

2
2002

MSU

This is to certify that the

dissertation entitled

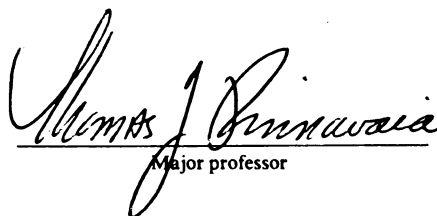
**Surfactant-Mediated Assembly of Crystalline
Mesoporous Aluminas: Synthesis, Characterization,
and Application in Hydrodesulfurization**

presented by

Randall Wayne Hicks

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in **Chemistry**


Major professor

Date July 2, 2002

LIBRARY
Michigan State
University

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.
MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE

**SURFACTANT-MEDIATED ASSEMBLY OF CRYSTALLINE MESOPOROUS
ALUMINAS: SYNTHESIS, CHARACTERIZATION, AND APPLICATION IN
HYDRODESULFURIZATION**

By

Randall Wayne Hicks

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

DOCTOR OF PHILOSOPHY

Department of Chemistry

2002

ABSTRACT

SURFACTANT-MEDIATED ASSEMBLY OF CRYSTALLINE MESOPOROUS ALUMINAS: SYNTHESIS, CHARACTERIZATION, AND APPLICATION IN HYDRODESULFURIZATION

By

Randall Wayne Hicks

Aluminas are utilized in many industrial applications, including as adsorbents, abrasives, ceramics, catalysts, and catalyst supports¹. Many different phases of aluminas exist, but due to its favorable combination of surface and textural properties, the most important phase is γ -alumina. Surface areas and pore volumes of conventional aluminas are typically less than 250 m²/g and 0.5 cc/g, respectively. Performance in catalytic applications is limited in part by these properties.

As has been shown in silica chemistry, the use of surfactants to aid in the assembly of a mesostructure leads to improvement in textural properties². Similar advances are anticipated in alumina chemistry, but to date, little progress has been made in this area. Since the disclosure of mesostructured aluminas in 1996³, all but a couple of subsequent reports have described compositions of mesostructured aluminas with amorphous walls. This limits their thermal and hydrothermal stability, and thus their potential use in catalytic applications.

The present work describes the synthesis of the first members of a new family of crystalline mesostructured aluminas prepared from the hydrolysis of aluminum sec-butoxide in the presence of either polyethylene oxide (PEO) or amine

surfactants as porogens. Members of this family exhibiting the γ -Al₂O₃ phase, denoted MSU- γ aluminas, have surface areas, pore sizes, and pore volumes in excess of 400 m²/g, 15 nm, and 1.5 cc/g, respectively⁴. In addition, forms of these aluminas have expressed thermal and hydrothermal stability. Mesostructured boehmites, MSU-B aluminas, have also been obtained using similar synthetic methods. In the synthesis of either alumina, the key step is the formation of an MSU-S/B surfactant-boehmite precursor, which is converted to the desired final product through calcination.

To demonstrate their usefulness, MSU- γ aluminas have been utilized as catalyst supports in dibenzothiophene hydrodesulfurization reactions. Conversions and selectivities superior to that of a commercial catalyst have been achieved. Their success in this capacity can be traced to the stability of the γ -Al₂O₃ phase, the ability to effectively disperse the active catalytic component, and increased accessibility to the active sites.

References

- (1) Misra, C. *American Chemical Society Monograph, Vol. 184: Industrial Alumina Chemicals*, 1986.
- (2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et al. *J. Am. Chem. Soc.* **1992**, *114*, 10834-10843.
- (3) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1102-1105.
- (4) Zhang, Z.; Hicks, R. W.; Pauly, T. R.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 1592-1593.

To my wife, Jennifer, for without her sacrifice this work would not be possible.

ACKNOWLEDGEMENTS

There are many people to thank for their contributions toward the completion of my doctoral degree during my time at MSU. First, I express gratitude to my research advisor, Dr. Thomas J. Pinnavaia, for his support, both intellectual and financial, over the last six years. There are two specific items that need mention. First, thanks for encouraging me to stay in the Ph. D. program when I was prepared to leave with a master's degree. I'm glad that I stayed. Second, thanks for not objecting to my desire to teach. I could have exclusively conducted research, but I feel that I'm better for having done both, even if it meant a longer tenure at MSU. So thank you for letting me do it my way.

Thanks to the department, especially Drs. Paul Hunter and Kathy Hunt, for allowing me to teach over the last year. I hope that the department found it as good an experience as I did. My success in the job market this year was largely a consequence of that opportunity.

Thanks to Chris Marshall at Argonne National Laboratory for the generous donation of time and facilities. The data obtained from the catalytic testing performed in his labs was crucial to the completion of this work.

Thanks to former Pinnavaia group members Peter Tanev for introducing me to aluminas and Tom Pauly for valuable discussions concerning my project. Thanks to Zhaorong Zhang for our collaborations over the last 2+ years. Having also worked on it, you're the only other person that truly knows how frustrating this project has been. To the rest of the current group members, thanks for

making lab life more enjoyable. You can now all feel free to steal my lab equipment and mess up my bench as much as you'd like.

Thanks to three friends that I met at MSU, Pete LeBaron, Paul Szalay, and Bill Scanlon. Graduate school would have been nearly intolerable without the good times that we had over the years.

Thanks to my family for their support, even if they weren't sure exactly what I was doing here. To all my parents, Charles (Linda) Hicks and Neva (Ron) Penix, thanks for preparing me for this experience. Thanks too, to my mother-in-law, Leone Beck, who has always provided words of encouragement.

Thanks to my brother, Ryan, and my other friends back home, Rick & Jess, Mark & Shelley, Vern, Frog, and John for support and much needed stress relief. I only wish that we had more time to spend together since I've been here.

Most importantly, thanks to my wife and my buddy, Jennifer. I am eternally grateful for the love and support that you have given me. I can't express here in words what that has meant. We've both had to make sacrifices so that I could finish what I started, more so for you, particularly over this last year. But it will all be worthwhile in the end. And soon, it will be our time again.

TABLE OF CONTENTS

LIST OF TABLES.....	x
LIST OF FIGURES.....	xi
LIST OF ABBREVIATIONS.....	xix
 Chapter 1: Introduction.....	 1
1.1. Classification of Aluminas.....	1
1.2. Transition Aluminas.....	5
1.3. Hydrodesulfurization.....	9
1.4. Mesostructures.....	18
1.5. Mesostructured Aluminas.....	21
1.6. Stabilization of Aluminas.....	23
1.7. Objectives and Rationale.....	26
1.8. References.....	28
 Chapter 2: Synthesis and Characterization of Mesostructured	
Boehmite.....	31
2.1. Introduction.....	31
2.2. Experimental.....	34
2.2.1. Synthesis.....	34
2.2.2. Characterization.....	35
2.3. Results and Discussion.....	36

2.3.1. Formation of MSU-S/B.....	36
2.3.2. General Properties of MSU-B Aluminas.....	39
2.3.3. Peptization.....	54
2.4. Mechanistic Aspects of MSU-B Alumina Synthesis.....	55
2.5. Conclusions.....	58
2.6. Future Directions.....	59
2.7. References.....	61

Chapter 3: Synthesis and Characterization of Mesostructured γ -

Al_2O_3.....	63
3.1. Introduction.....	63
3.2. Experimental.....	65
3.2.1. Synthesis.....	65
3.2.2. Characterization of MSU- γ Aluminas.....	67
3.3 Results and Discussion.....	68
3.3.1. MSU- γ Aluminas from PEO Surfactants.....	68
3.3.2. MSU- γ Prepared from Amine Surfactants.....	85
3.3.3 Stability of MSU- γ Aluminas.....	93
3.4. Conclusions.....	103
3.5. Future Directions.....	105
3.6. References.....	106

Chapter 4: Hydrodesulfurization Over MSU-γ Supported Catalysts.....	108
4.1. Introduction.....	108
4.2. Experimental.....	110
4.2.1. Sample Preparation.....	110
4.2.2. Reactor Design and Experimental Conditions.....	113
4.2.3. Characterization.....	115
4.3. Results and Discussion.....	116
4.3.1. Catalytic Reactions.....	116
4.3.2. Structural and Textural Properties of MSU- γ Catalysts.	119
4.3.3. Relationships Between Catalyst Structure and Performance.....	128
4.4. Conclusions.....	139
4.5. Future Directions.....	139
4.6. References.....	142
 Chapter 5: Concluding Remarks.....	 144

LIST OF TABLES

Table 2.1.	Synthetic parameters and textural properties of MSU-B Aluminas.....	44
Table 3.1.	Synthetic parameters and textural properties of MSU- γ aluminas prepared from aluminum sec-butoxide and PEO surfactants.....	72
Table 3.2.	Comparison of textural properties of calcined MSU- γ formed at 500 °C and calcined MSU- δ alumina formed at 800 °C.....	87
Table 3.3.	Textural properties of MSU- γ aluminas prepared through the calcination of MSU-S/B surfactant-boehmite compositions and MSU-B boehmites at 500 °C.....	92
Table 3.4.	Textural properties of doped MSU- γ aluminas prepared from aluminum sec-butoxide and P84. In each synthesis, the dopant was administered as a metal salt which was dissolved in the surfactant solution prior to addition of the aluminum sec-butoxide.....	94
Table 3.5.	Textural properties of MSU- γ aluminas prior to and after treatment at 600 °C in a 20% steam atmosphere for 5 hr.....	104
Table 4.1.	Results of HDS reactions over MSU- γ catalysts exhibiting distinctly different morphologies.....	117
Table 4.2.	Textural properties of MSU- γ alumina HDS catalysts.....	127

LIST OF FIGURES

Figure 1.1.	Family of alumina compounds.....	4
Figure 1.2.	Transformation sequence observed upon the thermal dehydration of aluminas (adapted from Wefers and Misra).....	6
Figure 1.3.	Activity of transition metal sulfides in DBT HDS plotted as a function of periodic position of the metal (adapted from Pecoraro and Chianelli).....	12
Figure 2.1.	Cross-sectional (upper) and three-dimensional (lower) depiction of the boehmite double-layer. The thickness of the double layer is ~ 12 Å.....	33
Figure 2.2.	Schematic of interactions leading to formation of MSU-S/B. Each slab represents one boehmite double layer. Lines on the boehmite layers represent hydroxyls forming hydrogen bonds to the surfactant micelles. Areas of overlapping boehmite layers indicate cross-linking through condensation of adjacent hydroxyls.....	38
Figure 2.3.	Representative low angle XRD patterns for the as-synthesized surfactant-boehmite composite, denoted MSU-S/B, prepared from aluminum sec-butoxide and dodecylamine in an alcoholic/aqueous medium as described by line 3 in Table 2.1 and the surfactant-free analog, MSU-B, obtained by calcination of the MSU-S/B composite at 325 °C for 10 hr.....	40
Figure 2.4.	Representative wide angle XRD patterns for MSU-S/B and MSU-B aluminas shown in Figure 2.3. Crystallographic planes contributing to the peaks are noted.....	41
Figure 2.5.	Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for MSU-B aluminas differing in surfactant concentration. The percentage given corresponds to the mass percent of dodecylamine in the surfactant solution. The three isotherms, offset by 200 cc/g for clarity, correspond from top to bottom to samples described in lines 3, 8, and 19 in Table 2.1. PSD curves are displayed in the same order as the isotherms.....	43

Figure 2.6.	Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for MSU-B aluminas prepared from aluminum sec-butoxide and dodecylamine at ambient temperature in alcoholic/aqueous solvents of varying ethanol content. The three isotherms, offset by 200 cc/g for clarity, correspond to MSU-B aluminas described in lines 1-3 of Table 2.1. PSD curves are displayed in the same order as the isotherms.....	46
Figure 2.7.	Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for MSU-B aluminas prepared from aluminum sec-butoxide and dodecylamine at different temperatures. The four isotherms, offset by 200 cc/g for clarity, correspond to MSU-B aluminas described in lines 3-6 of Table 2.1. PSD curves are displayed in the same order as the isotherms.....	47
Figure 2.8.	Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for MSU-B aluminas prepared from the hydrolysis of aluminum sec-butoxide in the presence of different amine surfactants as porogens. The six isotherms, offset by 200 cc/g for clarity, correspond to MSU-B aluminas described in lines 7-12 of Table 2.1. PSD curves are displayed in the same order as the isotherms.....	49
Figure 2.9.	Bright field TEM images (A and C) and electron diffraction patterns (B and D) of MSU-B materials prepared from aluminum sec-butoxide and dodecylamine as described in Table 2.1, (A) line 8 and (B) line 3. The open framework results from the random orientations of fundamental particles. Electron diffraction patterns, (B) and (D), corresponding to bright field images (A) and (C), respectively show diffuse rings, signifying the polycrystalline nature of the material. The reflections contributing to the pattern are labeled in (D).....	52
Figure 2.10.	²⁷ Al NMR spectrum of MSU-B prepared from aluminum sec-butoxide and dodecylamine prepared as described in Table 2.1, line 3. The resonance at 7 ppm is consistent with the structure of boehmite, in which all aluminum ions are in octahedral environments.....	53

