisting of 10 - 20 wt% palladium evenly dispersed as 1 - 5 nm crystallites on the surface of mesoporous silica supports.

4.3.2 Effects of Temperature and Pore Size on Heck Reaction Kinetics

To determine the efficacy of the different mesoporous silica supports, the Pd-TMS materials were used to catalyze the Heck coupling of 4-bromoacetophenone and n-butyrylacrylate using triethylamine as the basic co-reactant. The consumption of the limiting reagent, 4-bromoacetophenone, measured relative to the dodecane internal standard by gas chromatography, was used to determine the reaction conversion and turnover number (TON = moles of bromoacetophenone reacted per mole of palladium) and turnover frequency (TOF = d(TON)/dt). Selectivity for the cinnamic acid ester coupling product was
Figure 4.4 Heck coupling of bromoacetophenone with n-butyralcylate at (a) 130°C and (b) 160°C over Pd-TMS11 (▲, MCM-41 supported), Pd-TMS12 (O, SBA-15 supported), and Pd-TMS13 (■, MCF supported) catalysts. Reaction was performed in a dimethylacetamide solvent with a bromoacetophenone-to-Pd ratio of 5000 and a butylacrylate:triethylamine:bromoacetophenone ratio of 1.1:1.1:1.0. Dodecane was used as an internal standard.

~99% and the most significant impurity detected was butylacrylate-butylacrylate coupling products. The ratio of trans-to-cis isomers of the bromoacetophenone-butylacrylate coupling product was ~99:1 for all catalysts used in this study.

Reactions were initially run with Pd-TMS catalysts at 130°C and the results are shown in Figure 4.4(a). At 130°C, greater than 90% conversion of bromoacetophenone was obtained for all three catalysts (the initial molar ratio of bromoacetophenone-to-Pd was 5000 in all cases), and there was little difference in activity between the catalysts immobilized on the three different supports. The turnover frequency for all three catalysts, measured between 20% and 80% conversion of bromoacetophenone, was ~1 mol BrC₆H₄C(O)CH₃/mol Pd·s.

The rate of diffusion in liquids is approximately proportional to the temperature, while the reaction rate is ostensibly proportional to e⁻¹/Ｔ. Therefore, increasing the reaction temperature should greatly enhance the rate of the surface reactions relative to the rate of diffusion, and transport limitations in the three supports could be elucidated. The
Heck reaction results for Pd-TMS11, Pd-TMS12, and Pd-TMS13 at a reaction temperature of 160°C are shown in Figure 4.4(b), and indeed there were significant differences between the activities of the three catalysts. The turnover frequency (measured from 20 - 80% conversion) for Pd supported on MCF was ~ 8.0 mol BrC6H4C(O)CH3/mol Pd · s, while the TOFs for the supports with cylindrical pores (SBA-15 and MCM-41) were significantly lower at 3.5 and 2.4 mol BrC6H4C(O)CH3/mol Pd · s, respectively.

In order to define the temperature dependence of the catalyzed Heck reaction, we ran the Pd-TMS13 catalyst at five different temperatures (see Figure 4.5). The rate of reaction decreases dramatically between 130°C and 125°C, indicating a strong activation energy for the reaction. Another trend that can be noted in Figure 4.5 is the increase in the ‘initiation period’ with decreasing temperature. When the coupling of bromoacetophenone and butylacrylate was carried out over Pd-TMS13 at 160°C, the reaction reached its maximum rate almost immediately, as would be expected from the higher initial concentrations of reactants in
the batch process. As Figure 4.6 shows, however, the time at which the maximum reaction rate was reached increases with decreasing temperature. In fact, the reactions at 125°C and 120°C never reach a point at which the reaction rate begins to decrease, and so the Pd-TMS13 catalyzed Heck reaction appears to remain in the initiation period for the duration of the reaction at these low temperatures. Similar temperature dependences were observed for Pd-TMS11 and Pd-TMS12 catalysts (see Figure 4.7).

The existence of transient behavior at the beginning of homogeneous catalytic reactions is a common phenomenon since the active catalytic species is often formed under reaction conditions. For homogeneously catalyzed Heck reactions, the initiation period of low activity is associated with the reduction of Pd²⁺ catalyst precursors to Pd⁰ active species, and it is the rate of the catalyst activation that dominates initial reaction rates.⁹ Le Bars et al. have also noted an initial transient period before attaining peak activity when ~ 3-nm Pd colloids were used to catalyze the Heck reaction at 140°C, although no reason for the activation period was given.¹⁰ It is well

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**Figure 4.7** Temperature dependence of the Heck coupling reaction over (a) Pd-TMS12 (SBA-15 supported) and (b) Pd-TMS11 (MCM-41 supported). The reactions were run at 160°C (x), 130°C (■) and 120°C (●). The reactions were performed in a dimethylacetamide solvent with a bromoacetophenone-to-Pd ratio of 5000 and a butylacrylate:triethylamine:bromoacetophenone ratio of 1.1:1.1:1.0. Dodecane was used as an internal standard.
known that palladium will form a surface layer of PdO when exposed to air. Since our experiments and those of Le Bars et al. are run in air, the initiation periods in the reaction runs with Pd nanocluster catalysts are likely due to the reduction of the PdO surface species to active Pd⁰ species in the reaction solution, similar to the reduction seen in homogeneous catalysts. To test this hypothesis, we used a sample of Pd-TMS13 that had been oxidized in air at 400°C as a Heck catalyst and found a two-hour induction period before significant conversion was achieved at 160°C (see Figure 4.8).

From the temperature dependence of the Heck reaction rate over the three catalysts with different pore structures, it can be seen that the reaction rate increases less rapidly with temperature for Pd-TMS11 and Pd-TMS12. This deviation in reactivity between the three catalysts, despite the same active component and similar low-temperature reaction rates, indicates that diffusion limitations are indeed present in the SBA-15 and MCM-41 supported systems. The MCF support therefore provides superior activity for the Heck reaction by imposing less severe transport limitations. In an effort to fully demonstrate the activity of the Pd-TMS catalysts, two reactions were run at a bromoacetophenone-to-Pd molar ratio of 100,000 over Pd-TMS13 and Pd-TMS12 at 160°C (Figure 4.9). The Pd-TMS13 catalyst achieved a TON of 97,000 after 8 hours and the TOF for 20-80% conversion is ~ 7 mol bromoacetophenone/mol Pd · s, similar to the TOF of 8 mol bromoacetophenone/mol Pd · s obtained for the Pd-TMS13 catalyst in the 5,000 TON run at 160°C.

Since homogeneous catalysts are not subject to the same pore diffusion

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**Figure 4.8** Heck coupling activity of Pd-TMS13 catalysts without oxidation treatment (■) and with oxidation treatment at 400°C (○). The reactions were run at 160°C and were performed in a dimethylacetamide solvent with a bromoacetophenone-to-Pd ratio of 5000 and a butylacrylate:triethylamine:bromoacetophenone ratio of 1.1:1.1:1.0. Dodecane was used as an internal standard.
limitations as porous heterogeneous catalyst particles, it is useful to compare the activity of the best homogeneous Heck catalysts to that of our Pd clusters supported on mesoporous silicas. Shaw et al.\textsuperscript{11} have found that tri(1-naphthyl)phosphine-based homogeneous palladacycle catalysts were active for the Heck reaction but turnover numbers for the coupling of bromoacetylbenzene and bromocyanobenzene to styrene were below 200, and the highest TOF obtained was \(\sim 0.01\) mol bromoacetylbenzene/mol Pd \(\cdot\) s. Rosner et al.\textsuperscript{13} have performed detailed kinetic studies on nitrogen-based palladacycle catalysts originally synthesized by Granell et al.\textsuperscript{13} They reported that the nitrogen-based palladacycles obtained a TOF of 12,000 hr\(^{-1}\) (\(\sim 3.3\) s\(^{-1}\)) for the coupling of bromobenzaldehyde to \(n\)-butylacrylate, but they claimed that these catalysts could obtain a TOF of 50,000 hr\(^{-1}\) (\(\sim 14\) s\(^{-1}\)). Beller et al.\textsuperscript{5} used a colloidal Pd catalyst for the coupling of bromoacetophenone to butylacrylate with the temperature ranging from 140\(^\circ\)C to 160\(^\circ\)C in each reaction and achieved a maximum TOF of 24,000 hr\(^{-1}\) (6.7 s\(^{-1}\)). The best results for a colloidal Pd system, however, were obtained by Le Bars et al.\textsuperscript{10} who used poly(vinyl pyrrolidone) to stabilize Pd particles of 1.5 to 3 nm, and achieved a maximum TON of 100,000 with a TOF of 22 s\(^{-1}\) for the coupling of bromobenzaldehyde to butylacrylate at 140\(^\circ\)C. The maximum turnover number (97,000) and turnover frequency (\(\sim 8\) s\(^{-1}\)) measured from 20–80\% conversion, \(\sim 16\) s\(^{-1}\) obtained from the peak reaction rate (Figure 4.6)) for our Pd-TMS13 catalyst are comparable to those of the best homogeneous catalysts, and approach the TOF of the best nanometer-sized colloidal systems. The MCF-supported catalyst shows lower activity than the colloidal systems despite their nearly identical Pd cluster sizes, indicating that some diffusional limitations still existed in the MCF system. However, the Pd-TMS13 catalyst has the advantage that it can be easily separated from the reaction mixture and be reused.

