

**I. DEVELOPMENT OF FACILE ROUTE TO FLUORIDE-MEDIATED,
PURE-SILICA ZEOLITE THIN FILMS**

**II. REMOVAL OF STRUCTURE-DIRECTING AGENTS FROM
MOLECULAR SIEVES VIA THE USE OF PHOTOLABILE STRUCTURE-
DIRECTING AGENTS**

Thesis by

Heather K. Hunt

In Partial Fulfillment of the Requirements for the

Degree of

Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2010

(Defended 28 September 2009)

© 2010

Heather K. Hunt

All Rights Reserved

Acknowledgments

The time I have spent at Caltech has been equally the most challenging and the happiest of all of my life, and I know that I will always remember Caltech and the wonderful people that I have met here with great affection. Over the last five years, I have been privileged to interact and work with truly inspiring and talented educators, researchers, mentors, authors, and administrators, and I am sincerely grateful to all of them for their guidance and support. This thesis is the culmination of several years of effort that would not have been possible without them.

First and foremost, I would like to thank my advisor, Professor Mark E. Davis, for all of his support, financial and otherwise, throughout my time here. I have been very fortunate to work in his lab, and this work would not have been possible without his efforts, suggestions, and patience when not everything worked perfectly the first time. (Or even the second or third time.) I will always be grateful to him for giving me this opportunity. I would also like to thank the members of my Candidacy and Thesis Committees, Professor Richard Flagan, Dr. Stacey Zones, Professor Yushan Yan, and Professor Julia Greer for their suggestions, support, and kindness. Professor Flagan has always been ready to discuss research problems and suggest solutions to them. Dr. Zones, at Chevron, has provided steady support and guidance, despite his busy schedule, and has led me to a deeper understanding of zeolite science. Professor Yan, at University of California, Riverside, has been like a secondary advisor to me, and has provided me with not only a group full of talented and helpful graduate students to collaborate with, but has also given me excellent suggestions on the direction of my zeolite films research and manuscript

preparation. Lastly, but certainly not least, Professor Greer has provided me with encouragement, support, and advice, in addition to access to her lab. To all of you, thank you.

In addition to my committee, I would also like to thank Dr. Allen Burton, at Chevron, for his help with modeling, zeolite identification, and synthetic suggestions. Many an unusual behavior or result would remain unexplained if not for him. I would also like to thank Dr. Sonjong Hwang, our resident solid-state NMR expert, for his help with the NMR equipment, and his advice on interpreting NMR spectra. Dr. Dongchan Jang in the Greer group was very helpful in his explanation of and instruction on the mechanical testing of the zeolite films I prepared. Additionally, in the Yan group, two students, Minwei Sun and Chris Lew, were extremely helpful in the synthesis and characterization of the zeolite films and powders we studied; Chris was especially dedicated, running capacitance measurements on sample after sample, and always sending me detailed and thoughtful explanations of the results. Lastly, I would like to thank all the members of the Davis group, past and present, who have made my time here at Caltech both educational and entertaining. Specifically, I would like to thank Dr. Eric Margelefsky for his help with organic synthesis, and for always listening when I needed someone to complain to or someone to give encouragement. His willingness especially to escape lab for ice cream was very helpful. I would also like to thank Dr. Ray Archer, for our discussions on zeolite science, and Dr. John Carpenter, my long-suffering office mate, who put up with five years of my incessant nattering about any subject under the sun without once asking me to get a

grip. These three have broadened my research horizons, helped me fix any number of equipment problems in the lab, and were always willing to help me open autoclaves.

I would also like to thank the administrators of the Women's Center, the Women Mentoring Women program, and the Caltech Animal Team, for their support. These include Dr. Felicia Hunt, Portia Harris, Dr. Candace Rypisi, Linda Taddeo, and Dr. Mike Hucka. Being involved in these organizations has allowed me to serve the Caltech community, to organize events from seminars to socials, to interact with a variety of people outside my division, and to form what I know will be lasting friendships with truly caring people. I have greatly enjoyed my time on the boards of these organizations, as well as my time in other student organizations, such as the Caltech Project for Effective Teaching, and the Caltech Dance Club.