Figure 2.11.	Wide angle XRD patterns of MSU-S/B prepared from aluminum sec-butoxide and dodecylamine at 20 °C showing evolution of the boehmite phase over time. The presence of weak reflections assignable to boehmite after only 1 minute show that the formation of MSU-B does not proceed through an MSU-X type of intermediate with amorphous framework walls.....	57
Figure 3.1.	Representative wide angle powder XRD patterns of an MSU-S/B surfactant-boehmite composition made from aluminum sec-butoxide and the PEO surfactant P84 under reaction conditions described in Table 3.1, line 3 and the corresponding MSU- γ alumina prepared from calcination of the as-synthesized MSU-S/B at 500 °C for 4 hr.....	69
Figure 3.2.	Nitrogen adsorption-desorption isotherm and BJH adsorption pore size distribution (inset) of an MSU- γ alumina prepared from aluminum sec-butoxide and the PEO surfactant P84 as described in Table 3.1, line 3. Included for comparison is the same data for an alumina prepared without surfactant as described in Table 3.1, line 20. Isotherms are offset 200 cc/g for clarity and PSD curves are displayed in the same order as the isotherms.....	71
Figure 3.3.	^{27}Al NMR of calcined (500 °C) MSU- γ alumina prepared from aluminum sec-butoxide and P84 as described in Table 3.1, line 3. The two resonances at 6.7 ppm and 72 ppm are assigned to aluminum in octahedral and tetrahedral coordination, respectively. The peaks are in the approximate 75:25 ratio consistent with $\gamma\text{-Al}_2\text{O}_3$	74
Figure 3.4.	Bright field TEM image of (A) calcined (500 °C) MSU- γ alumina prepared from aluminum sec-butoxide and P84 as described in Table 3.1, line 3. (B) Lower magnification image of the same product and the corresponding electron diffraction pattern, with diffuse rings assignable to the [311], [400], and [440] crystallographic planes. (C) Dark field image of the same particles as in (B), but formed from an $\sim 7^\circ$ arc of the [440] diffraction ring. The crystal orientations contributing to the [440] ring appear as bright spots in the image.....	76

- Figure 3.5.** Nitrogen adsorption-desorption isotherms of MSU- γ aluminas prepared from aluminum sec-butoxide and P84 as described in Table 3.1, lines 3 and 6-10 showing the effect of solvent polarity on the textural properties. The volume percent of 2-butanol in the solvent is labeled for each isotherm. Isotherms are offset 300 cc/g for clarity. The BJH adsorption pore size distributions (inset) are in the same order as the isotherms.... 80
- Figure 3.6.** Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) for MSU- γ aluminas prepared from aluminum sec-butoxide and P84 as described in Table 3.1, lines 3 and 11-14 showing the effect of surfactant concentration (mass P84 / mass solvent) on the textural properties. The mass percent of P84 is labeled for each isotherm. Isotherms are offset 300 cc/g for clarity. The PSD curves are displayed in the same order as the corresponding isotherms..... 82
- Figure 3.7.** Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) for MSU- γ aluminas prepared from aluminum sec-butoxide and differing PEO surfactants as described in Table 3.1, lines 3 and 11-14. Isotherms are offset 200 cc/g for clarity. The PSD curves are displayed in the same order as the corresponding isotherms. 83
- Figure 3.8.** Nitrogen adsorption-desorption isotherm and wide angle powder XRD pattern (inset) of a calcined (800 °C) MSU- δ . The initial MSU-S/B surfactant-boehmite intermediate was prepared from aluminum sec-butoxide and the PEO surfactant P84 under conditions described in Table 3.1, line 13..... 86
- Figure 3.9.** TEM image of MSU- γ prepared through the calcination of MSU-B boehmite at 500 °C for 4 hr. The initial MSU-S/B surfactant-boehmite composition was prepared from aluminum sec-butoxide and dodecylamine (DDA) at a reaction stoichiometry of Al:DDA:EtOH:H₂O = 5:1:68.0:73.4 and a reaction temperature of 20 °C. The surfactant free MSU-B boehmite phase was obtained by calcining the MSU-S/B precursor at 325 °C for 10 hr. The electron diffraction pattern (inset) demonstrates the crystallinity of the framework of the mesostructure, as indicated by the diffuse rings attributable to the [311], [400], and [440] crystallographic planes of γ -Al₂O₃..... 90

- Figure 3.10.** Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) for MSU- γ aluminas prepared through the calcination (500 °C) of amine-mediated MSU-S/B surfactant-boehmite precursors (samples A and C) and surfactant free MSU-B precursors (samples B and D). The Al:DDA:EtOH:H₂O reaction stoichiometry was 5:1:68.0:73.4 for all samples. Reaction temperature was 20 °C for samples A and B and 45 °C for samples C and D. Isotherms are offset 300 cc/g for clarity. The PSD curves are displayed in the same order as the corresponding isotherms. 91
- Figure 3.11.** Wide angle powder XRD patterns of MSU- γ aluminas prepared from aluminum sec-butoxide and P84: pristine and doped with either lanthanum or cerium. Peaks marked with an asterisk are attributable to a cerium aluminate phase, CeAlO₃. The doped MSU- γ aluminas were prepared through the calcination (500 °C) of doped MSU-S/B precursors prepared as described in Table 3.1, line 13..... 96
- Figure 3.12.** Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) of MSU- γ aluminas: pristine and doped with either lanthanum or cerium. The doped MSU- γ aluminas were prepared through the calcination (500 °C) of doped MSU-S/B precursors prepared as described in Table 3.1, line 13. Isotherms are offset 400 cc/g for clarity. The PSD curves are in the same order as the corresponding isotherms..... 97
- Figure 3.13.** TEM images of MSU- γ aluminas prior to (A,C,E) and after steaming (B,D,F) at 600 °C for 5 hr in a 20% steam atmosphere. Images A and B are for pristine MSU- γ . Images C, D and E, F are for MSU- γ doped with 5% La³⁺ and 5% Ce³⁺, respectively. The MSU- γ aluminas were prepared as described in the caption to Figure 3.11. The scale bar represents 100 nm in all figures..... 100
- Figure 3.14.** Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) of pristine and doped MSU- γ aluminas after steaming for 5 hr at 600 °C in a 20% steam atmosphere. Samples were prepared as described in the caption to Figure 3.11. Isotherms are offset 300 cc/g for clarity. The PSD curves are in the same order as the corresponding isotherm..... 101

Figure 3.15.	Wide angle powder XRD patterns of pristine and doped MSU- γ aluminas after steaming for 5 hr at 600 °C in a 20% steam atmosphere. Peaks marked with an asterisk are attributed to CeAlO ₃ , cerium aluminate. Samples were prepared as described in the caption to Figure 3.11.....	102
Figure 4.1.	Schematic of the HDS reactor employed in the study. The liquid feed of dibenzothiophene in hexadecane was introduced to the gas feed, a mixture of hydrogen and nitrogen. The two feeds are passed through the preheater (set to 350 °C), where all feed is vaporized. Then the feed reactants are passed over the catalyst bed at 400 °C. Liquid products are condensed and collected while gas products are scrubbed in 2M NaOH prior to venting.....	114
Figure 4.2.	Reaction pathways of DBT in HDS reactions. The upper pathway involves direct desulfurization leading to the formation of biphenyl (BP). The lower pathway involves a hydrogenation step prior to desulfurization, leading to the formation of cyclohexylbenzene (CHB).....	118
Figure 4.3.	Wide angle XRD patterns for lath-12 MSU- γ alumina taken at various stages of the catalytic testing process. The γ -Al ₂ O ₃ phase is evident throughout the process and the lack of peaks assignable to MoS ₂ indicate that the active catalyst is present in small domains and is well dispersed on the support.....	120
Figure 4.4.	Wide angle XRD patterns for scaffold-12 MSU- γ aluminas taken at various stages of the catalytic testing process. The γ -Al ₂ O ₃ phase is evident throughout the process and the lack of peaks assignable to MoS ₂ indicate that the active catalyst is present in small domains and is well dispersed on the support.....	121
Figure 4.5.	Wide angle XRD patterns for the commercial Crosfield catalyst, taken at various stages of the catalytic testing process. The decrease in intensity of the peaks assignable to γ -Al ₂ O ₃ in the pattern of the sulfided sample may be due to the coating of the alumina surface by small domains of MoS ₂ . Peaks from γ -Al ₂ O ₃ and MoS ₂ in the pattern of the spent sample indicate that MoS ₂ particles may aggregate sufficiently to cause scattering and expose the surface of the support.....	122

Figure 4.6.	Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for lath-12 MSU- γ catalysts taken at various stages of the catalytic testing process. The pore volume steadily decreases as the catalyst is loaded, sulfided, and spent. Isotherms are offset 100 cc/g for clarity and PSD curves are displayed in the same order as the corresponding isotherms.....	124
Figure 4.7.	Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for scaffold-12 MSU- γ catalysts taken at various stages of the catalytic testing process. The pore volume decreases slightly as the catalyst is loaded, sulfided, and spent while the pore size is increased and the distribution broadened over the same conditions. Isotherms are offset 0, 100, 100, and 200 cc/g from bottom to top for clarity and PSD curves are displayed in the same order as the corresponding isotherms.....	125
Figure 4.8.	Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for the commercial Crofield catalyst taken at various stages of the catalytic testing process. The pore volume decreases slightly as the catalyst is sulfided and spent. However, the pore size and distribution remain relatively unaffected over the same conditions. Isotherms are offset 100 cc/g for clarity and PSD curves are displayed in the same order as the corresponding isotherms.....	126
Figure 4.9.	Bright field TEM images of the scaffold-12 MSU- γ catalyst (A) after loading and (B) after using in an HDS reaction for 3 hr at 400 °C and 400 psi. The scale bar represents 100 nm. The inset is an approximately 30 nm x 30 nm area of the catalyst. That the framework of the alumina is largely unaffected by the conditions of the HDS reaction provides evidence of its stability.....	130
Figure 4.10.	Bright field TEM images of the lath-12 MSU- γ catalyst (A) after loading and (B) after using in an HDS reaction for 3 hr at 400 °C and 400 psi. The scale bar represents 100 nm. The inset is an approximately 30 nm x 30 nm area of the catalyst. The local pore structure (inset) is compromised to some degree, as is shown by the decreased void space in (B) as compared with (A). The long range order of the alumina laths is lost after use in the HDS reaction.....	132

Figure 4.11. Bright field TEM images of the commercial Crosfield catalyst (A) after loading and (B) after using in an HDS reaction for 3 hr at 400 °C and 400 psi. The scale bar represents 100 nm. The inset is an approximately 30 nm x 30 nm area of the catalyst. Although the local pore structure (inset) appears to withstand the conditions encountered in the HDS reaction, it appears that there is some aggregation of the fundamental particles after use.....	134
Figure 4.12. The Daage-Chianelli rim-edge model of the MoS ₂ catalyst particle. Sulfur removal takes place on rim and edge sites while hydrogenation of the aromatic ring is restricted to rim sites only.....	136
Figure 4.13. Influence of morphology on the ratio of rim sites to total sites available on the edges of MoS ₂ particles. While increasing the stack height leads to a slight increase in the overall number of edge sites, the more pronounced effect is the decrease in the relative number of rim sites.....	138

LIST OF ABBREVIATIONS

4H-DBT	Ring hydrogenated analog of DBT, dibenzothiophene
BET	Brunauer Emmett Teller
BJH	Barrett Joyner Halender
BP	Biphenyl
s-BuOH	sec-butanol, 2-butanol
CHB	Cyclohexylbenzene
DBT	Dibenzothiophene
DDA	Dodecylamine
EO	Ethylene oxide
EPA	Environmental Protection Agency
EtOH	Ethanol
GC-MS	Gas chromatography - mass spectrometry
h-bond	Hydrogen bond
HDA	Hexadecylamine
HDS	Hydrodesulfurization
HMS	Hexagonal mesoporous silica
HOMO	Highest occupied molecular orbital
M41S	Mobil family of mesoporous silicas
MCM-41	Mobil composition of matter 41
MSU- δ	Mesoporous alumina comprised of a δ -Al ₂ O ₃ framework
MSU- γ	Mesoporous alumina comprised of a γ -Al ₂ O ₃ framework

MSU-B	Mesoporous alumina comprised of a boehmite framework
MSU-S/B	Surfactant-boehmite composition, precursor to MSU aluminas
MSU-X	Wormhole mesoporous aluminas (or silicas)
nm	nanometer
NMR	Nuclear magnetic resonance
OA	Octylamine
P/P_o	Relative pressure, P = pressure, P_o = saturation pressure
PEO	Polyethylene oxide
PO	Propylene oxide
ppm	parts per million
PSD	Pore size distribution
s-BuOH	sec-butanol, 2-butanol
surf	Surfactant
TalA	Tallow amine
Tal TetA	Tallow tetraamine
Tal TriA	Tallow triamine
TEM	Transmission electron microscopy
TMS	Transition metal sulfide
v/v	volume ratio
XRD	X-ray diffraction

Chapter 1

Introduction

1.1. Classification of Aluminas

Aluminas, a class of compounds comprised of aluminum, oxygen, and often hydrogen, are wonderfully interesting and diverse. The name *alumina* is broadly applied to all members of this group that includes the aluminum hydroxides, aluminum oxide hydroxides, and aluminum oxides. The properties of these compounds vary greatly, from powders that are relatively soft to larger crystals of extreme hardness, inert to readily reactive, free flowing to viscous, catalytically active to inactive. Regardless of nature, it is interesting that all of these aluminas, when heated to temperatures high enough and for periods of time long enough, are eventually converted to α -alumina or corundum, the only stable form of alumina.

Aluminas are commercially important chemicals. The world's primary source of aluminum is from the mineral bauxite, an impure hydrous ore of aluminum and other metals. Bauxite is refined to useful alumina chemicals through the Bayer process. The ore is first treated with hot concentrated sodium hydroxide to extract the aluminum hydroxides and remove the impurities. Crystalline aluminum hydroxide is then precipitated, washed, and thermally dehydrated to produce aluminum oxide¹. While most of the alumina produced is used in the production of metallurgical grade aluminum, a large amount is devoted strictly to alumina chemicals. According to the International Aluminum Institute, over 40

million tonnes of alumina was produced in 2001². Not surprisingly, aluminas find uses in a variety of applications including as fillers in plastics and paper, fire retardants, adsorbents, abrasives, ceramics, and perhaps most importantly, as catalysts and catalyst supports.