![Figure 4.9](image-url) Heck coupling reaction over Pd-TMS13 (■) and Pd-TMS12 (○). The reactions were run at 160\(^\circ\)C in a dimethylacetamide solvent with a bromoacetophenone-to-Pd ratio of 100,000 and a butylacrylate:triethylamine:bromoacetophenone ratio of 1.1:1.1:1. This Dodecane was used as an internal standard.
The similarity of the results between homogeneous, colloidal, and our heterogeneous catalysts could indicate that a dissolved Pd species was the active catalyst in all cases, so we performed two experiments to test the heterogeneity of our reaction. First, we quenched a reaction after ~ 20% conversion, filtered the solution to remove catalyst particles, and then heated the reaction solution back to 160°C. After 24 hours, the filtered reaction solution showed less than 5% further conversion, indicating that dissolved Pd species or free Pd colloids were unlikely to be the active species in our catalysts. For the second heterogeneity test, we made use of the fact that elemental mercury would form an amalgam with palladium and therefore poison Pd metal clusters, while distinct organometallic species should not be affected by the presence of elemental Hg. After 20% conversion had been reached for the coupling of bromoacetophenone to butylacrylate at 160°C, we added a drop of elemental Hg and found that no further reaction occurred, substantiating the heterogeneous nature of our active species.

4.3.3 Catalyst Recovery and Reuse

In addition to developing a support material that would provide reactivity equal to the best colloidal and homogeneous catalysts, we also desired to create a catalyst that could be easily separated from the reaction mixture and be reused in subsequent reactions. The Pd-TMS catalysts were removed from reaction mixtures by filtration, and were rinsed, dried and reused. Elemental analysis of the used catalysts showed no measurable loss in palladium, but 4 - 5 wt% carbon deposition was noted. Powder XRD experiments performed on the recovered Pd-TMS13 catalysts (Figure 4.10(b)) showed an increase in the intensity and a decrease in the width of

Figure 4.10 XRD patterns of Pd-TMS13 catalysts (a) before reaction, and after reaction (b) with no treatment, (c) with oxidation post-reaction treatment at 400°C and (d) with reduction-oxidation-reduction post-reaction treatments at 400°C.
Pd diffraction peaks, indicating an increase in the palladium crystallite size. Scherer's analysis revealed that the palladium grain size had grown from < 5 nm to 15 nm after reaction.

*a.* Bright field image

Si map  

Pd map

100 nm

*b.* Bright field image

Si map  

Pd map  

Br map

*Figure 4.11* STEM images and EDS elemental maps of Pd-TMS13 (a) before reaction, and (b) after reaction with no post-reaction treatment.

To obtain more detailed information on the agglomeration of the supported Pd, STEM and energy dispersive spectroscopy (EDS) were used to image the elemental distribution within the catalysts. Elemental mapping of the unused catalyst, shown in Figure 4.11(a), illustrates the uniform distribution of Pd throughout the catalyst surface. After reaction, however, the palladium has agglomerated into large clusters (~ 100 nm) comprised of smaller crystallites (10 - 20 nm). In addition to the aggregation of Pd, there was also a detectable concentration of bromine on the catalyst surface. Excess Br on the catalyst could occupy Pd coordination sites and prevent the Pd surface atom from rejoining the catalytic cycle if the Br is not removed with the base as shown in the Heck reaction cycle (Scheme 4.4). Oxidation-reduction cycles are known to remove poisoning halide
impurities from metal surfaces, so our recovered catalysts were subjected to reduction-oxidation-reduction treatments at 400°C to remove the excess bromine. EDS studies on the treated catalysts indicated that the majority of Br had been removed from these catalysts, but a small amount of bromine was still detectable on the Pd clusters themselves. The XRD patterns of the recovered catalysts that received post-reaction treatments are shown in Figures 4.10(c) and (d). When the recovered catalyst was only oxidized at 400°C, PdO grains of 20 nm were noted. When the catalyst was subjected to the full reduction-oxidation-reduction cycle, the Pd crystallite size was as large as ~ 100 nm.

The Pd-TMS catalysts recovered from reaction mixtures were reused in subsequent reactions with or without post-reaction treatments. Figure 4.12 shows that the activity of the recovered and untreated catalysts was an order of magnitude lower than the original catalyst. Not all of the decrease in activity could be attributed to the loss of Pd surface area, however, since the catalyst that was subjected to the post-reaction

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**Figure 4.12** Heck coupling activity of Pd-TMS13 catalysts in the first run (■), in the second run with no treatment (▲), and in the second run after reduction-oxidation-reduction treatment (○). The reactions were run at 160°C in a dimethylacetamide solvent with a bromoacetophenone-to-Pd ratio of 5,000 and a butylacrylate:triethylamine:bromoacetophenone ratio of 1.1:1.1:1.0. Dodecane was used as an internal standard.

**Figure 4.13** Heck coupling reaction over Pd-TMS13 catalysts run with a triethylamine:bromoacetophenone ratio of 1.1 (■, □) and 2.2 (○, ○). Filled symbols indicate the first reaction run with the catalyst, and open symbols indicate the second reaction run with the recovered and untreated catalyst. The reactions were run at 160°C in a dimethylacetamide solvent with a bromoacetophenone-to-Pd ratio of ~ 5,000 and a butylacrylate:bromoacetophenone ratio of 1.1:1.0. Dodecane was used as an internal standard.
reduction-oxidation cycle showed improved activity over the untreated catalyst despite the much larger Pd grain size of the former. We therefore conclude that the presence of bromine on the recovered catalyst had a significant detrimental effect on the catalytic activity. In order to ensure the more complete removal of bromine from the catalyst surface, reactions were run using twice the normal concentration of triethylamine (Figure 4.13). In the initial reaction with a base-to-bromoacetophenone ratio of 2.2, slightly higher conversions were achieved although the kinetics of the reaction were somewhat slower than when a base-to-bromoacetophenone ratio of 1.1 was used. In the second run, the conversion and kinetics of the recovered and untreated catalyst were superior when a higher base concentration was used. In fact, the activity was approximately equal to that of the treated recovered catalyst run at the lower base concentration (Figure 4.12).

The heterogeneous Pd-TMS catalysts were easily separated from the reaction mixtures and could be used for subsequent runs. However, palladium agglomeration and bromine poisoning significantly reduced the activity of the recovered catalysts. The use of higher base concentrations in the reaction solution or post-reaction treatments of the recovered catalysts was effective in partially restoring the activity of the catalysts, but a means of preventing or reversing the loss of palladium surface area during reaction has not yet been established.

4.4 Summary
We have used mesocellular silica foams as supports for heterogeneous Heck catalysts in order to determine the possible advantages of the MCF's large pores and high void fractions. The Heck reaction was selected because it is widely used in the synthesis of pharmaceuticals and fine chemicals, and because the rapid reaction rates obtained with homogeneous catalysts could lead to significant mass transport limitations in a heterogeneous catalyst. Our heterogeneous catalysts were synthesized by vapor grafting allylcyclopentadienyl-palladium complexes onto MCM-41, SBA-15 and MCF silica supports, followed by reducing the complexes to form nanometer-sized palladium clusters. The resulting Pd-TMS11 (MCM-41 supported), Pd-TMS12 (SBA-15 supported) and Pd-TMS13 (MCF supported) catalysts were used for the Heck coupling of bromoacetophenone to n-
butylacrylate in the presence of triethylamine. Pd-TMS13 achieved an impressive TOF of 8 - 16 s⁻¹, which compares favorably with the most active homogeneous Heck catalysts reported in the literature (TOF of 3.3 - 14 s⁻¹).¹²

At a reaction temperature of 130°C, there was little difference between the activities of the catalysts supported on silicas with different pore sizes. At 160°C, however, the activity of the MCF-supported catalyst was significantly better than those of the catalysts supported on SBA-15 and MCM-41. The high activity of Pd-TMS13 was attributed to the large pores and open pore structure of MCF that reduced diffusion limitations on the reaction rate.