I would also like to thank my friends for their constant support, and their willingness to drop anything if I needed help. My classmates, Shelby Hutchens, Heather McCaig, Arwen Brown, and Lisa Hochrein, have all been the best friends, partners in crime, and ardent supporters that I could have asked for when I came to graduate school. They have listened in sympathy and in laughter, and have always had time for tea. From them, I have learned a great deal about other research fields, and have been allowed to use equipment I never would have touched otherwise. With them, I have experienced all the joys and anguish of life and research at Caltech. Finally, I thank my husband, Nick Thurwanger, and my parents, Richard and Jennifer Hunt. Without their encouragement, their support, their patience, and in Nick's case, willingness to move halfway across the country, I would not

have made it to Caltech, let alone enjoyed my time here. To the three of you, I owe a debt of gratitude that I can only hope I can repay.

God bless all of you.

Abstract

This thesis consists of two projects related to the development of new routes to zeolite films. In an effort to expand the known library of pure-silica zeolites accessible in planar conformation, Part I details the development of a new synthetic technique, the vapor phase transport of fluoride, to produce pure-silica zeolite films with the LTA, CHA, STT, ITW and –SVR topologies. The films are characterized by X-ray diffraction, field emission scanning electron microscopy, X-ray energy dispersive analyses, and mechanical testing. Such pure-silica zeolite films could be useful in a variety of applications, due to their porosity, crystallinity, and general stability. For example, these materials could be employed as low dielectric constant materials, which are needed for microprocessors as the feature size is continually reduced. Upon investigation of the aforementioned zeolite powders and films, we find that the materials with the LTA topology have the lowest dielectric constant of all the pure-silica zeolites. Additionally, all the zeolites investigated, except STT, give k -values lower than predicted from their structures using the Bruggeman effective medium model, which has been commonly employed and found able to predict dielectric constants of amorphous silicas.

The second part of this thesis presents the development of an alternative method to thermal combustion to remove organics from zeolite pores, which can degrade zeolite films, using a photolabile structure-directing agent that can be removed from the zeolite pore space using UV photolysis. Here, the synthesis, photocleavage, and structure-directing ability of two different photolabile molecules (8,8-dimethyl-2-(2-nitrophenyl)-1,4-dioxo-8-azoniaspiro[4.5]decane hydroxide (P-SDA 1) and 1-(2-nitrobenzyl)-1H-

imidazole (P-SDA 2)), are presented and discussed. Cleavage of the photolytic P-SDA 1 is demonstrated in a homogeneous solution, and intercalated into a dealuminated zeolite FAU. The structure-directing ability of P-SDA 1 is evaluated via attempts to synthesize silicate and aluminosilicate zeolites, resulting in the formation of amorphous and layered materials. The structure-directing ability of P-SDA 2 is evaluated via attempts to produce aluminophosphate zeolites, resulting in several unknown crystalline phases, in addition to dense and hydrated phases. Lastly, complete photocleavage of P-SDA 2 within the crystalline, aluminophosphate materials is also demonstrated.

Table of Contents

Acknowledgements.....	iii
Abstract.....	vii
Table of Contents.....	ix
List of Tables.....	xii
List of Figures.....	xiii

Part 1: Development of Facile Route to Fluoride-Mediated, Pure-Silica Zeolite Thin Films.....1

Chapter 1: Introduction and Organization of Thesis Presentation.....	2
1.1 Introduction to Zeolites and Molecular Sieves.....	2
1.2 Synthesis and Formation of Zeolites.....	5
1.3 Zeolite Applications.....	9
1.4 Thesis Organization.....	10
1.5 References.....	12

Chapter 2: Introduction to Part I of Thesis.....	20
2.1 Introduction.....	20
2.2 Zeolite Film and Membrane Synthetic Strategies.....	23
2.2.1 Support Choice and Modification.....	24
2.2.2 Synthetic Strategies.....	25
2.2.2.1 Hydrothermal Techniques.....	26
2.2.2.2 Non-hydrothermal Techniques.....	32
2.2.3 Characterization Techniques.....	34
2.2.4 Defect Elimination.....	35
2.3 Development of New Synthetic Techniques.....	36
2.4 References.....	38

Chapter 3: In Situ Crystallization of Fluoride-Mediated, Pure-Silica Zeolite Thin Films.....44