As mentioned above, a range of composition is observed within the family of aluminas. They may be crystalline or amorphous. The crystalline aluminas are aluminum hydroxides, $\text{Al}(\text{OH})_3$, aluminum oxide hydroxides, AlOOH , and aluminum oxides, Al_2O_3 . There are three forms of the trihydroxides: gibbsite, bayerite, and nordstrandite. Of these, gibbsite is the most common and is the product of the Bayer process. In its structure, aluminum ions occupy 2/3 of the octahedral vacancies in the close packed lattice of hydroxide ions. Hydroxide ions are aligned so that the sequence of layer stacking is AB...BA...AB...BA. Bayerite is not found in nature, but has been prepared synthetically. Its structure is similar to that of gibbsite, but the layer sequence is AB...AB...AB. The third trihydroxide, nordstrandite, has a structure that is a composite of the previous ones. Alternating double layers of gibbsite and bayerite are stacked to form the structure¹. The best method to distinguish between these different crystalline phases is x-ray diffraction (XRD). In addition to the crystalline trihydroxides, amorphous $\text{Al}(\text{OH})_3$ also exists.

Two other members of the alumina family are aluminum oxide hydroxides, AlOOH , boehmite and diaspore. Boehmite occurs as a component of bauxite and can also be synthesized through neutralization of aluminum salts or hydrolysis of aluminum alkoxides around the boiling point of water³. The boehmite structure is

comprised of extended chains of AlOOH dimers. The chains form a double layer in which hydroxyls in one layer are positioned over the depressions between adjacent hydroxyls in the other layer. The oxygen ions are arranged in a cubic close packed lattice. Diaspore is found in nature associated with geologically older bauxite deposits and metamorphic rocks and it is therefore believed that high pressures and temperatures are required for its formation. Its structure is similar to that of boehmite in that the basic unit is the chain of AlOOH dimers, however, the oxygen atoms are arranged in a hexagonal close packed lattice. In denoting aluminas, the common crystallographic designation assigns a prefix of α - to the hexagonal phases and a prefix of γ - to the cubic phases. Therefore, boehmite is often represented as $\gamma\text{-AlOOH}$ and diaspore as $\alpha\text{-AlOOH}$.

The only thermodynamically stable oxide of aluminum is corundum, $\alpha\text{-Al}_2\text{O}_3$. It can be prepared by several methods, the most common being thermal degradation of other aluminas at temperatures over 1000°C . Corundum is also found in nature in igneous and metamorphic rocks. The α - designation is consistent with its hexagonally close packed oxygen lattice in which aluminum ions occupy $2/3$ of the octahedral holes. In gem quality crystals of corundum, trace impurities of chromium lead to the formation of rubies while iron and titanium impurities lead to sapphires. The family of these alumina compounds is summarized in Figure 1.1.

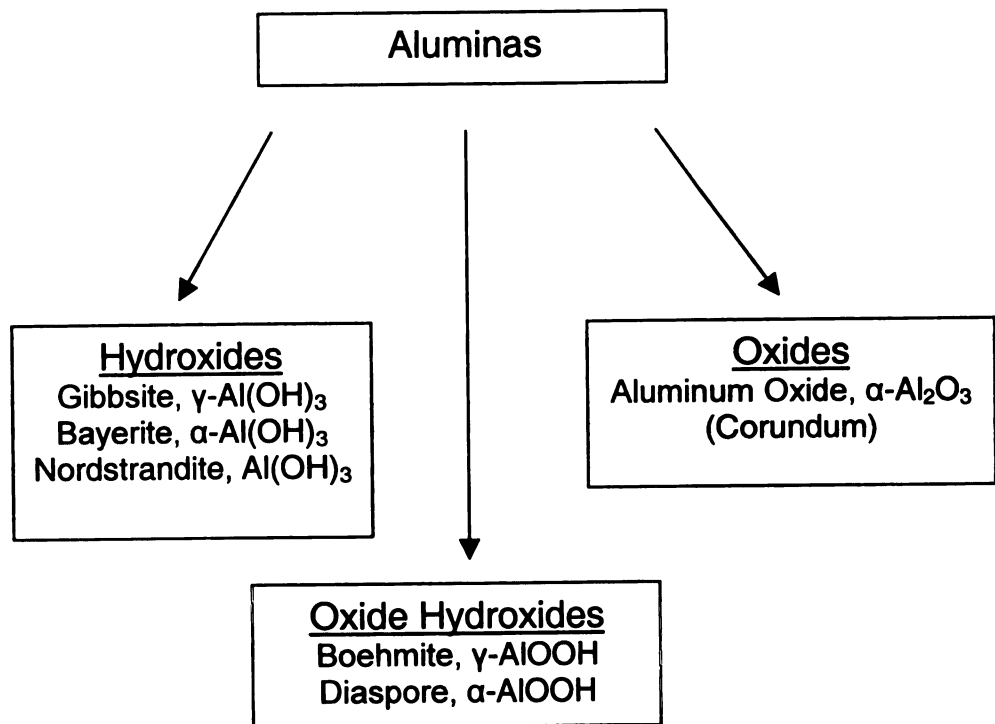


Figure 1.1. Family of alumina compounds.

1.2. Transition Aluminas

As mentioned previously, all aluminas eventually are converted to corundum upon heating at high temperatures. The appropriately named transition aluminas are disordered crystalline phases formed at temperatures of 250 – 800 °C during the transformation to α -Al₂O₃ at approximately 1100 °C. At least seven different transition aluminas have been reported: ρ (rho), X (chi), η (eta), γ (gamma), κ (kappa), θ (theta), and δ (delta). The particular phase observed depends upon both the precursor and the temperature to which that precursor is heated. Gibbsite is converted first to X at a temperature of 350 °C, then to κ around 750 °C while the other trihydroxides proceed through an η phase at lower temperatures, then to θ at temperatures over 800 °C. All of them are transformed to α beyond 1100 °C. The oxide hydroxide phases exhibit different transformation sequences than those of the trihydroxides. Boehmite is converted to γ around 500 °C, to δ above 750 °C, and then to θ above 900 °C before reaching α above 1000 °C. The behavior of diaspore is interesting in that it converts directly to α at a temperature of 500 °C. The similarity in the hexagonal packing of oxygen atoms in the dense structures of these phases, requiring therefore only minimal rearrangement upon transformation, is thought to be responsible for this observation. Within the group of transition aluminas, the nearly anhydrous θ , κ , and δ phases are more ordered than the other forms, as their formation requires higher temperatures¹. The transformation sequences are summarized in Figure 1.2.

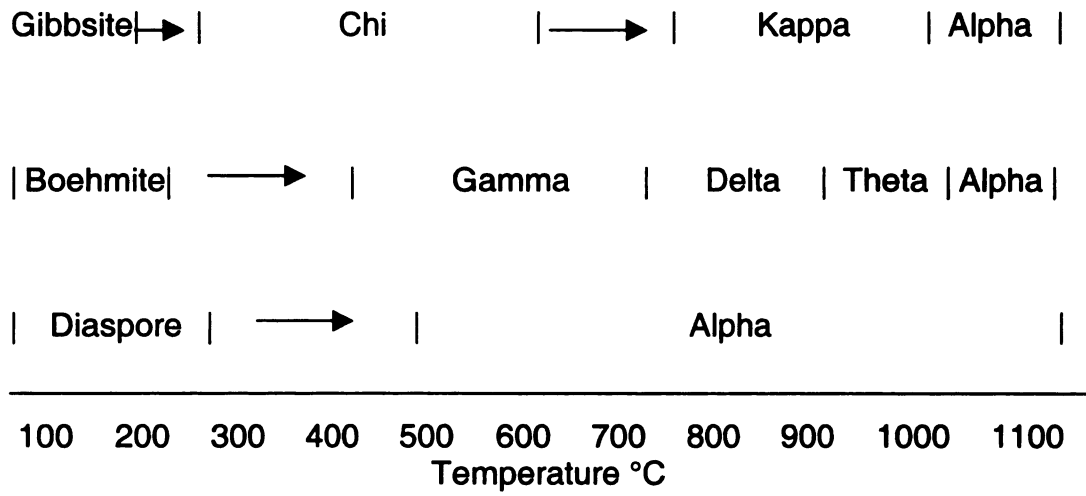


Figure 1.2. Transformation sequence observed upon the thermal dehydration of aluminas (adapted from Wefers and Misra³).

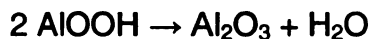
Despite the number of different phases, the structures of the transition aluminas are fairly similar with respect to each other. This in part explains the observed transformation sequence. χ - Al_2O_3 exhibits a highly disordered hexagonal packing of oxygen anions while the high temperature form of κ - Al_2O_3 is also hexagonal but more ordered. η - Al_2O_3 has a tetragonally distorted spinel structure in which $21\frac{1}{3}$ of the 24 cation vacancies are occupied by aluminum ions. The θ - Al_2O_3 structure is similar to that of the lower temperature η form. The structure of γ - Al_2O_3 is also of the spinel type, but it can be distinguished from that of the η form by its significantly larger tetragonal distortion. δ - Al_2O_3 is similar to γ , but it exhibits slightly greater long-range order³. In general, the identification of transition aluminas is best performed through XRD and ^{27}Al nuclear magnetic resonance (NMR). Each transition alumina has a slightly different XRD pattern, the higher temperature forms exhibiting sharper peaks than the others. ^{27}Al NMR can be used to distinguish the distribution of aluminum ions in the octahedral and tetrahedral vacancies of the oxygen lattice.

As the transition aluminas are disordered phases, dehydration upon heating and subsequent rearrangement of the lattices lead to the formation of porosity and internal surface area. While there is a loss of mass upon heating, the particle sizes remain the same, resulting in the development of porosity. In the dehydration of the trihydroxides, surface areas can reach as high as $350\text{ m}^2/\text{g}$ at lower temperatures before rapidly and continually declining toward the conversion to α - Al_2O_3 . For the oxide hydroxides, there is also an initial increase

in porosity leading to surface areas of 90-100 m²/g at a temperature of 500 °C that decreases to 15-20 m²/g upon heating at about 550 °C¹.

Upon the thermal dehydration of aluminas, the surfaces of the transition aluminas are altered extensively. The condensation of surface hydroxyls and their subsequent removal as water create a rough surface, exposing coordinatively unsaturated aluminum ions and leaving the remaining hydroxyl ions in various environments. This leads to acidic and basic sites on the surface of the alumina. While they are also used as adsorbents in liquid drying, water purification, and chromatographic columns, the combination of textural properties (pore volume and surface area) and surface properties leads to activity in catalytic applications. Consequently, transition aluminas are also referred to as activated aluminas.

Of all of the different phases, γ -Al₂O₃ is perhaps the most important and most widely utilized transition alumina. It is formed upon thermal dehydration of boehmite at temperatures ranging from 450 to 750 °C as described by the following equation:



γ - Al₂O₃ has been used as a catalyst in alcohol dehydration reactions to form alkenes and ethers and in isomerization reactions. γ - Al₂O₃ has also proven to be extremely useful as a catalyst support in numerous reactions due to its combination of heat resistance, chemical inertness, and favorable textural and surface properties. γ - Al₂O₃ can be produced with surface areas ranging from 185 – 250 m²/g with pore volumes typically around 0.20 cc/g^{1,3}.

Two primary methods are employed in the preparation of supported catalysts, impregnation and coprecipitation. In the incipient wetness impregnation method, a salt solution of the active species is deposited on the alumina and then thermally degraded to form the active catalyst. In the coprecipitation method, salt solutions of both the aluminum and active component are precipitated simultaneously, again followed by thermal degradation to produce the active catalyst. High surface area is a desirable property because a larger amount of active catalyst can be loaded onto the support. Many of the reactions in which alumina supported catalysts are used are important in the petroleum industry.

1.3. Hydrodesulfurization

One such reaction is the hydrodesulfurization (HDS) reaction, a crucial component of petroleum refining. Heteroaromatic sulfur organic molecules, common components of crude oil deposits, must be removed before fuels can be cleanly consumed. Fuels high in sulfur, when burned, produce acidic sulfur oxide species that lead to the production of smog and acid rain. Federal regulations put forth by the EPA are calling for a 97% reduction in sulfur content in fuels, from 500 to 15 ppm sulfur, by the year 2010⁴. At the same time that these constraints are put into place, lower sulfur content crudes are being depleted, making it necessary to rely upon feedstocks that contain larger amounts of sulfur. In addition, the presence of sulfur has a detrimental effect on other catalysts involved in downstream catalytic processing of feeds. Therefore, development of

improved methods for sulfur removal is pertinent both environmentally and economically.

In the HDS reaction, sulfur is removed from organic molecules as H_2S . Many studies of HDS processes are performed using thiophene or dibenzothiophene (DBT) as substrates. These molecules, as well as substituted and polyaromatic analogs, are representative of the sulfur containing compounds found in crude oil stocks. Sulfur removal in these larger molecules is especially challenging as steric effects come into play. Catalytic studies involving dibenzothiophene are therefore better indicators of potential performance using actual oil feedstocks. Reactions are usually performed in a catalytic reactor at temperatures ranging from 350 – 400 °C and pressures of 400 psi.

The catalysts employed in HDS reactions are transition metal sulfides (TMS). Many TMS show activity in HDS reactions, but because of their considerably lower cost, the HDS catalysts typically employed in industrial processes are either molybdenum or tungsten sulfides, combined with either nickel or cobalt sulfides, loaded on a $\gamma\text{-Al}_2\text{O}_3$ support. Some classic works by Chianelli and others⁵⁻¹⁴ over the last 20 years explain why these catalysts are effective, making them the preferred choice for use in the petroleum industry.