The activity of the supported Pd nanoclusters decreased precipitously below 130°C. The dramatic change in reactivity with changing temperature was associated with the high activation energy process of reducing surface palladium oxides to the Pd⁰ species that were most active for Heck catalysis. This hypothesis was confirmed through the use of heterogeneous palladium catalysts that had been fully oxidized to PdO by treatment in air at 400°C. The oxidized catalysts were initially inactive, but showed slightly improved activity after long exposures to the reaction mixture at high temperatures.

The heterogeneous Pd-TMS catalysts were easily separated from the reaction mixtures and could be used for subsequent runs. However, palladium agglomeration and bromine poisoning significantly reduced the activity of the recovered catalysts. The catalyst activity could be partially restored through the use of higher base concentrations in the reaction solution or post-reaction treatments of the recovered catalysts.
4.5 References


CHAPTER 5
Heterogeneous Asymmetric Hydrogenation

5.1 Introduction
Asymmetric hydrogenation is an important reaction for producing single enantiomer chemicals to satisfy the increasing demand for enantio-specific pharmaceuticals and fine chemicals. Numerous homogeneous catalysts, primarily transition metal complexes possessing bidentate chiral phosphine ligands to induce enantioselectivity, have been developed to hydrogenate prochiral alkenes and ketones to a specific enantiomer at enantiomeric excesses (ee) greater than 95%.

Despite the remarkable selectivity of the organometallic homogeneous catalysts, they have several major deficiencies. First, the homogeneous catalysts are very expensive (frequently costing in excess of $300/g) and are difficult to separate and recover from the reaction mixture. Improving the turnover numbers of these catalysts has made them more economically attractive, and yet the catalysts are still not reusable and can remain as impurities in the reaction products. In contrast, a properly designed heterogeneous catalyst could provide simple and complete separation (e.g., by filtration) and could remain active for multiple reaction cycles. An effective heterogeneous catalyst must possess catalytic activity and selectivity rivaling those of the homogeneous catalysts, and the support material must provide a large active surface area for reasonable active site densities, while not imposing mass transfer limitations on reaction rates. As for the Heck reaction, some of the most important uses of asymmetric hydrogenation are for the production of large pharmaceutical molecules. Thus, asymmetric hydrogenation provides another example in which heterogeneous catalysts with pore structures specifically tailored to accommodate large molecules could offer significant advantages in reaction kinetics.

A number of prior attempts to develop enantioselective heterogeneous catalysts have produced materials with good selectivity; schematic representations of some of these are shown in Figure 5.1. Davis and co-workers have synthesized metal-phosphine complexes that are soluble in polar solvents. These catalysts are first dissolved in a polar solvent and then wetted onto a support with a polar surface. Apolar solvents are used for the reaction and therefore the catalyst remains in the wetting layer of the support (Figure 5.1(a)).
Another method for heterogenizing asymmetric hydrogenation catalysts is to covalently bond the chiral phosphine ligands to a solid surface, most frequently through condensing alkoxyaryl-modified phosphines with surface silanol groups (Figure 5.1(b)). Recently, chiral phosphine ligands have been incorporated into polymer backbones to generate reusable asymmetric hydrogenation catalysts (Figure 5.1(c)). These methods are all restrictive as to the type of phosphine that can be used, since the chiral phosphine itself must be modified and new chemistries must be developed to incorporate a new chiral phosphine.
The objectives of our investigation into asymmetric hydrogenation reactions are two-fold: first, we endeavor to synthesize a homogeneous asymmetric hydrogenation catalyst with selectivity equivalent to the current homogeneous catalysts, and second, we wish to determine the effect of support pore size and structure on the activity of these catalysts. We have developed a novel method for immobilizing active and selective asymmetric hydrogenation catalysts onto mesoporous silica supports. Instead of immobilizing the homogeneous catalyst through the chiral phosphine ligand, we have synthesized a triethoxysilylpropylisonitrile compound that binds strongly to transition metals, and therefore can be used to hold the metal-phosphine complex onto a surface without modifying the chiral phosphine ligand. Using this ‘strong ligand’ immobilization procedure, we can generate a range of heterogeneous transition metal-chiral phosphine catalysts, such as \([S\text{-BINAP}]{\text{Ru}(C_{8}H_{11})(CNC}_{3}H_{6}(SiO_{2})_{n})}\text{BF}_{4}\) (4, Scheme 5.2). We have used the mesocellular foams (MCF),\(^6\) with pore sizes of \(\sim 30\) nm and surface areas of \(\sim 700\) m\(^2\)/g, as the supports for the immobilized catalysts.

**Scheme 5.1** BINAP-Ru-isonitrile synthesis
5.2 Experimental Procedures

In order to synthesize an active and selective heterogeneous asymmetric hydrogenation catalyst using the 'strong ligand' immobilization approach, we began with a homogeneous catalyst developed by Wiles et al. \([\text{BINAP}]\text{Ru}(\text{C}_8\text{H}_{11})(\text{NCCH}_3)\text{BF}_4\), 1, due to the high activity and selectivity of this complex for the asymmetric hydrogenation of a wide range of substrates,\(^7\) the extensive use of Ru-BINAP complexes in industry,\(^8\) and the weakly coordinated nature of the catalysts “spectator” (i.e. non-chiral) ligands that would make them easy to replace with a strong ligand in our reaction scheme. As shown in Scheme 5.1 and Figure 5.2, the BINAP (bis(diphenylphosphino)-1,1'-binaphthyl) ligand used to impart enantioselectivity to the transition metal active site consists of two naphthyl groups linked through a 1,1' bridge. The phosphorous atoms bind to the active metal, while the bulk of the diphenyl groups prevents racimization of the complex via rotation of the 1,1' carbon-carbon bond. As described below, we have investigated a number of different strong ligand chemistries for immobilizing the Ru-BINAP complex, and have tested the different formulations for catalytic activity. The catalysts were also immobilized on a number of different mesoporous supports to study the effects of support pore size and structure on the activity of the heterogeneous asymmetric hydrogenation catalysts.

![Figure 5.2 The structure of a BINAP-Ru-acetonitrile catalyst, 1, as determined by Wiles et al.\(^6\)](image)

5.2.1 Catalyst Synthesis and Characterization

The alkoxide precursor to the immobilized asymmetric hydrogenation catalyst, \([(\text{S-BINAP})\text{Ru}(\text{C}_8\text{H}_{11})(\text{NC}_3\text{H}_6\text{Si(OCC}_2\text{H}_5)_3)]\text{BF}_4\), 3, was synthesized as shown in Scheme 5.1. First, the acetonitrile “weak ligand” version of the catalyst, \([(\text{S-BINAP})\text{Ru}(\text{C}_8\text{H}_{11})(\text{CH}_3\text{CN})]\text{BF}_4\), 1, was synthesized according to the procedure of Wiles et al.\(^7\) Next, compound 1 (3.4 g,
0.035 mol) was dissolved in methylene chloride (Aldrich, 30 mL). To the orange solution, CNC$_3$H$_5$Si(OC$_2$H$_5$)$_3$ (2, Aldrich, 0.89 g) was added. The mixture was stirred at room temperature for 15 min and was concentrated under vacuum to ca. 15 mL. Pentane (Aldrich, 150 mL) was layered onto the yellow solution to give a yellow precipitate. The solid was filtered, washed with pentane (Aldrich) and dried to give 3.2 g of product. The calculated weight percentages for C$_6$H$_6$NO$_3$BF$_4$P$_2$RuSi are: 64.81 wt% C, 5.61 wt% H and 1.22 wt% N. The component weight percents experimentally determined by carbon, hydrogen and nitrogen analysis (QTI, Whitehouse, NJ) were: 63.90 wt% C, 5.87 wt% H, 1.57 wt% N. $^{13}$C and $^{31}$P nuclear magnetic resonance (NMR) analyses were used to confirm the structure of the compound. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 20°C): 8.40 (s, CH$_2$Si), 18.3 (s, CH$_3$), 59.0 (s, CH$_2$O), 20.1 (d), 23.4, 23.5, 23.8, 24.4, 25.3, 26.3, 27.1, 31.9, 34.5, 36.4, 41.1, 42.4, 47.0, 48.1, 48.6, 54.4, 57.5, 58.8, 59.0, 61.2, 65.1, 65.3, 70.0, 70.2, 92.8, 95.9, 100.8, 100.9, 109.6, 109.7. $^{31}$P($^1$H)NMR (162 MHz): 44.2 (d, JPP = 31 Hz), 43.3 (d, JPP = 29.6 Hz), 31.70 (d, JPP = 29.6), 30.9 (d, JPP = 31 Hz). Photoacoustic Fourier-transform infrared (PA-FTIR) analysis: 2154 cm$^{-1}$ (vCN).