Abstract.....	44
3.1 Introduction.....	45
3.2 Results and Discussion.....	51
3.2.2 Seeding and Diluting the Zeolite Precursor Gel.....	51
3.2.3 Vapor Phase Transport of Fluoride.....	56
3.3 Conclusions.....	67
3.4 Experimental.....	68
3.4.1 Synthesis of Structure-Directing Agent (4-methyl-2,3,6,7-tetrahydro-1H,5H-pyrido [3.2.1-ij] quinolinium hydroxide).....	68
3.4.2 Synthesis of ITQ-29 (LTA) Films and Powder Via Seeding / Diluting.....	69
3.4.3 Synthesis of ITQ-29 (LTA) Films and Powder Via Vapor Phase Transport of Fluoride.....	70

3.4.4 Characterization	72
3.5 References.....	73

Chapter 4: Investigation of Dielectric Properties of Fluoride-Mediated, Pure-Silica

Zeolite Thin Films	77
Abstract.....	77
4.1 Introduction.....	78
4.2 Results and Discussion	90
4.3 Conclusions.....	104
4.4 Experimental.....	105
4.4.1 Synthesis of Structure-Directing Agent A (1,2,3-trimethylimidazolium hydroxide)	105
4.4.2 Synthesis of Structure-Directing Agent B (N,N,N-trimethyl-1-adamantylammonium hydroxide)	105
4.4.3 Synthesis of Structure-Directing Agent C (Hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) hydroxide)	106
4.4.4 Surface Modification of the Substrates.....	107
4.4.5 Synthesis of Fluoride-Mediated, Pure-Silica Zeolite Films and Powder	107
4.4.6 Characterization	109
4.5 References.....	111

Part II: Removal of Structure-Directing Agents from Molecular Sieves Via the Use of Photolabile Structure-Directing Agents.....115

Chapter 5: Introduction to Part II of Thesis	116
5.1 Introduction.....	116
5.2 Photolabile Structure-Directing Agents.....	124
5.3 Photochemical Protecting Groups in Organic Synthesis	126
5.3.1 2-Nitrobenzyl Family.....	127
5.3.2 Benzyloxycarbonyl Family	130
5.3.3 3-Nitrophenyl Family.....	131
5.3.4 Phenacyl Family.....	132
5.4 Photofunctional Zeolites	133
5.5 Development of a Photolabile Structure-Directing Agent.....	135
5.6 References.....	

Chapter 6: Photolabile Structure-Directing Agents for Zeolite Synthesis.....142

Abstract.....	142
6.1 Introduction.....	142
6.2 Results and Discussion	145
6.2.1 P-SDA 1 Synthesis.....	145
6.2.2 Photolysis of P-SDA 1	150
6.2.3 Zeolite Synthesis Using P-SDA 1.....	155
6.3 Conclusions.....	160

6.4 Experimental.....	161
6.4.1 Synthesis of P-SDA 1	161
6.4.1.1 Ketalization Reaction.....	161
6.4.1.2 Amine Quaternization Reaction.....	162
6.4.2 Photocleavage of P-SDA 1	163
6.4.2.1 Homogeneous Cleavage of P-SDA 1.....	163
6.4.2.2 Photocleavage of P-SDA 1 Intercalated within Tosoh 390- HUA, a Dealuminated Zeolite X (Structure Code FAU) 163	163
6.4.3 Zeolite Synthesis with P-SDA 1	164
6.4.4 Characterization	166
6.5 References.....	167

Chapter 7 : An Imidazole-Based, Photolabile Structure-Directing Agent for the Synthesis of Aluminophosphate Zeolites	170
Abstract.....	170
7.1 Introduction.....	171
7.2 Results and Discussion	175
7.2.1 P-SDA 2 Synthesis.....	175
7.2.2 Aluminophosphate Zeolite Synthesis Using SDA 2.....	179
7.2.3 Aluminophosphate Zeolite Synthesis Using P-SDA 2	184
7.2.4 Photocleavage of P-SDA 2 within Aluminophosphate Material ..	190
7.3 Conclusions.....	196
7.4 Experimental.....	197
7.4.1 Synthesis of P-SDA 2	197
7.4.2 Synthesis of Aluminophosphate Zeolites with SDA 2 and P-SDA 2	198
7.4.3 Synthesis of Metal-Substituted Aluminophosphate Zeolites with SDA 2 and P-SDA 2	198
7.4.4 Photocleavage of P-SDA 2 in As-Made Aluminophosphate and Metal-Substituted Aluminophosphate Materials.....	199
7.4.5 Characterization	200
7.5 References.....	200
Chapter 8: Summary and Conclusions	203
1. Summary and Conclusions	203
2. Future Directions	211