Much work has been done toward characterizing transition metal sulfide catalysts. Several structure/function relationships have been derived as models for catalytic activity and selectivity have been proposed to explain the nature of these TMS materials. The primary factor in determining the utility of a TMS catalyst is in the electronic effect that is observed in these catalysts. That is,

correlations to and trends in activity in HDS can be made based upon the position of the metal in the periodic table. Pecoraro and Chianelli measured the activity of TMS catalysts in DBT HDS⁵. When the activity is plotted against the periodic position, a “volcano” plot is observed (Figure 1.3), where a maximum in the activity is seen for Group VIII metals⁶. This trend was explained based upon the metal-sulfur bond strengths. As first described by Sabatier in 1911, in order to be an effective catalyst in a given reaction, a species must form bonds of intermediate strength with the substrate⁷. In the case of HDS, the metal-sulfur bond should be strong enough that the substrate bind to the metal, but weak enough that the catalyst allows H₂S to desorb from the active site. If the heat of formation (M-S bond strength) is too strong, then the active site is in essence poisoned by the substrate. If too weak, then the substrate does not bind tightly enough to lead to C-S bond cleavage. The transition metals in the center of the d-block meet this requirement and are show the greatest activity in HDS. The activity for the 4d and 5d metals is considerably higher than the 3d metals which are relatively inactive in HDS. Additionally, the 3d TMS do not exhibit a volcano plot behavior, indicating that factors other than periodic position have an influence on catalytic activity as well.

Using transition metals in anionic octahedrally coordinated MS₆ⁿ⁻ clusters, Harris and Chianelli carried out calculations of the electronic structure of TMS in an attempt to better explain the observed HDS activities⁸. Several factors were identified to be responsible for these observations. Included were the degree of covalency of the TMS, a measure of M-S d-p orbital interaction and covalent

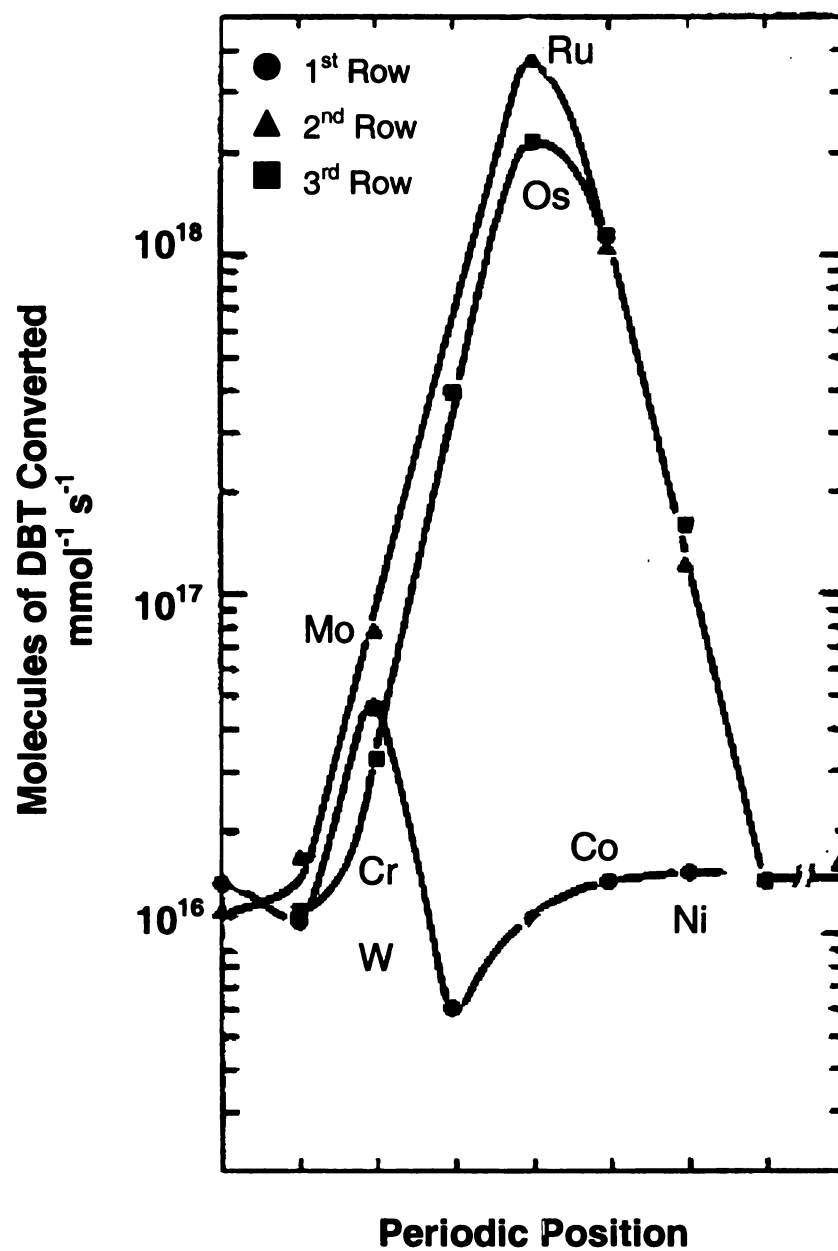


Figure 1.3. Activity of transition metal sulfides in DBT HDS plotted as a function of periodic position of the metal (adapted from Pecoraro and Chianelli)⁵.

bond strength of the M-S bond. The bond strength decreases on going across a period as more electrons are placed in antibonding orbitals. At the same time though, the degree of covalency increases as M-S orbital mixing increases. These factors are in line with the Sabatier principle. A third factor was identified, the symmetry and occupation of the highest occupied molecular orbital (HOMO). This effect is seen in bonding aspects of TMS. The activity is best when the HOMO in these clusters is a metal-based t_{2g} set of antibonding orbitals. The bonding to a thiophene molecule can be through the S atom in a σ -bonding mode or through the ring in a π -bonding mode. For 3d metals, the σ -bonding interactions are generally weak as the lone pair of electrons on the sulfur that is donated to the metal in bond formation is tied up in aromaticity. For 4d metals, there is a σ and π component to the bonding, thought to be a requirement for effective bonding of thiophene to transition metals. This is further supported by the fact that thiophene can act as a π -acceptor ligand and backbonding from the metal to an antibonding π^* orbital on thiophene is observed, weakening the C-S bond and thereby increasing activity. These three factors were grouped into a single activity parameter that correlated well with activity.

As mentioned previously, although other TMS exhibit greater activity in HDS catalysis, it is the MoS_2 that is the industry workhorse. When promoted by a second metal such as Co, there is an increase in the electron density, and hence activity, of the primary metal. This is the primary function of the promoter. A model similar to the previous one designed for unpromoted catalysts took into account a second 3d metal, using $\text{MoM}'\text{S}_9{}^{n-}$ clusters to study the electronic basis

for promotion⁹. As the metal was varied across the period, the t_{2g} set of orbitals decreases in energy relative to the higher 4d t_{2g} set. Upon reaching cobalt in the series, the 4d t_{2g} set is at an energy between the t_{2g} and e_g sets of the 3d metal. Cobalt has seven d electrons, six of which entirely fill the t_{2g} set while the seventh is now placed in the t_{2g} set of Mo, formally donating to Mo and increasing its electron density. The same effect is observed for nickel. All of the copper orbitals lie below the Mo orbitals and electrons are withdrawn from the molybdenum in this case. Other 3d metals had no effect. While this model does not predict the exact location of the promoter atoms, it is assumed that they are linked to the molybdenum atoms through a bridging sulfur atom. Furthermore, as electrons are transferred from antibonding Co or Ni orbitals to antibonding Mo orbitals, the Mo-S bond is weakened as the Co-S bond is strengthened. A sulfur shared between the two metals will have an intermediate M-S strength and, in accord with Sabatier's principle, should exhibit maximum activity.

There are several possible locations available to the promoter atom in the MoS_2 catalyst. If the catalyst is supported on, for example, alumina, the cobalt may be embedded in the upper layer of the support, a phase denoted as $\text{Co:Al}_2\text{O}_3$. Cube-like domains of Co_9S_8 have also been observed as a component of catalysts. Topsøe and Clausen identified a third phase as well, the so-called Co-Mo-S structure, a mixed Co-Mo sulfide phase in which the three elements are in close proximity to one another¹⁰. Through the use of Mössbauer spectroscopy, the type and quantity of cobalt structures were determined. It was found that the Co-Mo-S structure was the catalytically active phase as trends in activity

correlated favorably with the amount of this phase present in the catalyst. It was determined by use of analytical electron microscopy that the most common position of the cobalt is on the edge of an MoS₂ layer. This position for Co is now generally accepted and has led to the view that MoS₂ itself can be treated as a support for the promoter, allowing for a high content of cobalt and improved activity.

In addition to electronic considerations in catalyst performance, a geometric effect is also observed. This has to do with the nature of the crystal structure of the catalyst. For example, RuS₂ has an isotropic structure whereas MoS₂ has an anisotropic structure. The ruthenium catalyst's structure is cubic and there exists a correlation between HDS activity and the surface area of the catalyst. On the other hand, the molybdenum structure is a layered one in which the sheets are stacked only 2 – 10 nm thick, but extend 100 – 300 nm in a direction perpendicular to the layer stack. Accordingly, activity does not correlate to surface area of the MoS₂ catalyst. While the basal planes of this material contribute greatly to the surface area, they do not have an effect on activity in HDS. However, oxygen chemisorption correlates well with HDS activity for both. In the case of the MoS₂, oxygen was shown to accumulate on edges of the particles, indicating that the edge planes contain the catalytically active sites¹¹.

While the electronic and geometric effects have an impact on the activity of an HDS catalyst, the crystal structure also plays a role in selectivity. Daage and Chianelli considered the two-site nature of the edges of MoS₂ particles in developing the rim-edge model^{12,13}. In HDS of DBT, predominantly two products

are formed: biphenyl (BP) and cyclohexylbenzene (CHB). BP is formed from direct desulfurization of DBT while CHB is formed when DBT is first hydrogenated before undergoing desulfurization. MoS_2 was prepared under various thermal conditions, leading to samples with varying degrees of crystallinity. The layer stack height was determined by measuring the width of the 002 peak in the powder XRD pattern. It was found that as the particles became increasingly crystalline and the stack height increased, there was a severe decrease in the rate constant for the hydrogenation reaction. It was proposed then that hydrogenation occurs only on rim sites, those which are at the edge of the basal planes. Desulfurization occurs on both rim and edge sites, the latter located at the edge of internal layers. A convenient feature of this model is that the number of rim sites is dependent only upon the stack height, not the shape of the particles. Thus, selectivity is governed by height within the particle, activity by the diameter of the particle.

The active sites of the HDS catalyst are sulfur vacancies at the edges of the MoS_2 particles. In promoted catalysts, it is likely that the active sites are sulfur vacancies near cobalt that is in the Co-Mo-S phase. A clear mechanism to explain HDS catalysis has yet to be developed. Information used in developing a mechanism has come from solid-state chemistry, organometallic chemistry, and surface science studies. Many model systems use thiophene as the substrate. Prins et al. suggest the following as a possibility¹⁴. Adsorption of the thiophene sulfur atom onto the active site occurs first, followed by a four-electron reduction process to yield butadiene and hydrogen sulfide. The electrons for the reduction

are supplied either by four one-electron or two two-electron oxidations of molybdenum. In any model, thiophene (or DBT) can bind to the active site in two manners: one-point end-on adsorption through sulfur or side-on adsorption through a carbon-carbon double bond. The proposed side-on adsorption mechanism involves the formation of persulfide ions. One support for this mode is that persulfide ions are found in the structures of RuS_2 , OsS_2 , two of the highest activity TMS catalysts, and in the sulfides of cobalt and nickel, the common promoters of activity.

For the larger DBT molecule and its substituted analogs, steric hindrance may become a factor in deciding which mode of adsorption is most likely. Daage and Chianelli address this in their report of the rim-edge model¹². The HDS reaction proceeds through a vertical ($\text{S } \eta^1$) adsorption mode that can occur on all edge sites. The hydrogenation reaction progresses through a flat adsorption mode that requires a larger surface area of the catalyst. This is unlikely to occur on the edge in general, but at the rim, where part of the molecule will dangle in space. For thiophene, end-on adsorption is common, but for larger molecules such as DBT, a planar adsorption is preferred.

While the theoretical studies described above are based on unsupported catalysts, it is a common practice to use a catalyst support in actual HDS reactions. Alumina is the support of choice in this reaction for several reasons. The material can withstand the temperatures and pressures involved in the HDS reaction. The support itself is inert and is not involved in the reaction. This is important in terms of selectivity and efficiency, where acidity can lead to cracking

reactions and increased consumption of costly hydrogen. Additionally, the surface area of conventional γ - Al_2O_3 is high enough that the catalyst can be dispersed effectively, leading to a larger number of catalytically active sites. The use of an alumina support is also cost effective in two ways. First, alumina itself is inexpensive. Second, the use of the support allows for the dilution of the metal, allowing for a less expensive catalyst. One concern with supported catalysts is that the active sites of the catalyst that are in contact with the support may be inaccessible, thus lowering the activity of the catalyst. If the generally accepted rim-edge model is envisioned and the MoS_2 interacts with the support through the basal planes, then the sites that are blocked would be rim sites, on which hydrogenation occurs. Therefore, selectivity would be improved. However, if the MoS_2 particles attach to the support in other manners, then edge sites could become buried, lowering the activity.