The procedure used to immobilize 3 on mesoporous silica is shown in Scheme 5.2. In one example of this synthesis, MCF was used as the support. MCF (BET surface area: 750 m$^2$/g, median pore size: 350 Å, pore volume: 2.3 cm$^3$/g, elemental analysis: 0.36 wt% C, 0.60 wt% H, 0.32 wt% N) was first dried at 5x10$^{-2}$ mmHg vacuum and 140°C for 12 hours. To the MCF, 3 (1.0 g), toluene (Aldrich, 150 mL) and water (0.12 mL) were added. The mixture was heated with stirring in a 95°C oil bath for 12 hours. The yellow slurry was filtered to remove the colorless toluene solution. The solid was washed with methanol (Aldrich, 3 x 40 mL), methylene chloride (Aldrich, 20 mL), and then methanol (20 mL) again, to remove any physically adsorbed complex. The resulting yellow

![Scheme 5.2 Synthesis of heterogeneous asymmetric hydrogenation catalyst](image-url)
powder, 4, was dried at 95°C for 1 hour, yielding 3.40 g of product. Elemental analysis was performed on 4 to give 16.77 wt% C, 1.61 wt% H, 0.57 wt% N, 0.68 wt% P, 2.24 wt% Ru.* BET surface area (494 m²/g), BJH adsorption pore volume (1.28 cm³/g), and median pore diameter (328 Å) of the heterogeneous catalysts were measured using nitrogen adsorption, and PA-FTIR analysis was performed, primarily to track the distinct isonitrile peak at 2154 cm⁻¹ (νCN).

Compound 3 was also fixated on commercial silica gel. Large-pore silica gel received from Strem Chemicals (BET surface area: 248 m²/g) was dried at 140°C under vacuum for 12 h. Aside from the support material, the fixation procedure was identical to that on MCF. Elemental analysis of the sample gave 12.27 wt% C, 1.09 wt% H, 0.40 wt% N, 0.59 wt% P, 1.8 wt% Ru.* The support parameters after fixation were BET surface area: 291 m²/g, BJH adsorption pore volume: 1.13 cm³/g, and median pore diameter: 316 Å.

5.2.2 Catalytic Testing

Hydrogenation of terminal olefins by silica-supported catalysts was carried out in the high-pressure reactor shown schematically in Figure 5.3, and the specific hydrogenation reactions investigated are shown in Scheme 5.3. For kinetic studies, methyl 2-acetamidoacrylate (MAA) 5 (Aldrich, 150 mg) or dimethylitaconate (DMI) 7 (Aldrich, 20 g) was dissolved in methanol (Aldrich, 250 mL) and the solution was transferred to the autoclave. The reactor and the mixture were purged with argon and then with hydrogen. The hydrogen pressure was increased to 150 psi with a stirrer speed of 1000 rpm. The increase in H₂ pressure was used to blow 20 mg of the catalyst 4 from an air-free holding tube into the reactor. The progress of the reaction was monitored by gas chromatography (GC, Hewlett Packard 5890) or by in situ FTIR spectroscopy (ASI ReactIR). Analytical conditions: column: dimethylated β-cyclodextran (30 m x 0.32 mm) from Advance Separation Technologies, Inc.; oven temperature: 110°C; carrier gas: 25 psi helium; GC detector: FID. Following the reaction, the mixture was removed and centrifuged under argon to recover the catalyst powder. The yellow powder was then rinsed with methanol, centrifuged, and recovered (all under argon) before being reused.

*Elemental analysis for Ru, performed using acid digestion/thermal decomposition sample preparation for inductively coupled plasma (ICP) analysis as performed by QTI (Whitehouse, NJ) produced unreliable results for catalysts 3 and 4, with Ru contents ranging from 0.4 wt% to 2.0 wt%. This is believed to be due to incomplete dissolution of the sample. ICP analysis using laser ablation sample preparation was performed at Hydro-Quebec, (Quebec, Canada) and produced more repeatable results ranging from 1.5 wt% to 3.0 wt% depending on the sample, error in the Ru measurement was still ± 0.25 wt%.
Figure 5.3 Schematic diagram of high-pressure hydrogenation reactor.

Scheme 5.3 Asymmetric hydrogenation reactions
The second reaction run was performed under identical conditions except the mass of all reactants used was halved. The homogeneous complex 3 was also run under conditions identical to the first heterogeneous catalyst run, except the total mass of catalyst used was 8 mg, so as to maintain a constant molar ratio of reactants to Ru (i.e. all reactions were run at constant total turnover number).

5.3 Results and Discussion

5.3.1 Homogeneous Acetonitrile Asymmetric Hydrogenation Catalysts

Initially the homogeneous acetonitrile Ru-BINAP catalyst 1 was synthesized according to the procedure of Wiles et al., and the activity of this catalyst for the hydrogenation of methylacetamidoacylate was measured to confirm successful reproduction of the results of Wiles et al. and to establish baseline conditions for the testing of novel heterogenized catalysts. The catalytic results obtained using 1 at 150 psig H₂ are shown in Figure 5.4. As was found by Wiles and Bergens, the turnover frequency of catalyst 1 was relatively low at room temperature, ~ 0.0001 s⁻¹, and the enantiomeric excess (ee) for the hydrogenation of methylacetamidoacylate was ~ 67% (R). In order to increase the reaction rate, we raised the reaction temperature to 60°C. At elevated reaction temperatures, we observed a slight decrease in selectivity (ee ~ 65%), which has been reported previously in the literature. However, raising the reaction temperature to 60°C dramatically increased the hydrogenation rate.

![Graph](image)

**Figure 5.4** Conversion of methylacetamidoacylate over catalyst 1 at 60°C (■) and 25°C (○).

Hydrogen pressure had a more dramatic effect than temperature on the enantioselectivity of the reaction. At low H₂ pressures, ~ 4 psig, the ee for the hydrogenation of methylacetamidoacylate was nearly 80% (R) at 60°C. Previous studies have reported a significant decrease in ee with increasing H₂ pressure, but the exact mechanism is still under debate. At 60°C, the hydrogenation rate at 150 psig H₂ was an order of
magnitude higher than that at 4 psig. The higher rate would allow us to more easily differentiate the effects of pore size and structure on the kinetics of the reaction. We also found, through the testing of the homogeneous acetonitrile-Ru-BINAP catalyst, that the reaction rate was not significantly affected by hydrogen pressure or stirring speed when the $H_2$ pressure was maintained above 100 psig and the stirring speed was kept above 750 rpm. The Autoclave Engineers reactor used in these experiments is not only rated for high-pressure use, but also fitted with a gas mixing impeller that circulates gas from the head space through the reaction solution. With this forced convection of small bubbles of hydrogen through the solution, the gas-liquid transport rate is greatly enhanced, thereby eliminating the hydrogen diffusion rate limitations commonly observed in asymmetric hydrogenation studies. Above 100 psig of pure $H_2$, the saturation concentration of hydrogen in methanol is 0.05 M (actually measured at 55°C by Koneripalli et al.)."1 Given the 0.01 M concentration of methylacetamidoacrylate used in these experiments, there was a large excess of $H_2$ and the expected independence of the reaction rate with increasing hydrogen pressure. Therefore, all subsequent reactions were run using methanol as the solvent at 60°C under a pure hydrogen atmosphere of 150 psig with a stirring speed of 1000 rpm, unless otherwise noted.

5.3.2 Comparison of Three Strong Ligands for the Heterogenization of Ru-BINAP Catalysts to Silica Surfaces

In the derivation of asymmetric hydrogenation catalysts, and indeed most conventional asymmetric catalysts, the most complex step of the procedure is the synthesis of the bidentate chiral ligand that imparts enantioselectivity to the catalyst. Modification of the bidentate chiral phosphines of asymmetric hydrogenation catalysts, as is required by most other heterogenization methods, not only demands laborious modification and repetition of the most difficult steps in the catalyst synthesis in order to develop the optimal catalyst formulation, but also holds the possibility of significantly decreasing the enantioselectivity of the catalyst. By not modifying the chiral bidentate phosphine ligand, the strong ligand approach allows for the use of commercially available chiral phosphines and should maintain the enantioselectivity of the original homogeneous catalyst. Furthermore, a number of different immobilization chemistries can be investigated through the use of commercially available or easily synthesized strong ligands.
We have investigated the effect of strong ligand chemistry on immobilized catalyst activity by using silicon alkoxide modified with thiol 9, phosphine 11, and isonitrile 13 ligands (all of which bind strongly to transition metals) to tether Ru-BINAP complexes to the surface of MCF silica supports. The chemical structures of the three strong ligands as well as the generalized immobilization method used to synthesize all three heterogenized catalysts are shown in Scheme 5.4. The synthesis method for these initial heterogenized catalysts consisted of first immobilizing the strong ligand onto the silica support, and then introducing a Ru-BINAP complex with a weakly bound spectator ligand that exchanged with the strong-binding surface ligand to generate a free weak ligand in
solution and the immobilized complex. The catalysts were then rinsed with methanol to remove remnant weak ligands, and stored under air-free conditions to prevent the oxidation of the BINAP phosphines.