List of Tables

Chapter 3

Table 3.1 Energy dispersive spectrometry (EDS) data of the amorphous precursor film supported on OH-(100) Si demonstrates that the film is pure-silica, with the carbon content appearing due to the TMAOH and SDA in the precursor gel. EDS data for the calcined sample indicates that the carbon content has been completely removed.	65
---	----

Chapter 4

Table 4.1 Dielectric constant (k) of various pure-silica zeolite powders measured at 2 GHz	98
Table 4.2 Synthesis conditions for zeolite films and powders.....	109

Chapter 6

Table 6.1 Synthesis conditions for zeolite synthesis using P-SDA 1 as the structure-directing agent	158
---	-----

Chapter 7

Table 7.1 Results of $AlPO_4$ syntheses attempted with SDA 2 (A = amorphous, DP = dense phase, #1 = ATS / unknown phase, #2 = AFI / tridymite).....	180
Table 7.2 Results of magnesium-substituted aluminophosphate runs using SDA 2 at 150, 175, and 200 °C (A = Amorphous).....	182
Table 7.3 Results of attempted aluminophosphate zeolite syntheses with P-SDA 2 as the structure-directing agent (3 = unknown hydrated phase, 4 = unknown phase, 5 = unknown phase, 6 = ATS / unknown phase, 7 = ATV / dense phase, DP = dense phase)	185
Table 7.4 Results of attempted metal-substituted, aluminophosphate zeolite syntheses with P-SDA 2 as the structure-directing agent.....	190

List of Figures

Chapter 2

- Figure 2.1 Schematic representation of the three categories of nanostructured, planar zeolite and zeolite-based configurations..... 22
- Figure 2.2 Synthetic strategies for the formation of zeolite and zeolite-based films and membranes 26
- Figure 2.3 Models of zeolite and zeolite-based film formation for in situ synthetic techniques 28
- Figure 2.4 Silicalite (MFI) polycrystalline film grown via *in situ* techniques showing a loose layer of MFI crystals on the surface..... 29
- Figure 2.5 Schematic of the vapor phase transport method for film formation... 31

Chapter 3

- Figure 3.1 Schematic of the synthesis process of fluoride-mediated zeolite films by the seeding / diluting modification to in situ crystallization..... 49
- Figure 3.2 Schematic of the synthesis process of fluoride-mediated, pure-silica zeolite LTA films by the vapor phase transport of fluoride..... 50
- Figure 3.3 PSZ ITQ-29 (LTA) film synthesis attempts using various substrates, seed amounts, and dilutions 53
- Figure 3.4 Al-free ITQ-29 (LTA) film synthesis attempts using various substrates, seed amounts, and dilutions 54
- Figure 3.5 (a) Substrate submerged in ITQ-29 precursor gel of appropriate molar composition, (i) Stir to hydrolyze the TEOS; (b) Substrate subjected to dip-coating, (ii) Dip-coat substrates, 5x, in the hydrolyzed gel to create amorphous precursor film; (c) Coated substrate and bulk precursor gel placed inside vacuum desiccator, (iii) Evaporate ethanol produced during hydrolysis and excess H₂O; (d) Amorphous precursor film and solid (dry) gel; (e) Introduce dry gel into Teflon®-lined Parr Autoclave after addition of HF (aq) to dry gel, introduce coated substrate (no HF present in amorphous film) into autoclave on elevated Teflon® platform, and crystallize via VPTM..... 57
- Figure 3.6 X-ray diffraction patterns of as-made, calcined and polished PSZ LTA film samples on OH-(100) Si demonstrates phase crystallization of the precursor film using the VPTM of fluoride..... 62
- Figure 3.7 FE SEM micrographs of (a) surface of calcined PSZ LTA film; (b) a thin section of calcined PSZ LTA film showing ~ 115 μm thick film; (c) surface of calcined PSZ LTA film after mechanical polishing; (d) a thin section of calcined PSZ LTA film after polishing showing ~ 1.7 μm thick film..... 64
- Figure 3.8 Load / displacement curves for the PSZ ITQ-29 films on (100) Si wafers indicate that different elastic moduli are obtained at different indentation sites 66