1.4. Mesostructures

Since the disclosure of mesostructured silica molecular sieves by Mobil researchers in 1992^{15,16}, there has been much work done in the development of these materials. The original work employs cationic surfactant micelles to template silicate oligomers into mesostructures. Removal of the surfactant creates the final products, the M41S family of materials. These materials are characterized by their uniform and tunable pore sizes from $\sim 15 - 100 \text{ \AA}$, large pore volumes, and high surface areas in excess of $1000 \text{ m}^2/\text{g}$. The principal

member of this family, MCM-41, possesses hexagonal pores with long-range order. Therefore, the mesoporous molecular sieves can be viewed as large-scale analogs to microporous zeolites.

Noting the impact that mesostructured silicas have had in catalysis, similar improvements may be anticipated with the use of mesostructured aluminas. Particularly, these aluminas could be utilized as catalyst supports in HDS. The larger pore volumes and surface areas of these materials when compared to conventional aluminas would allow for better dispersal of catalyst and increased access to active sites. Additionally, larger amounts of catalyst may be loaded onto the support without the blockage of pores. With this additional loading of catalyst and increased number of accessible active sites, the loss of active some sites due to contact with the support can be tolerated.

Following Mobil's work, Stucky and coworkers identified the important steps in the formation of mesostructured silicas through electrostatic pathways¹⁷. First, there is multidentate binding of silicate oligomers to the surfactant. Second, the oligomers polymerize in the interface region. Third, charge matching between inorganic and organic species dictates the extent to which the reaction proceeds. These factors were then used to extend Mobil's original synthetic pathway into four general electrostatic pathways leading to mesoporous materials¹⁸. In addition to silica, mesostructures of antimony, tungsten, iron, lead, zinc, and aluminum oxides could also be prepared from these pathways, although not all materials were thermally stable.

Work from the Pinnavaia group established two additional pathways based upon hydrogen bonding interactions between neutral inorganic precursors and neutral primary amine surfactants¹⁹. The materials afforded differed from their predecessors. Both materials exhibited uniform pores, but, owing to the relatively weaker hydrogen bonding forces that govern the assembly of the materials in latter work, long range order was not observed. These disordered silicas, named HMS, were characterized by the wormhole structural motif that arose. Additionally, the wall thickness of materials prepared in this manner was greater than that of materials synthesized from electrostatic pathways, where wall thickness is determined by charge matching. The neutral assembly pathway imposes no such restriction. The textural properties, however, were comparable to those of the previously described materials. Additionally, surfactant molecules could be removed (and recycled) from the as-synthesized HMS materials through solvent extraction, as opposed to calcination which is required to remove surfactant from electrostatically prepared materials. A study by Tanev²⁰ compared the properties of the two types of materials and reported that HMS materials, due to the thicker framework walls, exhibit improved thermal stability. The smaller particle size of HMS leads to the formation of complimentary textural porosity, facilitating access to framework-confined mesopores.

Another neutral assembly pathway, similar to the previously mentioned one, was also discovered²¹. The composition of materials formed from these neutral pathways could also be specified by selecting the appropriate inorganic

precursor. Dative bonding pathways to tantalum and niobium oxide mesoporous materials were proposed by Antonelli and Ying^{22,23}.

In the ten years that have passed since Mobil's initial report, the development and proliferation of mesostructured silica materials has been widespread. To quantify this explosion of research in this field to some extent, consider that a literature search for reports of mesoporous silica since 1992 will result in over 1,800 references while a similar search for mesoporous aluminas will yield less than 8% of that amount. The 8% is exaggerated to some degree, as many of the references describe aluminas prepared by conventional, non-templating, methods or alumina in mixed metal oxide materials. The results of the search are especially discouraging, noting the extensive use of aluminas in catalysis. It is also a testament to the elusiveness of the ability to synthesize these materials. While the increased utility of mesoporous silicas in catalytic applications has already been realized²⁴, a similar increase in the use of mesoporous aluminas is anticipated in the near future.

1.5. Mesostructured Aluminas

Many aluminas are porous by nature. The transition aluminas formed through thermal dehydration of aluminum hydroxides are examples. However, the pore size in these materials is not uniform; a broad distribution of sizes is observed. This leads to necking that can limit access to the pores. Mesoporous aluminas assembled through templating pathways offer narrower pore size distributions

and improved textural properties. Bagshaw and Pinnavaia first reported a mesoporous alumina synthesized in this manner²⁵. A series of aluminas, titled MSU-X, were synthesized from hydrolysis of aluminum sec-butoxide in the presence of nonionic surfactants. After calcination, these materials exhibited surface areas up to 535 m²/g and pore volumes up to 0.68 cc/g with uniform pore sizes. The wormhole frameworks were thermally stable to temperatures of 500 °C. The 5-coordinate aluminum centers detected by ²⁷Al NMR spectrum, a property of amorphous aluminas, suggests that Lewis acid sites may be present in these materials.

Other reports of mesoporous alumina quickly surfaced following Bagshaw's initial communication. Yada and coworkers synthesized alumina mesophases from aluminum nitrate and sodium dodecyl sulfate^{26,27}. A lamellar phase can be converted into a disordered hexagonal phase during hydrolysis of the aluminum salt by urea. Although the hexagonal phase is not evident by XRD after calcination at 600 °C, a low angle peak is observed, indicating that a disordered mesoporous phase is present.

A report from Davis' group described the formation of mesoporous aluminas prepared from the hydrolysis of aluminum alkoxides in the presence of carboxylic acids as structure directors²⁸. Although the materials were calcined at relatively low temperatures for short durations, surface areas up to 710 m²/g were reported. The pore size exhibited by these materials was near 20 Å regardless of surfactant chain length.

Reporting a generalized synthesis strategy leading to large pore mesoporous metal oxides, Stucky and coworkers provided an example of a mesoporous alumina²⁹. Nonionic surfactants were used to template the oxide from an aluminum chloride precursor. The homogenous sol formed was allowed to gel in an open Petri dish at 40 – 60 °C. The resulting alumina, once calcined, showed an average pore size of 140 Å with a pore volume of approximately 0.35 cc/g. The framework walls of the alumina were amorphous.

A contribution from Gabelica and coworkers indicated a novel approach to mesoporous aluminas³⁰. Mixing of anionic and cationic surfactants was employed to achieve better charge matching between the inorganic and organic phases. Aluminum salts and Keggin ions were precipitated in the presence of these surfactant mixtures to yield aluminas with surface areas up to 810 m²/g, an unprecedented value. Remarkably, there has been no further work reported stemming from this group's initial report. The pore size and pore volume reported for the high surface area alumina were 27 Å and 0.61 cc/g, respectively. The material was comprised of a regular arrangement of pores with amorphous walls, as judged by XRD and the ²⁷Al NMR.

1.6. Stabilization of Aluminas

All of the previously described aluminas are comprised of amorphous frameworks. While these materials were generally thermally stable up to 500 °C, they may not remain stable under certain catalytic conditions where higher

temperatures and pressures and hydrothermal conditions are encountered. Over time and with extended use under these conditions, alumina particles can grow in size and sinter, suffering structural and textural modification. Transition alumina phases are only metastable and will eventually be converted to $\alpha\text{-Al}_2\text{O}_3$ under extreme thermal conditions. A concomitant loss of textural properties is observed with this structural transformation. To combat these effects, aluminas have been doped with small percentages of lanthanides, typically 1 – 5% lanthanum and cerium. This has been carried out primarily by two methods. Coprecipitation of the two oxide precursors or incipient wetness impregnation of lanthanide containing salts can afford the stabilized materials. There are also two explanations for the resulting stability of the doped materials. Shaper³¹ and Beguin³² concluded that a lanthanum aluminate compound covered the surface of the alumina. Oudet³³ proposed that a LaAlO_3 perovskite type structure behaves similarly. In each case, the stabilization is due to strong interactions between the lanthanide structure and the alumina, inhibiting the conversion to $\alpha\text{-Al}_2\text{O}_3$. Alternatively, it was proposed by Burtin³⁴ that stability was due to the occupation of lanthanide ions in cationic vacancies of the spinel type lattice of alumina. Braun et al. also concluded similarly in their doping work³⁵. In this manner, the lanthanide ions fortify the alumina structure and limit the amount of diffusion of aluminum ions on conversion to corundum. Other metal ions have been used in stabilization, however, lanthanum and cerium have consistently shown the best results. Cerium exhibits two common oxidation states, Ce^{3+} and Ce^{4+} . Oxidation to the higher state can lead to the formation of CeO_2 and its

leaching from the alumina. Lanthanum exhibits only the La^{3+} oxidation state and is therefore a better stabilizer. The stabilization of MSU-X aluminas has been achieved through lanthanide doping³⁶. Indeed, textural properties were improved in doped aluminas as compared to the pure aluminas.

In addition to the stabilization of amorphous aluminas, it is of interest to synthesize mesoporous crystalline aluminas in an effort to improve catalytic properties. Owing to the crystallinity, these materials exhibit inherent stability when compared to their amorphous analogs. The first report of such an alumina was recently made by Pérez-Pariente and coworkers³⁷. In a synthesis similar to that of MSU-X alumina, aluminum alkoxides were hydrolyzed with nonionic surfactants and dipropylamine to yield a thermally stable, crystalline mesoporous alumina. The synthesis was altered to include thermal aging of the freshly made gel. Upon calcination, mesoporosity was retained within the crystalline product. The XRD pattern of the calcined product showed peaks assignable to a transition alumina phase, confirming a crystalline phase. Additionally, unlike many of the amorphous aluminas, there was no peak in the ^{27}Al NMR corresponding to 5-coordinate aluminum centers. Surface areas in excess of $500 \text{ m}^2/\text{g}$ and pore volumes of 0.91 cc/g were attained. The degree of crystallinity and the textural properties were compromised after calcination at 700°C .

1.7. Objectives and Rationale

As can be inferred from the reports summarized above, the synthesis and application of mesoporous aluminas are areas that are ripe for exploration and development. One objective of this study is to synthesize novel mesoporous aluminas. Alumina is perhaps the world's most widely used catalyst support. As such, new materials with improved structural and textural properties would be a welcome addition to the alumina family. Noting the unstable nature of the amorphous aluminas, the focus here is on crystalline aluminas. To date, only one example of a crystalline mesostructured alumina has been reported. Although these materials promise to be more stable than their amorphous relatives, corundum, $\alpha\text{-Al}_2\text{O}_3$, is the only phase of alumina that can be considered truly stable. Therefore, doping of lanthanides and transitional metals into the alumina frameworks in an effort to improve thermal and hydrothermal stability, with retention of textural properties, will also be explored. The doping of ions into the frameworks of these aluminas can also stabilize a particular phase. This is important in many catalytic applications where the elevated temperatures required for catalysis initiate phase transitions of the alumina, accompanied by degradation of textural properties. Additionally, the incorporation of transition metal ions may introduce catalytically active centers into the alumina. Whatever strategy is employed for stabilization, the goal is to produce high performance mesoporous aluminas.

Finally, another goal is to demonstrate the value and utility of these newly designed aluminas. Especially of interest is the ability of these materials to function as catalyst supports in hydrodesulfurization reactions. Crystalline aluminas offer the necessary stability under the conditions used in HDS reactors. Aluminas with improved properties give hope that more effective and efficient routes to sulfur removal will be found, enabling the petroleum and automotive industries to meet the demands of government and society. This is an increasingly crucial need as high quality oil feedstocks are consumed, leaving heavier and dirtier stocks as the primary fuel source.

1.8. References

- (1) Misra, C. *American Chemical Society Monograph, Vol. 184: Industrial Alumina Chemicals*, 1986.
- (2) International Aluminum Institute, 2002.
- (3) Wefers, K.; Misra, C. "Oxides and Hydroxides of Aluminum," Alcoa Laboratories, 1987.
- (4) In *New York Times*: New York, NY, 2000.
- (5) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430-445.
- (6) Chianelli, R. R. *NATO ASI Ser., Ser. C* **1983**, *105*, 361-378.
- (7) Sabatier, P. *Ber. Deutsch Chem. Ges.* **1911**, *44*, 2001.
- (8) Harris, S.; Chianelli, R. R. *J. Catal.* **1984**, *86*, 400-412.
- (9) Harris, S.; Chianelli, R. R. *J. Catal.* **1986**, *98*, 17-31.
- (10) Topsoe, H.; Clausen, B. S. *Catal. Rev. - Sci. Eng.* **1984**, *26*, 395-420.
- (11) Tauster, S. J.; Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1980**, *63*, 515-519.
- (12) Daage, M.; Chianelli, R. R. *J. Catal.* **1994**, *149*, 414-427.
- (13) Daage, M.; Chianelli, R. R.; Ruppert, A. F. *Stud. Surf. Sci. Catal.* **1993**, *75*, 571-584.
- (14) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev. - Sci. Eng.* **1989**, *31*, 1-41.
- (15) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et al. *J. Am. Chem. Soc.* **1992**, *114*, 10834-10843.
- (16) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature (London)* **1992**, *359*, 710-712.