The results for the hydrogenation of methylacetamidoacrylate over the heterogeneous thiol-, phosphine-, and isonitrile-Ru-BINAP catalysts are shown in Figure 5.5. The [(S-BINAP)Ru(C₆H₅)₂(C₃H₆SiO₂)]BF₄ 12 catalyst showed poor activity for the hydrogenation of methylacetamidoacrylate, reaching only a few percent conversion after more than a day, despite the fact that the ee produced by the phosphine strong ligand catalyst was nearly the same as that of the homogeneous acetonitrile-Ru-BINAP complex. Both the thiol-Ru-BINAP 10 and the isonitrile-Ru-BINAP 4 catalysts showed significantly higher activity than the phosphine strong ligand catalyst, and the ee of all catalysts were above 60%. However, the thiol and isonitrile catalysts showed very different kinetic behavior. The thiol catalyst had a high initial activity, and the rate of reaction decreased as the reaction progressed. The rate of hydrogenation over the isonitrile catalyst, on the other hand, increased with time to approximately twice that of the initial rate over the thiol catalyst. After the initiation period, the rate of hydrogenation over the isonitrile catalyst appeared to be independent of the MAA concentration. The zero-order kinetics of the isonitrile-Ru-BINAP catalyst are discussed in greater detail in Section 5.3.5.

Since the isonitrile strong ligand catalyst 4 showed the highest activity of the three heterogeneous asymmetric hydrogenation catalysts, we selected this catalyst for further study. The fact that all three heterogeneous catalysts showed less than 5% deviation from the ee of the previously developed homogeneous catalysts indicates that the strong ligand immobilization technique was successful at maintaining the enantioselectivity of the homogeneous compound.
5.3.3 Comparison of the Homogeneous Isonitrile Catalyst to Isonitrile Catalysts Immobilized on Different Silica Supports

The isonitrile-Ru-BINAP catalyst 4 that showed the highest activity in the screening studies was then immobilized on 3 different silica supports: SBA-15, MCF, and commercial large-pore silica gel (Strem Chemicals). The catalyst was heterogenized using a slightly different technique than that used in the screening studies. First, the homogeneous isonitrile-Ru-BINAP complex was synthesized as shown in Scheme 1, and then the compound was attached to the surface of the silica support as shown in Scheme 2. This approach allowed the complex to be carefully purified by techniques such as recrystallization before it is immobilized, and therefore led to fewer impurities in the resulting heterogeneous catalysts.

Physical characterization data for the silica supports before catalyst fixation are provided in Table 5.1. The Strem large-pore silica sample had a median pore size of 464 Å prior to

<table>
<thead>
<tr>
<th>Table 5.1 Pore characteristics and compositions of isonitrile-Ru-BINAP heterogeneous catalysts</th>
</tr>
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<tbody>
<tr>
<td>Support Material</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>SBA-15</td>
</tr>
<tr>
<td>Mesoporous Foam</td>
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</tbody>
</table>

BET Surface Area

<table>
<thead>
<tr>
<th></th>
<th>before fixation</th>
<th>after fixation</th>
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</thead>
<tbody>
<tr>
<td>SBA-15</td>
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<td>18 Å</td>
</tr>
<tr>
<td>Mesoporous Foam</td>
<td>350 Å</td>
<td>328 Å</td>
</tr>
<tr>
<td>Strem Gel</td>
<td>464 Å</td>
<td>316 Å</td>
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</tbody>
</table>

Median Pore Size

<table>
<thead>
<tr>
<th></th>
<th>before fixation</th>
<th>after fixation</th>
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<tbody>
<tr>
<td>SBA-15</td>
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<td>25%</td>
</tr>
<tr>
<td>Mesoporous Foam</td>
<td>86%</td>
<td>75%</td>
</tr>
<tr>
<td>Strem Gel</td>
<td>80%</td>
<td>70%</td>
</tr>
</tbody>
</table>

C/H/N/P Wt Ratio

|                  | 54.2/6.4/1/4.5 | 48.8/5.4/1/4.0 | 53.4/4.0/1/4.3 |
fixation, which is larger than the 350 Å pore size of the MCF used to derive Ru-TMS13c. However, the Strem silica has a broader distribution of pore sizes that was weighted toward smaller pores, along with an irregular pore structure consisting of large pores that were sometimes accessible only by means of smaller pores. MCM-41 was not used as a support because it lost nearly all of its pore volume and had a surface area of < 15 m²/g after fixation of the isonitrile-Ru-BINAP complex, presumably because of the complete blockage of the small pores by the large organometallic compound. The three large-pore silica supports (SBA-15, MCF, and Strem silica gel) all possessed similar weight percentages of nitrogen and phosphines, indicating similar active site loadings. The direct measurement of the Ru concentration in the catalysts via ICP involved significant uncertainties, and multiple measurements for each sample gave values ranging from 0.4 wt% to 3.5 wt%. Therefore, the Ru content was predicted from the nitrogen and phosphorous data assuming one mole of Ru per mole of nitrogen and per two moles of phosphorous. Since the values obtained from nitrogen and phosphorous data were in good agreement, this was determined to be a reasonable method of estimating the true Ru loading. The Ru loadings on all three large-pore silica supports were approximately 2 wt%, allowing for direct comparison of the activity of the resulting catalysts.

The asymmetric hydrogenation of methylacetamidoacrylate was used as a test reaction to compare the activity of isonitrile-Ru-BINAP catalysts immobilized on SBA-15, MCF, and Strem large-pore silica gel (Figure 5.6). Two reactions were run under identical conditions for each catalyst to determine the reproducibility of the results. MCF supported catalysts showed slightly (10%) higher activity in both reaction runs, but given the experimental errors present in the determination of the Ru loading, this difference did not appear to be statistically significant. Also, the measurement of the amount of catalyst added (~ 20 ± 1 mg) resulted in some experimental uncertainty.

In addition to the similarities in reaction rates, the ee's obtained from all three catalysts were essentially the same (ee = 62%, 65% and 64% for Ru-BINAP catalysts immobilized on SBA-15, MCF and Strem silica gel, respectively). The similarities in the selectivities of the three different catalysts indicate that the functional form of the organometallic complex had not changed, suggesting that there were not significant pore restriction effects that would otherwise have distorted the catalytic complex.
The homogeneous complex \([\text{[(S-BINAP)Ru(C_8H_{11}O)(CNC_3H_6Si(OCH_2CH_3)_3)BF_4]}\) was also run under conditions identical to those for the heterogenized catalysts (see Figure 5.6). From these results, it is evident that the heterogeneous catalysts maintained essentially the same selectivity as the homogeneous complex (ee = 65% (S)), and that the heterogeneous catalysts were actually more active than their homogeneous counterpart. All three heterogeneous isonitrile catalysts gave turnover frequencies about 4 times greater than the homogeneous isonitrile catalyst. Both the heterogeneous and homogeneous isonitrile-Ru-BINAP catalysts showed nearly zero-order kinetics up to 98% conversion, after an induction period.

A second vinylic substrate, dimethyl itaconate 7, was also used in catalytic tests of the Ru asymmetric hydrogenation catalysts. Higher reaction rates and enantioselectivities were achieved with DMI as the substrate, and so to test the full capabilities of the heterogeneous isonitrile-Ru-BINAP catalysts, reactions were run in concentrated solutions of DMI (0.5 M in methanol). At the higher substrate concentrations used in the DMI experiments, we were able to use \textit{in situ}-FTIR to monitor the reaction, although GC samples were still taken at various times to corroborate the FTIR data and to determine the ee. The results of the catalytic tests using the DMI substrate are shown in Figure 5.7.
The asymmetric hydrogenation reaction again showed an initial period of low activity, followed by nearly zero-order kinetics with respect to the DMI concentration. The basic shape of the conversion curve for the DMI substrate was the same as that for the MAA substrate. Catalytic tests using other substrates such as α-methylene-γ-butyrolactone and γ-methylene-γ-butyrolactone also showed initial activation periods followed by zero-order kinetics, indicating that the behavior was not attributable to a specific substrate, but rather, was typical of the isonitrile-Ru-BINAP catalysts. The DMI hydrogenation data obtained from the in situ FTIR detector allowed for more detailed observation of the kinetics at high conversions. From Figure 5.7, it can be seen that the hydrogenation rate did not decrease until greater than 97% conversion had been reached. The maximum turnover frequency reached with the MCF-supported isonitrile-Ru-BINAP catalyst is ~ 650 h⁻¹ (0.18 s⁻¹), the ee measured for this reaction was 77%.