Chapter 4

- Figure 4.1 Cartoon of a parallel-plate capacitor with a dielectric medium polarized by an electric field, E 80
- Figure 4.2 (a) Metal-insulator-metal structures used for parallel-plate capacitance measurements; (b) Schematic of a time-domain reflectometer (TDR) coupled with transmission line for dielectric measurements of powder samples (used with permission)⁷ 81
- Figure 4.3 (a) LTA framework, viewed along the [001] axis; (b) CHA framework, viewed normal to the [001] axis; (c) STT framework, viewed normal to the [100] axis; (d) ITW framework, viewed along the [100] axis;³⁷ (e) -SVR framework, viewed along the [001] axis (courtesy of A. Burton, Chevron) 89
- Figure 4.4 X-ray diffraction patterns of calcined and polished (a) PSZ CHA films on (100) Si; (b) PSZ STT films on (100) Si; (c) PSZ ITW films on (100) Si; (d) PSZ -SVR films on (100) Si 91
- Figure 4.5 FE SEM micrographs of (a) surface of calcined PSZ CHA film; (b) surface of calcined PSZ STT film; (c) surface of PSZ CHA / STT intergrowth; (d) calcined, polished PSZ STT film; (e) surface of calcined PSZ ITW film; (f) surface of calcined PSZ -SVR film; (g) surface of calcined, polished PSZ -SVR film; (h) thin section of a typical PSZ STT film after mechanical polishing, showing $\sim 1.7 \mu\text{m}$ thick film with variable height 94
- Figure 4.6 k -values obtained for PSZ thin film of *MRE, MFI, BEA*, and LTA topologies made by *in situ* (MFI and BEA*) and vapor phase transport methods (*MRE and LTA) 96
- Figure 4.7 Effective dielectric constant of pure-silica CHA measured over a range of frequencies 98
- Figure 4.8 Effective dielectric constant of pure-silica STT measured over a range of frequencies 99
- Figure 4.9 Effective dielectric constant of pure-silica ITW measured over a range of frequencies 99
- Figure 4.10 Effective dielectric constant of pure-silica -SVR measured over a range of frequencies 100
- Figure 4.11 k -values obtained for fluoride-mediated, PSZ powders of MFI, ITW, FER, -SVR, STT, CHA, and LTA topologies via TDR 103

Chapter 5

- Figure 5.1 Schematic representation of the results of thermal stresses on zeolite films during calcination: (a) cracking at film / substrate interface if film is not well-adhered to substrate, (b) cracking within film if film is well-adhered to substrate 118
- Figure 5.2 Schematic of zeolite film patterning using UV / ozonolysis photochemical “calcination” treatment to remove occluded organics 120
- Figure 5.3 Cleavage reaction of ketal-containing structure-directing agent into smaller fragments²¹ 122

Figure 5.4	Recyclable structure-directing agent route – (1) zeolite synthesis; (2) cleavage of the organic molecules inside the zeolite pores; (3) removal of the cleaved fragments; (4) recombination of the fragments into the original SDA molecule ²	122
Figure 5.5	Various acid-cleavable ketal structure-directing agents ²¹	123
Figure 5.6	Examples of the 2-nitrobenzyl family of photochemical protecting groups: (a) 2-nitrobenzyl group, (b) 2-nitrobenzyloxycarbonyl, and (c) 2-nitrophenylethyleneglycol	128
Figure 5.7	Schematic of the 2-nitrobenzyl group cleavage mechanism via hydrogen abstraction	130
Figure 5.8	Examples of the benzyloxycarbonyl family of photochemical protecting group: (a) benzyloxycarbonyl group, and (b) 3,5-dimethoxybenzyloxycarbonyl	131
Figure 5.9	Examples of the 3-nitrophenyl photochemical protecting group: (a) 3-nitrophenylhydroxide, and (b) 3-nitrophenyloxycarbonyl	132
Figure 5.10	The phenacyl photochemical protecting group family	132
Figure 5.11	P-SDA 1, 8,8-dimethyl-2-(2-nitrophenyl)-1,4-dioxa-8-azoniaspiro[4.5]decane	136
Figure 5.12	P-SDA 2, 1-(2-nitrobenzyl)-1H-imidazole	137