- (17) Monnier, A.; Schuth, F.; Huo, Q.; Kumar, D.; Margoless, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; et al. *Science (Washington, D. C., 1883-)* **1993**, *261*, 1299-1303.
- (18) Huo, Q.; Margoless, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schueth, F.; Stucky, G. D. *Nature (London)* **1994**, *368*, 317-321.
- (19) Tanev, P. T.; Pinnavaia, T. J. *Science (Washington, D. C.)* **1995**, *267*, 865-867.
- (20) Tanev, P. T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2068-2079.
- (21) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science (Washington, D. C.)* **1995**, *269*, 1242-1244.
- (22) Antonelli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 426-430.
- (23) Antonelli, D. M.; Ying, J. Y. *Chem. Mater.* **1996**, *8*, 874-881.
- (24) Corma, A. *Chem. Rev. (Washington, D. C.)* **1997**, *97*, 2373-2419.
- (25) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1102-1105.
- (26) Yada, M.; Machida, M.; Kijima, T. *Chem. Commun. (Cambridge)* **1996**, 769-770.
- (27) Yada, M.; Hiyoshi, H.; Ohe, K.; Machida, M.; Kijima, T. *Inorg. Chem.* **1997**, *36*, 5565-5569.
- (28) Vaudry, F.; Khodabandeh, S.; Davis, M. E. *Chem. Mater.* **1996**, *8*, 1451-1464.
- (29) Yang, P.; Zhao, D.; Margoless, D. I.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 2813-2826.
- (30) Valange, S.; Guth, J. L.; Kolenda, F.; Lacombe, S.; Gabelica, Z. *Microporous Mesoporous Mater.* **2000**, *35-36*, 597-607.
- (31) Schaper, H.; Doesburg, E. B. M.; Van Reijen, L. L. *Appl. Catal.* **1983**, *7*, 211-220.
- (32) Beguin, B.; Garbowski, E.; Primet, M. *Appl. Catal.* **1991**, *75*, 119-132.

- (33) Oudet, F.; Courtine, P.; Vejux, A. *J. Catal.* **1988**, *114*, 112-120.
- (34) Burtin, P.; Brunelle, J. P.; Pijolat, M.; Soustelle, M. *Appl. Catal.* **1987**, *34*, 239-254.
- (35) Braun, S.; Appel, L. G.; Zinner, L. B.; Schmal, M. *Br. Ceram. Trans.* **1999**, *98*, 77-80.
- (36) Zhang, W.; Pinnavaia, T. J. *Chem. Commun. (Cambridge)* **1998**, 1185-1186.
- (37) Gonzalez-Pena, V.; Diaz, I.; Marquez-Alvarez, C.; Sastre, E.; Perez-Pariente, J. *Microporous Mesoporous Mater.* **2001**, *44-45*, 203-210.

Chapter 2

Synthesis and Characterization of Mesostructured Boehmite

2.1. Introduction

Much effort has been invested in the development of alumina phases for industrial use. Heavy interest lies in the production of transition aluminas with favorable surface and textural properties. The primary target phase is $\gamma\text{-Al}_2\text{O}_3$. This phase is achieved by thermal dehydration of boehmite¹. Noting the importance of $\gamma\text{-Al}_2\text{O}_3$ as a catalyst and catalyst support, one can appreciate that boehmite is also a commercially important chemical. However, comparatively few reports on the synthesis of boehmite can be found in the literature.

Aside from its most important use as the precursor to $\gamma\text{-Al}_2\text{O}_3$, boehmite has other uses as well. Boehmite has served as a component in the synthesis of aluminum containing anionic clays or layered double hydroxides² and carboxylate alumoxanes³. It has been used infrequently as a catalyst support and as a catalyst itself. The lack of applications of boehmite as a catalyst stems from the widespread use of pseudoboehmite in this capacity. The differences in these two materials are discussed below.

Boehmite is an aluminum oxide hydroxide (AlOOH). The structure of boehmite is comprised of close packed oxide and hydroxide ions in which double chains of AlOOH molecules extend along the a-axis. These units are stacked in the direction of the b-axis where hydroxyls of one layer are located over the

depressions between adjacent hydroxyls in the other layer (Figure 2.1)⁴. Hydrogen bonding holds the double layers together.

Pseudoboehmite, or gelatinous boehmite, can be classified as alumina structurally similar to that of boehmite, but having a greater water content and smaller particle size than boehmite. Aluminum alkoxides are generated as byproducts in the formation of linear alcohols by the Ziegler process. Hydrolysis of these alkoxides results in the production of pseudoboehmite, available commercially under the name of Catapal¹. This material has a high surface area and is easily converted to a useable sol form by peptizing with dilute (typically nitric) acid⁵. In this respect, it is discernable from boehmite. When deciding which material to use in applications where a soluble aluminum source is desired, this property makes pseudoboehmite the material of choice.

Not surprisingly, the terms boehmite and pseudoboehmite are often incorrectly used in the literature. In addition, both have also been referred to as aluminum hydroxides, causing even more confusion. There has been some debate as to the actual differences in the two materials. Boehmite contains 15% H₂O by mass where pseudoboehmite has been found to contain up to 30% H₂O. The location of the excess water in the structure was originally thought to be contained in the region between the double layers. However, d-spacings found for the 020 peak in the XRD patterns of the materials were not large enough to accommodate such an excess volume of water^{6,7}. This leads to the currently accepted idea that pseudoboehmite is structurally identical to boehmite, differing only in its smaller crystallite size and higher water content. In this model

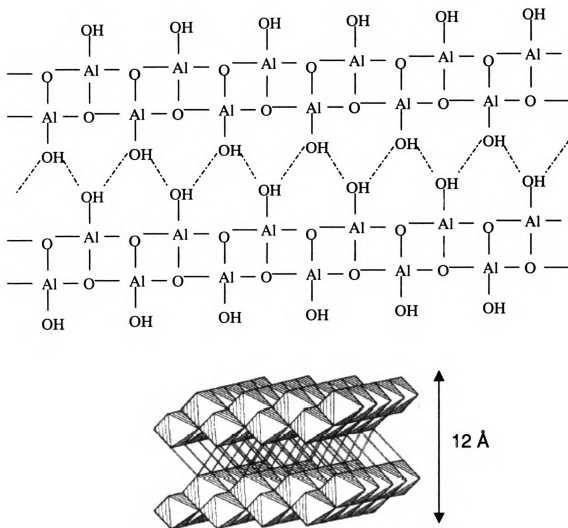


Figure 2.1. Cross-sectional (upper) and three-dimensional (lower) depiction of the boehmite double-layer. The thickness of the double layer is ~ 12 Å.

of pseudoboehmite, the increased number of terminal hydroxyl groups accounts for the excess water. The smaller the crystals, the greater the number of hydroxyls present.

Traditionally, boehmite is synthesized by the neutralization of aluminum salts under hydrothermal conditions⁴. Unlike the γ -Al₂O₃ and the other transition aluminas, boehmite is relatively non-porous. Mesoporous aluminas prepared in the presence of surfactants have been reported in the literature, however, all but a few describe materials that are amorphous⁸⁻¹⁴. Similarly, the use of surfactants to direct the formation of mesostructured boehmite is reported here. The novelty of this approach lies in the choice of the inorganic precursor and the surfactants employed in the synthesis and the method of surfactant removal. The use of aluminum sec-butoxide allows for formation of a boehmitic alumina phase during synthesis. Primary and tallow amine surfactants decompose at a temperature that allows for their removal via calcination without the concomitant conversion of boehmite to γ -Al₂O₃.

2.2. Experimental

2.2.1. Synthesis

The synthesis of mesostructured boehmite was executed as follows: The surfactant, a primary or tallow amine (see footnote to Table 2.1), was dissolved in a solution of ethanol and water (75/25 v/v) at ambient temperature. To this solution, aluminum sec-butoxide was added under vigorous stirring by the use of

a magnetic stirrer. The mixture was either allowed to stir at ambient temperature or was transferred to a temperature controlled shaker bath for 20 hours in a sealed vessel. Precipitates formed upon hydrolysis of the alkoxide were recovered by vacuum filtration, washed with water and ethanol, and allowed to dry at ambient temperature. The final surfactant-free products were obtained by calcining the as-synthesized products in air at 325 °C for 10 hours. Alternatively, surfactant could be removed by ethanol extraction at 80 °C. While the amounts of the starting materials were varied, a typical synthesis had the following molar ratios:

5.0 Al(s-BuO)₃ : 1.0 Surfactant : 28.7 Ethanol : 31.0 Water

2.2.2. Characterization

Powder diffraction patterns were collected on a Rigaku Roteflex Diffractometer using Cu K_α radiation ($\lambda = 0.154$ nm). Intensity was calculated in counts per second every 0.02 degrees 2 θ . Sweep rates were varied from 2 – 8 degrees 2 θ /min.

Nitrogen adsorption – desorption isotherms were collected on a Micromeritics TriStar 3000 sorptometer at 77K. Samples were degassed at least 12 hours at 150 °C under a vacuum of 10⁻⁶ torr prior to analysis. Surface areas and pore sizes were determined by the BET¹⁵ and BJH¹⁶ methods, respectively.

TEM images were collected on a JEOL 100CX microscope with a CeB₆ filament at an accelerating voltage of 120 kV. Samples were prepared by sonicating a suspension of the powder in ethanol for 20 min. One to two drops of

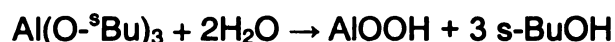
the suspension were then placed on a carbon coated holey film that was supported on a 3mm, 300 mesh copper grid.

^{27}Al NMR spectra were collected on a Varian 400 VRX solid – state NMR spectrometer. Samples were placed in a zirconia rotor and spun at 4 kHz with a pulse width of 0.5 μs and a pulse delay of 0.5 s. Chemical shifts were referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$ which is assigned a value of 0 ppm.

2.3. Results and Discussion

2.3.1. Formation of MSU-S/B

Addition of the aluminum sec-butoxide to the surfactant solution results in rapid hydrolysis of the alkoxide, instantly forming a precipitate of a surfactant – boehmite composition, denoted MSU-S/B. The conversion of the alumina species is as follows:



It has been reported that the formation of boehmite requires hydrothermal conditions¹. Although these reactions are performed at ambient temperature, two reasons may help to explain the presence of boehmite as a product of the reactions. First, the hydrolysis of the alkoxide is exothermic and a considerable amount of heat is released. The volume of the solution in the reaction mixture is not great enough to disperse this heat and initially the temperature in the reaction vessel is much greater than ambient temperature. Second, and more importantly, by providing multiple sites for the formation of hydrogen bonds between amine

head groups and boehmite hydroxyls, the use of the surfactant aids in the growth of particles. Boehmite particles will terminate with an exposed layer of hydroxide groups at the surface. These groups readily form h-bonds with the surfactant head groups (Figure 2.2). In contrast, hydrolysis of aluminum alkoxides in the absence of surfactant leads to the formation of pseudoboehmite. Indeed, this is one method of commercial production of pseudoboehmite.

Upon calcination, the surfactant is removed and the as-synthesized MSU-S/B is converted to a mesostructured boehmite, denoted MSU-B. Noting the transformation sequence upon dehydration of aluminas, the conversion of boehmite to $\gamma\text{-Al}_2\text{O}_3$ occurs at temperatures of 400 °C⁴. Consequently, if calcination is performed above 400 °C, the structural integrity of the boehmite phase is compromised. The use of primary and tallow amines is key in this regard because they will degrade at temperatures below 400 °C and can therefore be removed at lower calcination temperatures. Also upon calcination, particles may sinter leading to growth of larger crystals at the expense of smaller ones. This helps to ensure that the oxide framework is comprised of boehmite and not pseudoboehmite.

Calcination could also be performed at higher temperatures. In fact, MSU-B materials were stable to calcination at 350 °C for short durations. At longer periods or at 400 °C, the onset of conversion from boehmite to $\gamma\text{-Al}_2\text{O}_3$ was observed as judged by the appearance of peaks assignable to $\gamma\text{-Al}_2\text{O}_3$ in the wide angle XRD patterns. Therefore, milder conditions were preferred and

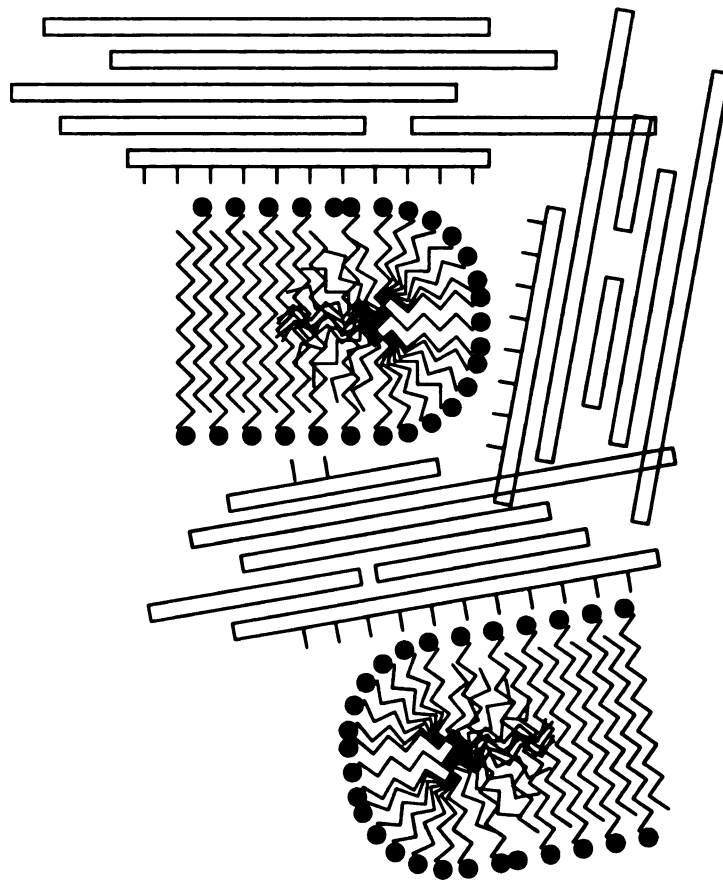


Figure 2.2. Schematic of interactions leading to formation of MSU-S/B. Each slab represents one boehmite double layer. Lines on the boehmite layers represent hydroxyls forming hydrogen bonds to the surfactant micelles. Areas of overlapping boehmite layers indicate cross-linking through condensation of adjacent hydroxyls.

calcination was performed at the lowest temperature possible to preserve the boehmite phase while still removing the surfactant.