Given the low turnover frequency of the heterogenized asymmetric hydrogenation catalysts, the similarity of the activity of the catalysts is to be expected despite the difference in the pore structures of the supports since the diffusion rate of the reactants in methanol is significantly higher than the measured reaction rate. To illustrate the kinetic limitation of the heterogeneous isonitrile-Ru-BINAP catalysts, we can compare the DMI reaction rate of a single catalyst particle to the concentration gradient required within the particle to generate a matching diffusive flux of DMI. A typical particle of MCF is ~ 200 μm in diameter and the ruthenium loading is approximately 2 wt%. Given the measured MCF pore volume of ~ 2 cm³/g, the density of a MCF particle is ~ 0.43 g/cm³ and the moles of Ru within a particle of 200-μm diameter is 3.3x10⁻¹⁰ mol Ru/particle.
Using the maximum TOF of 0.18 mol DMI reacted per mol Ru per second, the typical
catalyst particle reacts 5.5x10^{-11} mol of DMI per second. The diffusive flux of DMI to the
catalyst particle required to balance this reaction rate is \( \sim 4.4 \times 10^{-8} \text{ mol DMI/cm}^2 \cdot \text{s} \). The
diffusivity for DMI in methanol can be calculated from the Wilke-Chang equation,\(^{13}\)

\[
D_{12} = 7.4 \cdot 10^{-10} \frac{T(XM_2)^{1/2}}{\mu V_1^{0.6}}
\]  \hspace{1cm} (5.1)

in which \( D_{12} \) is the diffusivity of solute 1 in solvent 2, \( T \) is the temperature in K, \( X \) is the
solvent association parameter, \( M_2 \) is the molecular weight of the solvent in g/mol, \( \mu \) is
the viscosity of the solvent in poise, and \( V_1 \) is the molar volume of the solute in cm\(^3\)/g.
The association parameter for methanol is 1.9,\(^{14}\) the temperature is 333 K, the viscosity
of methanol is 0.00547 poise, and the molar volume of DMI is 140.7 cm\(^3\)/mol, leading
to a \( D_{\text{DMI-MeOH}} \) of 1.8x10\(^{-5} \) cm\(^2\)/s. With a known diffusivity, diffusional distance (the radius
of a particle \( \sim 100 \mu \text{m} \)) and the required flux to match the reaction rate, we can calculate
the necessary concentration gradient within the particle. The necessary \( \Delta C_{\text{DMI}} \) is 2.4x10\(^{-5} \)
mol DMI/cm\(^3\). Given that the initial concentration of DMI is \( \sim 0.0005 \) mol/cm\(^3\) and
assuming no external transport limitations, the ratio of the concentration at the particle
surface to that predicted at the particle core is 0.95. This very small concentration
gradient leads to a very high catalyst effectiveness factor (reactivity in catalyst
particle/reactivity at bulk solution concentration). In addition, there is little evidence for
concentration dependence for the catalyst activity, indicating that the catalyst activity is
not diffusion limited.

Several tests were run to confirm the heterogeneity of the reactions over the silica-
supported catalysts. The reaction solutions were filtered to remove the catalyst particles,
and ICP was performed on the resulting solutions. No Ru was detected above the exper-
imental sensitivity of 10 ppm. Reaction solutions that were filtered under air-free
conditions (to maintain the activity of any solubilized catalyst species) were reintroduced
to the reactor along with additional methylacetamidoacrylate reactant. The solutions
were run under 150 psi H\(_2\) and 60°C, but showed less than 5% of the heterogeneous
catalyst activity. In addition, PA-FTIR spectroscopy was used to confirm the presence of
the immobilized isonitrile-Ru-BINAP catalysts on the surface of the silica support both
before and after reaction. PA-FTIR spectra of the mesoporous material were taken before
the immobilization of the Ru complex (Figure 5.8(b)), after the immobilization of the Ru
complex (Figure 5.8(c)), and after reaction and rinsing with methanol (Figure 5.8(d)). An
infrared spectrum of the homogeneous catalyst (Figure 5.8(a)) was included for comparison. The isonitrile vibration at ~ 2100 cm⁻¹ and the naphthal vibrations from BINAP at ~ 700 cm⁻¹ were still present after the reaction, indicating that the catalyst remained immobilized on the silica surface.

As the ultimate proof of their utility, the heterogeneous isonitrile-Ru-BINAP catalysts were successfully recovered and reused with little loss in activity or enantioselectivity in subsequent runs. The catalyst was recovered by centrifugation rather than filtration to avoid any loss of material in the filter. The catalyst powder was then rinsed with methanol, centrifuged again and recovered (all under argon) before being reused. The results of two sequential hydrogenation runs with the same catalyst are shown in Figure 5.9, which demonstrated that the immobilized organometallic catalysts could be reused without significant loss of activity or selectivity.

**Figure 5.8** PA-FTIR spectra of (a) homogeneous isonitrile-Ru-BINAP catalyst 3, (b) unmodified MCF support, (c) heterogenized isonitrile-Ru-BINAP catalyst 4 before reaction, and (d) catalyst 4 after reaction.

**Figure 5.9** Conversion of MAA in sequential reaction runs with the same catalyst: first run (■), second run (□). The ee in both reactions was 65%.
5.3.4 Asymmetric Hydrogenation Mechanism

In order to better understand the reaction mechanism of the strong ligand immobilized heterogeneous catalysts, we performed further kinetic tests on the well-characterized homogeneous acetonitrile-Ru-BINAP catalyst 1. Catalyst 1 was run in a concentrated solution of DMI and monitored using in situ FTIR spectroscopy to provide more detailed kinetic information on this catalyst under conditions identical to those used for the hydrogenation of DMI over the heterogenized Ru catalysts. Figure 5.10 shows the results of asymmetric hydrogenation of DMI over the acetonitrile-Ru-BINAP “weak ligand” catalyst. The ee for the reaction was 78%.

The shape of the conversion curve shown in Figure 5.10 is essentially the same as that for the hydrogenation of MAA at lower concentrations, with a high initial reaction rate that decreases as the substrate concentration decreases. As noted previously, this is the opposite result of what is observed for the heterogeneous “strong ligand” catalysts, for which the initial kinetics are very slow followed by near zero-order kinetics to very high conversions. However, the similar enantioselectivities of the homogeneous “weak ligand” catalyst and the heterogeneous “strong ligand” catalyst suggest that the form of the catalyst transition states should be nearly identical. The acetonitrile-Ru-BINAP asymmetric hydrogenation reaction mechanism and intermediate structures determined by Wiles and Bergens are valuable for elucidating the behavior of the immobilized isonitrile-Ru-BINAP catalysts, which should have a similar reaction mechanism and intermediate structures, but have radically different kinetics.

The [[(BINAP)Ru(C₈H₁₁)(NCCH₃)]BF₄ complex 1 is fully coordinated, and therefore not catalytically active. The cyclooctadiene (COD, C₈H₁₄) ligand must be hydrogenated to cyclooctane (as

![Figure 5.10](image-url)
shown in Scheme 5.5) before the Ru complex can catalyze the hydrogenation of other olefins. Given that the Ru in complex 1 is coordinatively saturated, one of the ligands must temporarily leave the Ru coordination sphere for \( \text{H}_2 \) to be able to enter and hydrogenate the COD ligand. Since both BINAP and COD are strongly coordinated to Ru through multiple bonds, they do not frequently leave the coordination sphere, however, the acetonitrile ligand is highly labile and is readily replaced by hydrogen. Once the hydrogen has coordinated to Ru, the COD ligand can be reductively eliminated and replaced by either acetonitrile or solvent ligands. This process yields a coordinatively unsaturated compound, 14, that is an active hydrogenation catalyst.

The catalyst activation mechanism can be used to explain why the acetonitrile-Ru-BINAP catalysts have high initial activities while the isonitrile-Ru-BINAP catalysts have long activation periods. As discussed above, the labile acetonitrile ligand allows hydrogen to quickly bond to Ru and activates the catalyst. On the other hand, the isonitrile ligand was specifically chosen because it binds very strongly to transition metals. Therefore, none of the ligands in complexes 3 or 4 dissociates rapidly to allow hydrogen insertion and the activation process is dramatically inhibited. It is interesting to note that the catalyst heterogenized through “strong” thiol ligands demonstrated kinetics more reminiscent of the homogeneous acetonitrile-Ru compound. This is likely due to the
Scheme 5.6 Hydrogenation reaction mechanism

fact that the thiol ligands bind less strongly to Ru than isonitrile ligands (as evidenced by the higher metal leaching observed in the thiol-bound catalysts).