Chapter 6

Figure 6.1	(a) Acid-cleavable structure-directing agent 8,8-dimethyl-2-phenyl-1,4-dioxa-8-azoniaspiro[4,5]decane hydroxide; (b) potential photolabile structure-directing agent, 8,8-dimethyl-2-(2-nitrophenyl)-1,4-dioxa-8-azoniaspiro[4.5]decane hydroxide	145
Figure 6.2	Proposed synthetic route for the preparation of P-SDA 1: (i) ketalization reaction; (ii) quaternization of the secondary amine; (iii) ion exchange of the quaternary amine counter-ion	146
Figure 6.3	¹ H NMR spectrum of P-SDA 1 in its iodide salt form	148
Figure 6.4	TGA data of P-SDA 1 prior to conversion of quaternary ammonium iodide salt form to quaternary ammonium hydroxide material	149
Figure 6.5	Photolysis mechanism of P-SDA 1, generating 2-hydroxy-1-(2-nitrosophenyl)ethanone and 1,1-dimethyl-4-oxopiperidinium	151
Figure 6.6	¹³ C CPMAS NMR spectra of: (a) P-SDA 1 in the iodide salt form; (b) P-SDA 1 intercalated into the pure-silica zeolite with the FAU structure; (c) results of initial attempts to photocleave P-SDA 1 intercalated into the pure-silica FAU material demonstrate that cleavage did not occur, as the NMR data did not change	153
Figure 6.7	TGA data of P-SDA 1 intercalated in pure-silica zeolite FAU	154
Figure 6.8	IR spectra of (a) P-SDA 1; (b) P-SDA 1 subjected to photolysis while intercalated in pure-silica zeolite FAU	155
Figure 6.9	Schematic representation of P-SDA 1 in zeolite BEA* (docking calculations performed by A. Burton at Chevron)	156

Figure 6.10 ^{13}C CPMAS NMR spectrum of P-SDA 1 in materials containing MFI crystals shows the molecule is still intact	159
---	-----

Chapter 7

Figure 7.1 (a) 1-(2-nitrobenzyl)-1H-imidazole (P-SDA 2) ; (b) 1-benzyl-1H-imidazole (SDA 2)	173
Figure 7.2 Photolysis of P-SDA 2 proceeds via an intramolecular hydrogen abstraction from the carbon-hydrogen bond ortho to the nitro group to yield carbonyl and nitroso groups in the ortho position	173
Figure 7.3 IR absorbance spectrum of P-SDA 2	176
Figure 7.4 ^{13}C CP MAS NMR spectrum of P-SDA 2 at a spin rate of 6,000	177
Figure 7.5 TGA data for P-SDA 2	178
Figure 7.6 XRD patterns of aluminophosphate zeolites made with SDA 2: (bottom) ATS / unknown phase; (top) AFI / tridymite dense phase	180
Figure 7.7 Framework schematic of the aluminophosphate zeolites phases: (a) ATS, viewed along the [001] axis; (b) AFI, viewed along the [001] axis with projection down the [001] axis on the upper right ¹⁸	181
Figure 7.8 XRD pattern of the ATS phase from the compositions in Table 7.2 ...	183
Figure 7.9 XRD patterns of as-made aluminophosphate materials produced using P-SDA 2 as the structure-directing agent: (a) phase 3; (b) phase 4; (c) phase 5; (d) phase 6; and calcined phase 5: (e) ATV / dense phase	186
Figure 7.10 ^{13}C CPMAS NMR spectrum of the as-made, crystalline, aluminophosphate phase 5 produced using P-SDA 2 as the structure-directing agent	187
Figure 7.11 TGA data of the as-made, aluminophosphate phase 5, produced using P-SDA 2 as the structure-directing agent	188
Figure 7.12 ^{13}C CPMAS NMR spectrum of as-made, aluminophosphate material produced using P-SDA 2 as the structure-directing agent, after UV irradiation	191
Figure 7.13 TGA data of the cleaved and extracted aluminophosphate material .	192
Figure 7.14 XRD patterns of: (bottom) the as-made phase 5 sample; (top) the photocleaved phase 5 sample	193
Figure 7.15 IR spectra of photocleaved and extracted phase 5 sample	193
Figure 7.16 SEM micrographs of: (a) photocleaved phase 5 crystals and aggregates; (b) calcined ATV / dense phase material crystals and aggregates	195
Figure 7.17 Synthesis of P-SDA 2 via photochemical protection of the amino functionality of the imidazole	197