Calcination is a convenient method of removing the surfactant, although the surfactant is destroyed in the process. Surfactant removal and recovery can be achieved through ethanol extraction if desired. However, the small amounts of primary and tallow amines used and their costs, compared to other more expensive surfactants such as polyalkylene oxides, do not warrant their recovery. Calcination also ensures that hydroxyls on the boehmite surface are condensed, eliminating water and fortifying the structure of MSU-B.

2.3.2. General Properties of MSU-B Aluminas

MSU-B aluminas were characterized by powder XRD, nitrogen adsorption, TEM, and ^{27}Al NMR. Figures 2.3 and 2.4 show the low angle and wide angle powder XRD patterns, respectively of as-synthesized MSU-S/B and MSU-B materials, prepared under conditions as described in Table 2.1, line 3. From peaks in the wide angle patterns it is evident that the alumina is present in the boehmite phase. This occurs invariably in all samples prepared in the method described above. However, while a low angle peak is observed for this sample, this is not always the case. As discussed in greater detail below, MSU-B materials derived from alkoxide are not formed through a true templating mechanism. Therefore, low angle peaks that are typically taken as evidence of mesophase formation due to pore-to-pore correlation distances in the synthesis of mesoporous materials cannot be relied upon here.

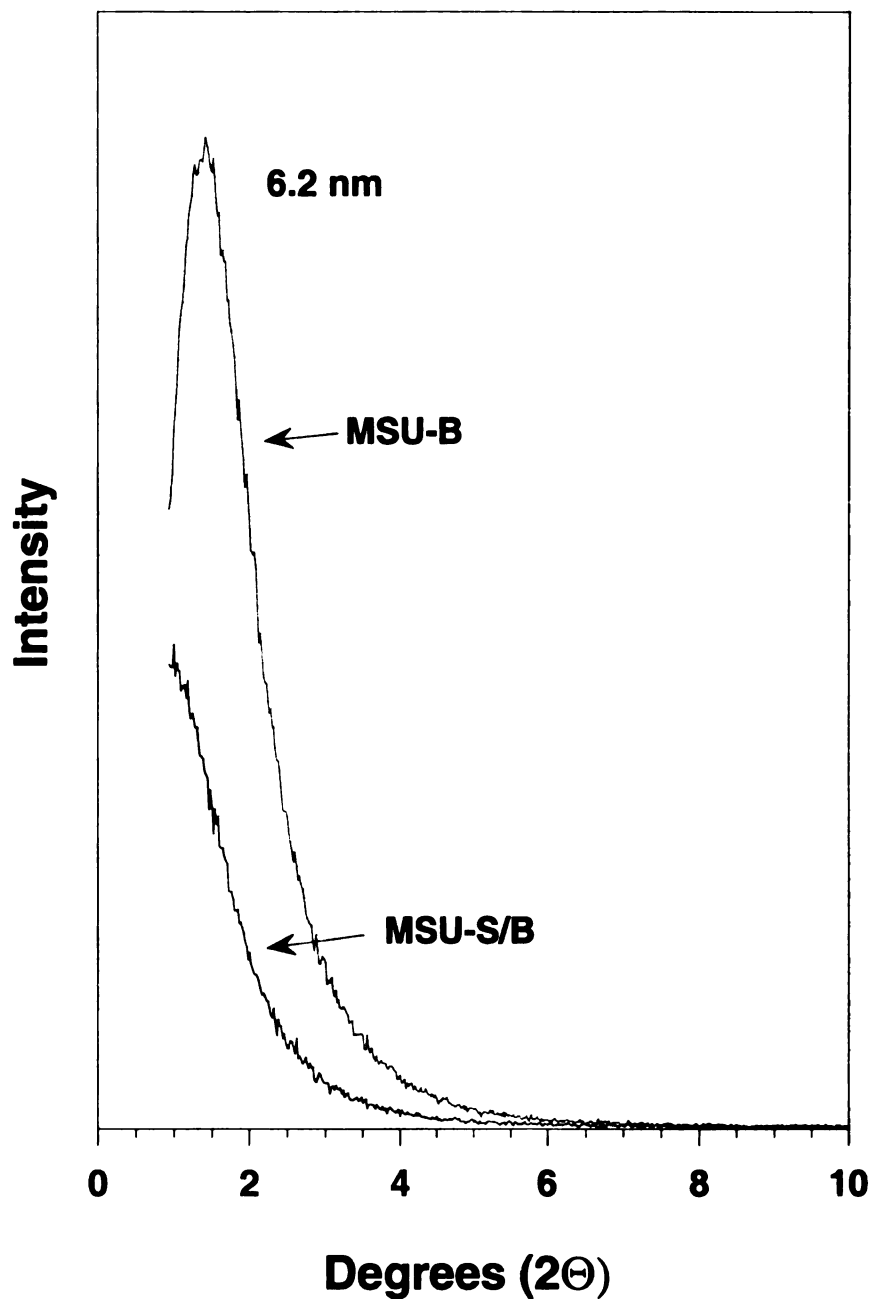


Figure 2.3. Representative low angle XRD patterns for the as-synthesized surfactant-boehmite composite, denoted MSU-S/B, prepared from aluminum sec-butoxide and dodecylamine in an alcoholic/aqueous medium as described by line 3 in Table 2.1 and the surfactant-free analog, MSU-B, obtained by calcination of the MSU-S/B composite at 325 °C for 10 hr.

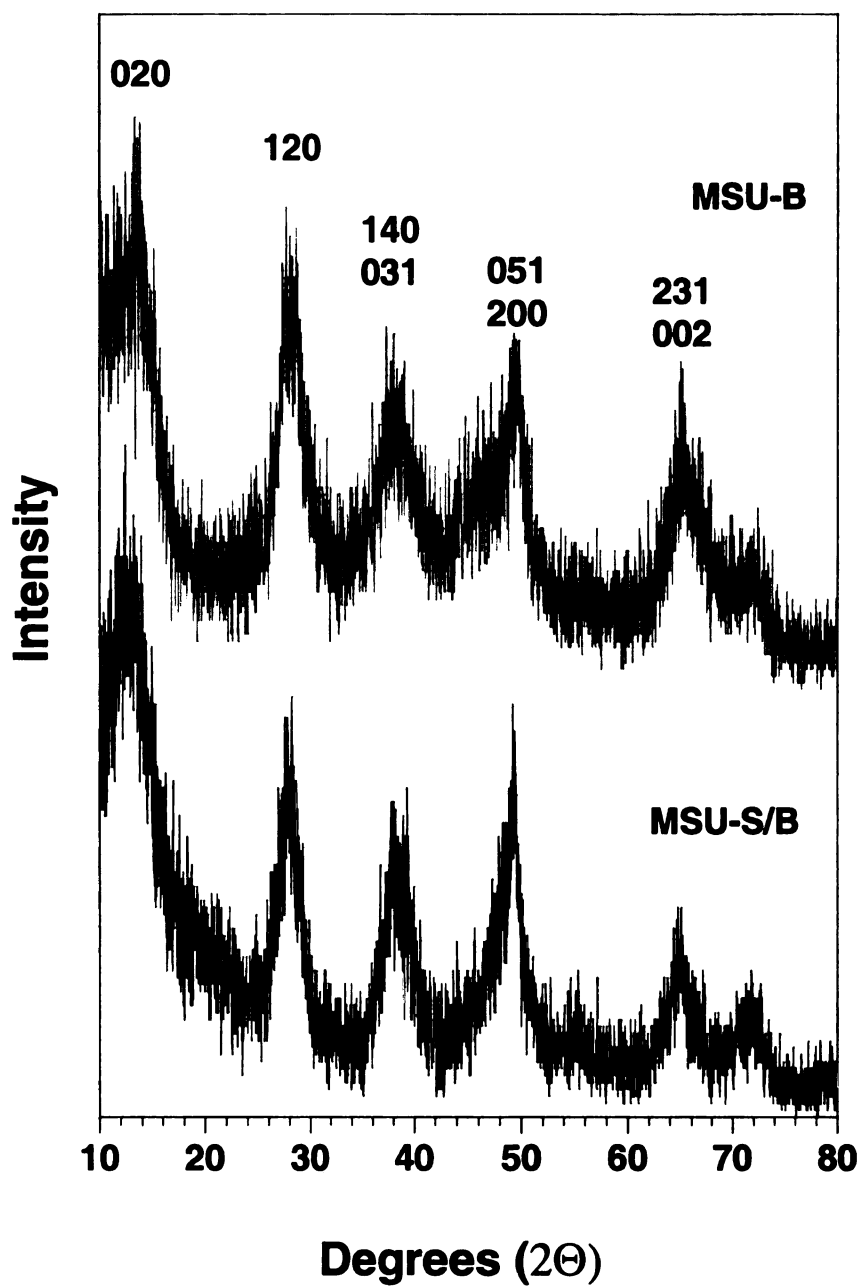


Figure 2.4. Representative wide angle XRD patterns for MSU-S/B and MSU-B aluminas shown in Figure 2.3. Crystallographic planes contributing to the peaks are noted.

In the particle assembly of these materials, the morphology of the oxide formed does not necessarily reflect the shape of the surfactant micelle. Rather, it is believed that a low angle peak, when observed, is due to the thickness of fundamental particles. While the observance of the peak itself is not always reproduced from one reaction product to another under identical reaction conditions, the d-spacings extracted from the peak position are not. The height of the boehmite double layer is approximately 12.2 Å. The recurring values of the observed d-spacings of calcined samples are approximately integer multiples of 12 Å. It appears that 5 – 7 double layers per particle is most common as suggested by the position of the low angle reflection that occurs most frequently at 2θ values corresponding to d-spacings of 60, 72, and 84 Å. There is more variance in the d-spacings of the MSU-S/B samples, but there may be some water or alcohol intercalated between the layers that causes the repeat distance to differ from that of the theoretical value of 12 Å.

The nitrogen adsorption – desorption isotherms of MSU-B materials are shown in Figure 2.5. These isotherms correspond to aluminas prepared with varying surfactant concentrations under conditions described in lines 3, 8, and 19 of Table 2.1. The isotherms for MSU-B most closely resemble the Type IV isotherm defined by Sing^{17,18} and associated with mesostructured materials. The lack of a well-defined step in the adsorption branch indicates that the pore size distributions are somewhat broad. This is in line with the particle assembly pathway leading to formation of the material. Although not well defined, the isotherms indicate that MSU-B materials have more uniform porosity as

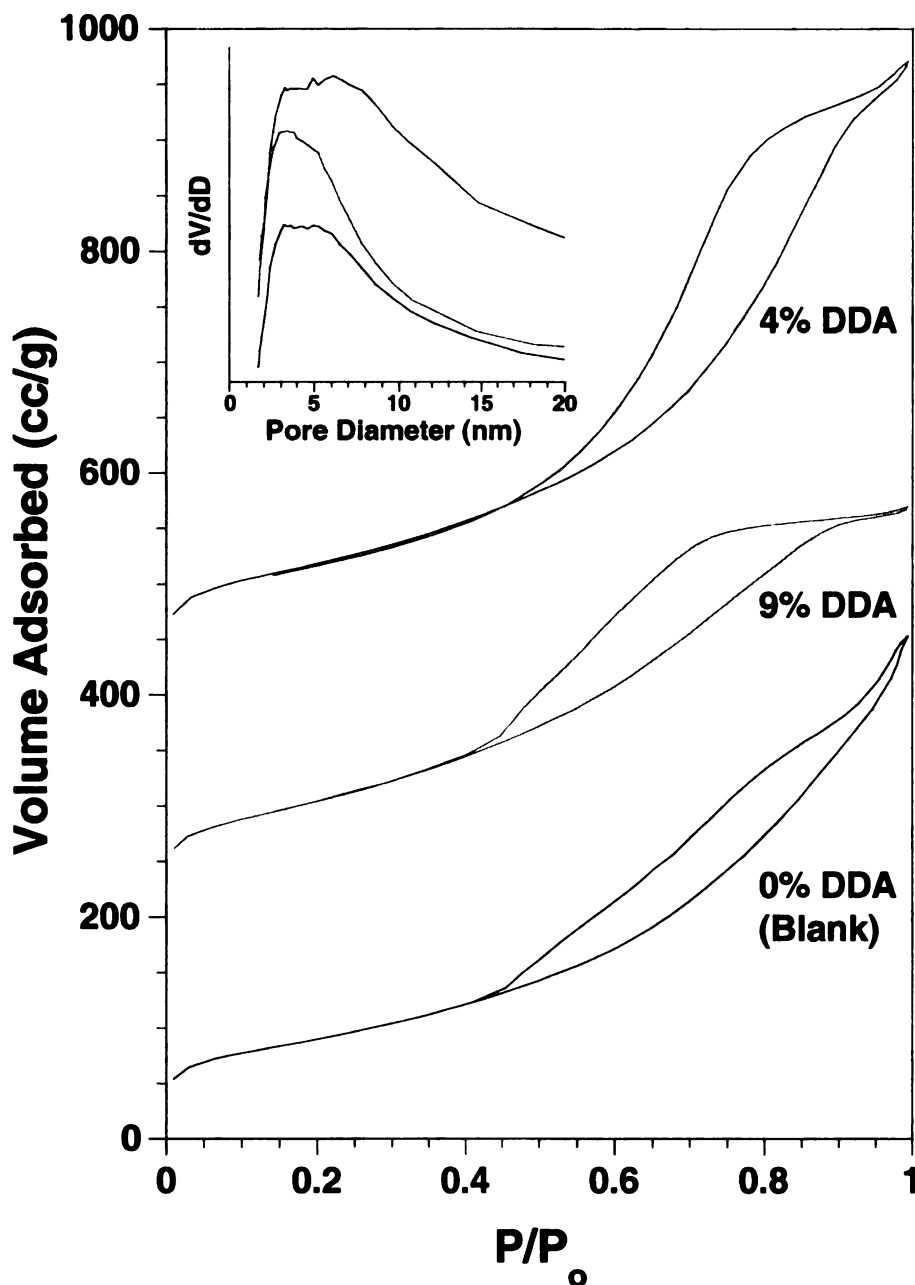


Figure 2.5. Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for MSU-B aluminas differing in surfactant concentration. The percentage given corresponds to the mass percent of dodecylamine in the surfactant solution. The three isotherms, offset by 200 cc/g for clarity, correspond from top to bottom to samples described in lines 3, 8, and 19 in Table 2.1. PSD curves are displayed in the same order as the isotherms.