Following the formation of the catalytically active species, 14, the asymmetric hydrogenation proceeds as shown in Scheme 5.6. First, the substrate coordinates to the Ru complex, and the coordinated hydrogen is inserted into the olefin bond to form the reaction intermediate 15. By the addition a H₂ molecule, the substrate is reductively
eliminated to form the hydrogenation product and one hydrogen is left bound to the Ru complex, thus re-forming the active species 14. Wiles and Bergen found that the reductive elimination of the bound substrate was the rate-limiting process. The kinetics of this reaction mechanism can be approximated by

$$S + C \xrightleftharpoons[k_2]{k_1} SC \xrightarrow{k_3} P + C$$  \hspace{1cm} (5.2)

in which $S$ is the substrate, $C$ is the catalytically active species 14, $SC$ is the reaction intermediate 15, and $P$ is the hydrogenation product. This expression leads to the well-known Michaelis-Menten rate equation,\textsuperscript{15}

$$-r_S = \frac{k_3 [C_T] [S]}{k_2 + k_3} = \frac{V_{\text{max}} [S]}{K_M + [S]}$$  \hspace{1cm} (5.3)

in which $[C_T]$ is the total concentration of active catalyst. Combining the Michaelis-Menten rate equation with the constant volume batch reactor design equation,

$$\frac{d[S]}{dt} = r_S$$  \hspace{1cm} (5.4)

we obtain,

$$\frac{[S]_0 - [S]}{\ln \left( \frac{[S]_0}{[S]} \right)} = -K_M + V_{\text{max}} \frac{t}{\ln \left( \frac{[S]_0}{[S]} \right)}$$  \hspace{1cm} (5.5)

where $[S]_0$ is the initial substrate concentration and $t$ is the time.

Applying Equation 5.5 to the DMI hydrogenation data using the homogeneous acetonitrile-Ru-BINAP catalyst (excluding the first 20 min of the reaction) yielded an excellent fit, as shown in Figure 5.11. $V_{\text{max}}$ for the reaction was ~ 250 mol DMI/L·mol Ru·min, $K_M$ was determined to be 3850 mol DMI/L·mol Ru and so $k_3 \sim 1 \text{ s}^{-1}$. Using these values, the reaction rate versus time curve predicted by the Michaelis-Menten expression was plotted against the experimental data in Figure 5.12(a). Aside from the fast initial rate, the reaction rate was accurately predicted by the Michaelis-Menten equation.
Since the heterogeneous isonitrile-Ru-BINAP catalyst should follow the same reaction mechanism as the homogeneous acetonitrile-Ru-BINAP catalyst, we have also used the Michaelis-Menton model to analyze the heterogeneous reaction kinetics. A comparison of the rate data from the "zero-order" regime of the isonitrile-Ru-BINAP catalyst with the Michaelis-Menton equation is provided in Figure 5.12(b). Because the initial rate data are dominated by the activation kinetics, this regime has been excluded from the curve fit. From equation 5.3, it is evident that if $K_m << [S]$, the rate is effectively zeroth order in substrate concentration.

A small $K_m$ is indicative of a very stable reaction intermediate, i.e. the formation rate of the intermediate ($k_1$) is high compared to the decomposition and forward reaction rates ($k_2$ and $k_3$, respectively). Assuming that the reaction intermediate for the isonitrile-Ru-BINAP catalyst is the same as that for the acetonitrile-Ru-BINAP catalyst shown in Scheme 5.6, the strong ligand once again appears to hinder the reaction. The coordination of hydrogen to the reaction intermediate is sterically inhibited, but in the case of 15, the acetonitrile ligand easily dissociates to allow hydrogen ingress. The isonitrile ligand does not dissociate and therefore inhibits the forward reaction, suggesting a small $k_3$ (therefore, both $K_m$ and $V_{max}$ should be considerably lower than for the acetonitrile catalyst). A Michaelis-Menton expression with a $V_{max}$ of 50 mol/L-mol Ru-min and a $K_m$ of 500 mol/L-mol Ru (less than 1/5 the corresponding values for the acetonitrile-Ru-BINAP catalyst) accurately fits the nearly zero-order kinetics, followed by a strongly concentration-dependent regime at low substrate concentrations.

Because the heterogeneous and homogeneous versions of the isonitrile-Ru-BINAP catalyst should have the same structure, the greater activity of the heterogeneous version is more difficult to explain. The increased rate of hydrogenation over heterogenized
catalysts could be due to a hydrogen spill-over effect, in which hydrogen adsorbed on the surface of the silica support increases the hydrogen concentration in the immediate vicinity of the fixed catalyst and thereby increases the reaction rate. We were, however, operating under conditions of excess hydrogen and had not observed significant variations in the reaction rates with hydrogen pressure. It therefore seemed unlikely that further increasing the local hydrogen concentration would increase the reaction rate. An analogous explanation for the higher activity of the heterogeneous catalyst was the adsorption of the olefinic substrate on the surface of the support, resulting in an increased local substrate concentration. However, the reaction rate over the isonitrile-Ru-BINAP catalysts is independent of substrate concentration; substrate “spill-over” effect should therefore not significantly alter the reaction rate. We hypothesized that the increased reaction rate of the heterogeneous catalyst was due to “pre-activation” of the isonitrile-Ru-BINAP catalyst through partial or full dissociation of the COD ligand during the high-temperature immobilization process. We were not, however, able to identify free COD or cyclooctane in the immobiliza-

**Figure 5.12** (a) Reaction rate of DMI over homogeneous catalyst 1 (■) compared to Michaelis-Menton model predictions (-) and (b) reaction rate of DMI over heterogeneous catalyst 4 (■) compared to Michaelis-Menton model predictions (-).
tion solution, nor were we able to sufficiently characterize the heterogenized catalyst by MAS-NMR or NEXAFS* to firmly establish a change in the Ru species after immobilization.

5.3.5 Comparison of Isonitrile Catalysts to Other Heterogeneous and Homogeneous Asymmetric Hydrogenation Catalysts

The best results from the isonitrile-Ru-BINAP catalyst supported on MCF are compared to published results on both homogeneous catalysts and other heterogeneous catalysts in Table 5.2. The most active homogeneous catalyst found in the literature for the asymmetric hydrogenation of terminal olefins was a trans-2,5-diethyl phospholane-based Rh complex (Rh-DuPHOS) synthesized by Burk and co-workers. The Rh-DuPHOS attained a maximum turnover number of 60,000 and a turnover frequency of 5000 h⁻¹, each of which was an order of magnitude higher than the corresponding value for Ru-TMS13. In comparison to the homogeneous acetonitrile-Ru-BINAP catalyst, the heterogenized isonitrile-Ru-BINAP catalyst also showed catalytic activity that was nearly an order of magnitude lower. While the activity of Ru-TMS13 was not as high as the best homogeneous asymmetric hydrogenation catalysts, it was superior to the best heterogeneous catalysts reported in the literature. The reusable asymmetric hydrogenation catalyst consisting of BINAP ligands incorporated into a polymer backbone (see Figure 5.1(c)) had been run to only 400 total turnovers at a rate of 20 turnovers per hour. The

<table>
<thead>
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<th>Homogeneous Rh-DuPHOS</th>
<th>Polymer-Supported Ru-BINAP</th>
<th>MCF-Supported Isonitrile-Ru-BINAP (Ru-TMS13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TON</td>
<td>50000</td>
<td>200</td>
<td>7000</td>
</tr>
<tr>
<td>TOF (h⁻¹)</td>
<td>5000</td>
<td>40</td>
<td>650</td>
</tr>
<tr>
<td>Reuseable</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
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* NEXAFS experiments were performed at Brookhaven National Laboratory with the assistance of Henry Hwu.
lower activity values for the heterogeneous systems reported in the literature could have resulted from several causes. First, other studies did not run at as high a hydrogen pressure, and good gas-liquid transport was seldom achieved. Also, while the strong ligand immobilization method slowed the kinetics of the hydrogenation reaction, the catalyst active site was otherwise left unchanged; whereas other heterogenization methods tended to alter the biphosphine ligand itself, which has negative consequences on both selectivity and activity.

5.4 Summary
Ru-BINAP asymmetric hydrogenation catalysts have been immobilized on mesoporous silica supports using the "strong ligand" immobilization technique. By replacing labile spectator ligands with a siloxane modified ligand that binds strongly to transition metals, we have been able to anchor the asymmetric hydrogenation catalyst to the support without altering the chiral phosphine ligand that imparts enantioselectivity to the catalyst. Several different strong ligands were investigated, and it was determined that the isonitrile ligand provided the highest activity, with no measurable Ru leaching and no change in enantioselectivity in the resulting heterogenized catalyst relative to the homogeneous catalyst. The heterogeneous isonitrile-Ru-BINAP catalyst was more active than the homogeneous version of the same catalyst, and could be reused with little loss in activity or selectivity.

While the heterogeneous isonitrile-Ru-BINAP catalyst was more active than other heterogeneous catalysts reported in the literature, it was less active than the homogeneous catalysts with more labile ligands. The "weak ligand" acetonitrile-Ru-BINAP catalyst upon which the heterogeneous catalyst was based has ~ 5 times greater activity and the same enantioselectivity. The Michaelis-Menton model—developed by Wiles and Bergens—could be applied to the reaction mechanism for asymmetric hydrogenation over the acetonitrile-Ru-BINAP catalysts. The resulting kinetic expression fit well to the experimental rate data. The reaction rate of heterogeneous strong ligand catalyst could also be modeled using the Michaelis-Menton equation. However, the inability of the isonitrile to dissociate from the Ru complex inhibited the formation of the catalytically active species, leading to very slow initial kinetics, and inhibited the hydrogen insertion step that drove
the catalytic reaction to completion, resulting in zero-order kinetics with respect to the olefin substrate. The net result of the concentration-independent reaction rate over the heterogeneous catalyst was that the pore structure of the support had little effect on the reaction rate since the reaction was kinetically limited, rather than diffusion limited.
5.5 References
9 Gao, H.; Angelici, R. J. Organometallics 1999, 18, 989.
       (b) Wiles, J. A.; Bergens, S. H. Organometallics 1999, 18, 3709.
CHAPTER 6
Recommendations for Future Work

6.1 Future Directions for Mesocellular Silica Foams
We have synthesized mesocellular silica foams (MCF) with void fractions of > 0.85 and pore sizes of ~ 30 nm. In this work, the MCF materials were applied as catalyst supports for palladium nanoclusters that were used as Heck catalysts and for organometallic complexes that were used as asymmetric hydrogenation catalysts. Future work utilizing MCF materials could be directed in two major areas: optimizing the mesoporous silicas for non-catalytic applications (such as separations and electrochemistry), and improving the catalytic properties of the materials.

With high void fractions and pore sizes in a regime appropriate to many biological molecules, the MCF materials are well suited for use as molecular sieves and separations media. To form an ideal chromatographic material, however, MCF needs to be processed into contiguous films or particles of uniform dimensions. In this work, MCF was formed as particles with diameters of 10 - 500 μm, but the concentrations of silica precursor and polymer template in the MCF synthesis mixture were found to have a significant impact on the morphology of the material. Further research into manipulating the phase segregation and gellation of the water/acid/Pluronic/silica system could result in continuous films, which then must be carefully calcined and dried to produce a separation membrane. With their open pore structure and random pore orientation, the MCF materials could yield filters capable of separating proteins with low pressure drop and without the need to orient the film. Also, MCF precipitation conditions could be modified to narrow the particle size distribution. Alternatively, a MCF coating could be applied to commercially available monodisperse silica particles. Porous particles of uniform size are necessary to reduce channeling and peak broadening in packed-column chromatographic applications. If MCF particles with uniform diameters could be synthesized, significant improvements in separations would be expected given the high void fraction of the materials (allowing the solute molecules more facile access to the pores, thus reducing bypass), high surface areas, and easily modified surface chemistry (ensuring strong interactions between solute molecules and tailored MCF surfaces). MCF materials could also provide significant improvements in the area of composite polymer electrolytes. Silica-PEO composites are currently being researched as more robust replace-
ments for solid polymer electrolytes in rechargeable batteries and in fuel cells. Silica additions to polymer electrolytes result in increased conductivities and enhanced high-temperature stabilities. In turn, the improved high-temperature performance of the electrolyte allows fuel cells, for example, to be operated more efficiently.

The other direction for future work involves refining the application of MCF as a catalyst support. The catalysis performed thus far was aimed at demonstrating that MCF could reduce transport limitations in fast reactions (e.g. Heck catalysis), and that complex catalyst compounds used in enantioselective reactions (e.g. asymmetric hydrogenation) could be immobilized on these supports without loss in selectivity. Work remains on improving the stability of the heterogeneous Pd-TMS13 Heck catalyst, and on enhancing the activity of the Ru-TMS13 asymmetric hydrogenation catalyst. Furthermore, reactions with both fast kinetics and high selectivities should be investigated to take full advantage of the unique properties of the MCF support.

6.2 References


3 Honma, I.; Takeda, Y.; Bae, J. M. Solid State Ion. 1999, 120, 255.
Novel mesocellular silica foam (MCF) materials have been synthesized with pore sizes of up to 350 Å, pore volumes of > 2 cm$^3$/g (void fractions of > 0.85) and surface areas of ~ 700 m$^2$/g. MCF materials were formed using triblock copolymer (PEO-PPO-PEO, Pluronic) micelles to template the formation of the mesoporous silica structures from acidic solutions of tetraethoxysilane. The combination of the polymer amphiphile with hydrophobic swelling agents (such as trimethylbenzene) resulted in larger pore sizes and more open pore structures than had previously been obtained with surfactant templates. The large pores and high void fractions of MCF make the material ideally suited for use as a catalyst support.

The basic properties of the swollen triblock copolymer micelles were investigated to provide a better understanding of their templating behavior. Small-angle neutron scattering (SANS) was used to determine the size, shape and internal structure of the Pluronic micelles. Since the complex structure of the swollen micelles (consisting of an oil-filled core surrounded by a well-hydrated corona) required a large number of fit parameters to model the SANS data, a pseudo-equilibrium thermodynamic model for micelle formation was employed to predict all but two of the fit parameters. The thermodynamic model predicted the compositions and dimensions of the micelle core and corona within 10% of their experimental values, and the micelle polydispersity fit parameter was corroborated using dynamic light scattering to provide further confidence in the physical significance of the fit parameters. The good agreement between theory and experiment gave us a reliable structure for the swollen micelles. Knowledge of this structure was used to investigate the effects of changing polymer and oil types on the size of the swollen micelles, and therefore to select the best systems for templating large pores in silica sol-gels.

The SANS experiments showed that the swollen Pluronic micelles were spherical. However, when silicon alkoxides were added to micellar solutions containing only small amounts of oil, SBA-15 materials consisting of cylindrical pores packed in hexagonal arrays ($H_1$ phase) were formed. At an oil-to-polymer mass ratio of ~ 0.2, the MCF materials (consisting of spherical cells connected by windows) were produced. We
determined that the SBA-15 structure forms as a result of the silica-induced dehydration of the PEO that constitute the micellar coronas. The dehydration of the PEO blocks leads to the precipitation of a polymer-silica-rich phase with a composition similar to that of the H2 liquid crystalline phase in concentrated polymer solutions. The fact that the silica condenses slowly under the acidic conditions of our experiments means that the polymer has time to adopt its equilibrium conformation in the newly formed polymer-silica-rich phase before the material solidifies. The mesostructure change from cylindrical to spherical geometry is driven by the need to decrease micellar surface-to-volume ratio as more oil is added to a solution with a fixed amount of polymer, and thereby decrease the oil-water interfacial free energy as well as the PPO block deformation free energy in the aggregate core. Thus, we have found two key factors in determining the pore size and structure of Pluronic-templated silica materials that were not previously well understood. First, there must be sufficient silica present in solution to displace the water bound to the PEO blocks and precipitate the polymer aggregates. Second, because the silica condenses slowly under acidic conditions, it is the equilibrium structure of the concentrated precipitate, not the original solution, that determines the pore structure of the final material.

To demonstrate the utility of the MCF materials, we have used MCF as a catalyst support for two different reactions: the Heck reaction and asymmetric hydrogenation. The Heck reaction was selected because it is widely used in the synthesis of pharmaceuticals and fine chemicals, and because the rapid reaction rates obtained with homogeneous catalysts could lead to significant mass transport limitations in a heterogeneous catalyst. Palladium metal clusters were vapor-grafted onto MCF and several other large-pore silicas, to generate active Heck catalysts. The activities of these heterogeneous “Pd-TMS” catalysts were equal to those of the best homogeneous organometallic catalysts reported in the literature for the coupling of bromoacetophenone to n-butylacrylate. At 160°C, the activity of the MCF-supported catalyst was better than that of catalysts supported on mesoporous silicas with smaller pores, such as MCM-41 and SBA-15. The high activity of the MCF-supported catalyst was attributed to its large pores and open pore structure that reduced diffusion limitations on the reaction rate due to restricted diffusion of reactants in small pores.
Asymmetric hydrogenation was chosen as a model reaction because the highly selective reaction requires the use of large and complex organometallic catalysts, which can only be heterogenized in large pores. We developed a 'strong ligand' heterogenization method that allowed us to anchor asymmetric hydrogenation catalysts to silica surfaces without modifying the chiral ligands that impart enantioselectivity to the active metal center of the catalyst. The resulting heterogeneous asymmetric hydrogenation catalysts had the same selectivity as homogeneous catalysts, proving that immobilization within the large pores of MCF did not distort the active complexes. However, the slow reaction rate of asymmetric hydrogenation meant that the reactions were kinetically, not transport, limited and therefore, the activity of MCF-supported catalysts was not significantly higher than those supported on commercially available large-pore silica gels.