Table 2.1. Synthetic parameters and textural properties of MSU-B aluminas.

	Surfactant ^a	Al/Surf/EtOH/H ₂ O Molar Ratio	Temp ^b (°C)	S _{BET} (m ² /g)	Pore Size ^c (nm)	Pore Volume (cc/g)
1	DDA	5 : 1 : 20.1 : 196	20	380	5	0.59
2	DDA	5 : 1 : 42.6 : 138	20	428	3	0.72
3	DDA	5 : 1 : 68.0 : 73.4	20	456	4.5	0.95
4	DDA	5 : 1 : 68.0 : 73.4	45	497	3.5	0.84
5	DDA	5 : 1 : 68.0 : 73.4	65	460	5	0.82
6	DDA	5 : 1 : 68.0 : 73.4	95	451	4	0.69
7	OA	5 : 1 : 20.0 : 21.6	20	325	5	0.47
8	DDA	5 : 1 : 28.7 : 31.0	20	378	3	0.59
9	HDA	5 : 1 : 37.4 : 40.4	20	391	3.5	0.59
10	Tal A	5 : 1 : 46.2 : 49.9	20	410	2.5	0.60
11	Tal TriA	5 : 1 : 64.0 : 69.0	20	429	2	0.60
12	Tal TetA	5 : 1 : 72.8 : 78.7	20	436	2.5	0.61
13	OA	2.2 : 1 : 20.0 : 21.6	20	452	5	0.81
14	DDA	3.1 : 1 : 20.0 : 21.6	20	418	5	0.63
15	HDA	4.0 : 1 : 20.0 : 21.6	20	434	3	0.64
16	Tal A	4.0 : 1 : 20.0 : 21.6	20	410	3	0.60
17	Tal TriA	5.9 : 1 : 20.0 : 21.6	20	462	3	0.63
18	Tal TetA	6.9 : 1 : 20.0 : 21.6	20	459	3	0.61
19	None	5 : 0 : 28.7 : 31.0	20	322	4	0.71

^a DDA = dodecylamine, OA = octylamine, HDA = hexadecylamine, Tal A = tallow amine, Tal TriA = tallow triamine, Tal TetA = tallow tetraamine

The tallow amine structure is generalized by the following formula:



Where R = a mixture of alkane groups ranging from C₁₂-C₁₈ and x = 0, 1, 2, or 3 for tallow amine, diamine, triamine, and tetraamine, respectively.

^b Ambient temperature taken as 20 °C

^c BJH pore diameter as measured from the adsorption branch

compared to the sample prepared without surfactant. The shape of the isotherm of the blank sample does not proceed through an inflection point at any partial pressure above 0.2. In this manner, its behavior most closely resembles a Type II isotherm, exhibited by non-porous materials.

A summary of textural properties of MSU-B aluminas is provided in Table 2.1. Included also are the textural properties for one sample prepared in absence of surfactant. From the data, it can be seen that surface areas of MSU-B aluminas in the approximate range of 380 – 460 m²/g, pore sizes 2.0 – 5.0 nm, and pore volumes 0.60 – 0.95 cc/g. Entries in lines 1-3 of the table correspond to samples in which the surfactant solution becomes higher in ethanol content. Based upon XRD evidence, more surfactant is incorporated into the mesostructure at higher ethanol content. Free surfactant peaks appear around 20 degrees 2 θ in the wide angle powder XRD patterns (not shown) of precipitates borne out of low ethanol content solvents. Judging by the textural properties of these samples, surface area, pore size, and pore volume all increase at higher ethanol content. The more surfactant incorporated into the mesostructure, the greater the void left upon its removal. The isotherms are provided in Figure 2.6.

The third through sixth entries in Table 2.1 are for samples of identical stoichiometry aged at different temperatures. Figure 2.7 provides the isotherms for these aluminas. While the surface areas seem random, both pore size and volume steadily decrease with an increase in aging temperature. At higher temperatures, less surfactant is incorporated into the mesostructure.

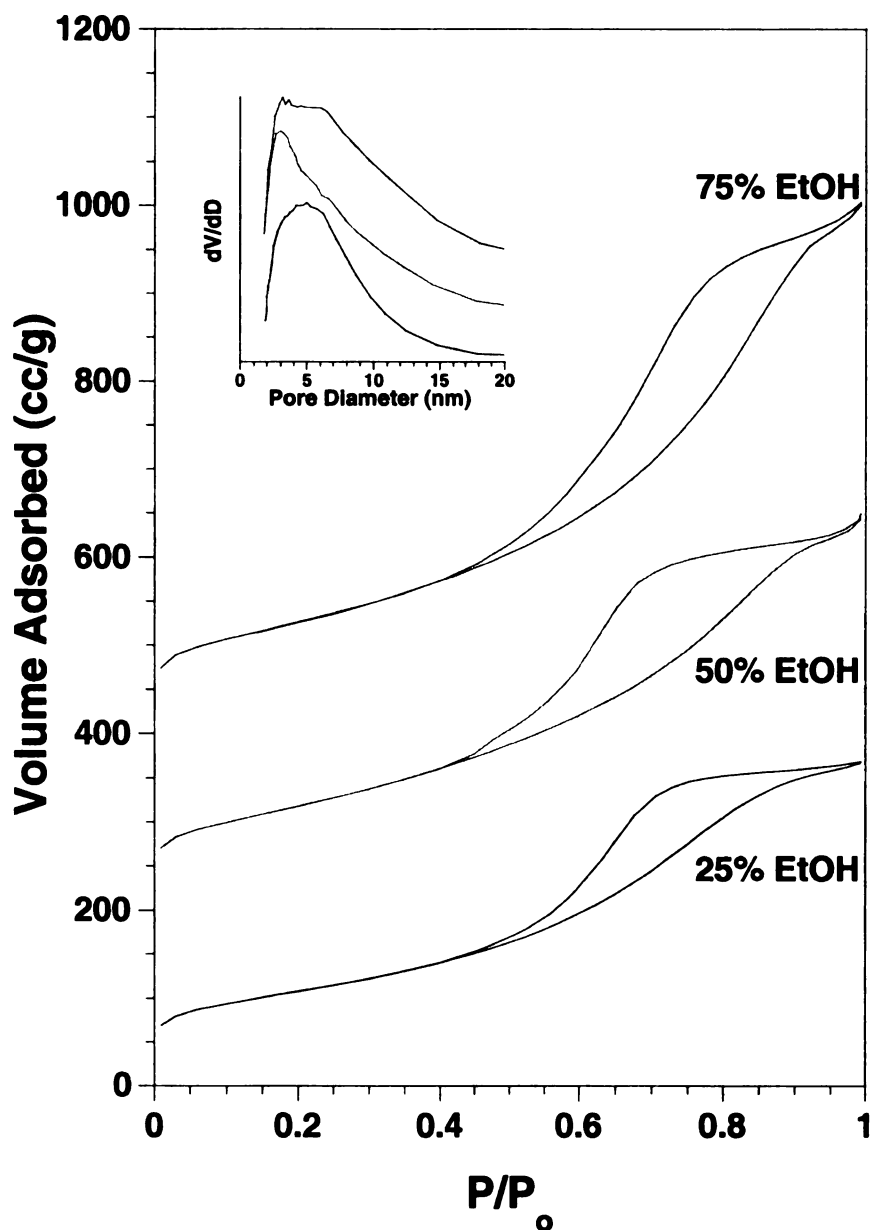


Figure 2.6. Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for MSU-B aluminas prepared from aluminum sec-butoxide and dodecylamine at ambient temperature in alcoholic/aqueous solvents of varying ethanol content. The three isotherms, offset by 200 cc/g for clarity, correspond to MSU-B aluminas described in lines 1-3 of Table 2.1. PSD curves are displayed in the same order as the isotherms.

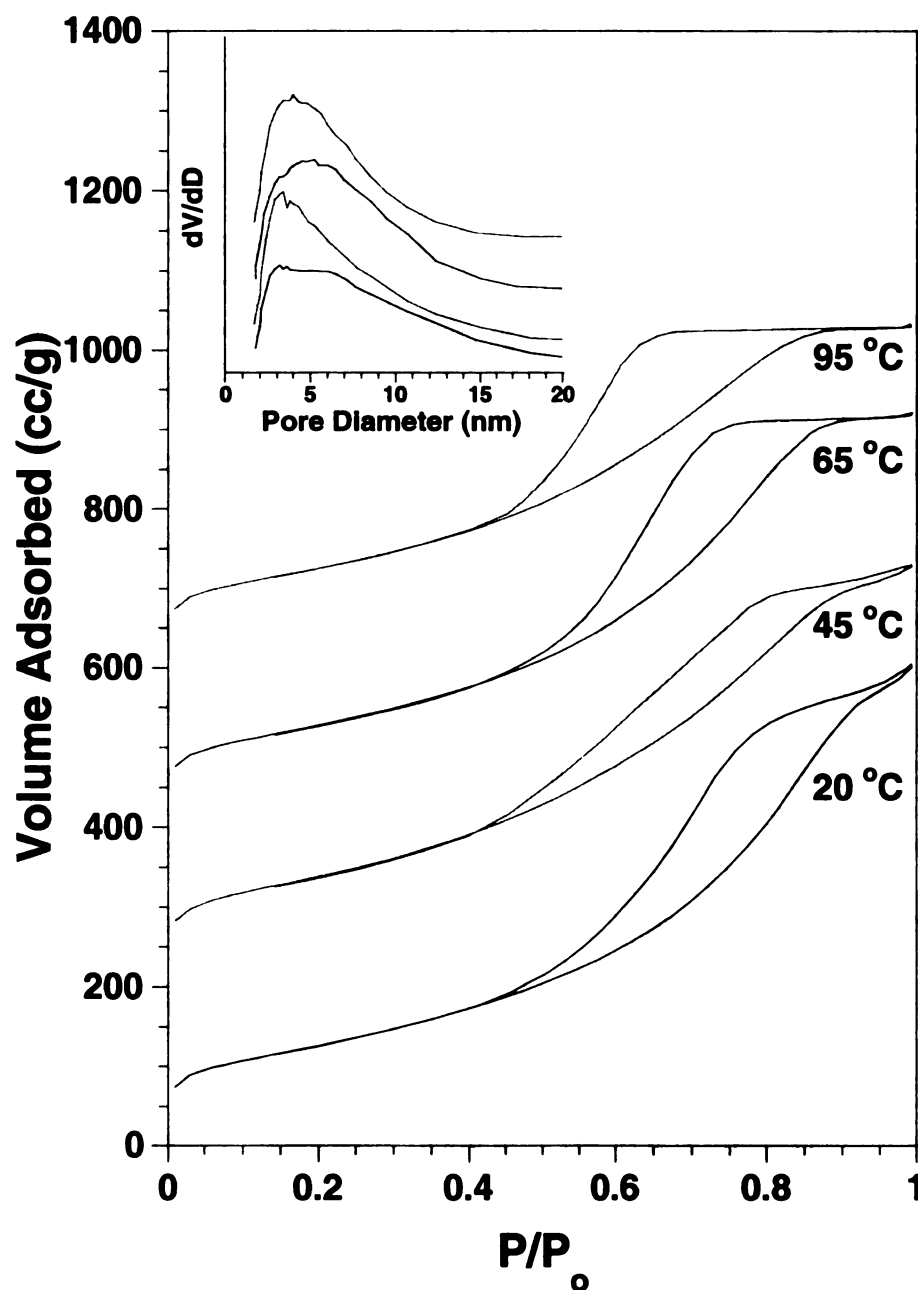


Figure 2.7. Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for MSU-B aluminas prepared from aluminum sec-butoxide and dodecylamine at different temperatures. The four isotherms, offset by 200 cc/g for clarity, correspond to MSU-B aluminas described in lines 3-6 of Table 2.1. PSD curves are displayed in the same order as the isotherms.

Filling of pores also occurs at lower partial pressures for products of higher temperature reactions, signifying larger particle growth.

Entries in lines 7-18 of Table 2.1 are for aluminas prepared from different amine surfactants under otherwise identical processing conditions. Nitrogen adsorption – desorption isotherms for these MSU-B samples are provided in Figure 2.8. The aluminum to surfactant molar ratio was held constant at 5:1 and the surfactant solution in each case was 9% by mass surfactant (lines 7-12). Then this series of experiments was repeated, maintaining a constant aluminum to surfactant mass ratio (lines 13-18). It is interesting that the pore size and pore volume are approximately constant regardless of the size, mass, or molar mass of the surfactant. The surface areas do vary, but not predictably. There is a steady increase with increasing surfactant size in the constant molar ratio products, but they do not correlate well with surfactant size in the latter case. In traditional templated syntheses, pore sizes and volumes increase with increasing size of the surfactant molecule. That the pore size remains nearly constant under a range of synthetic conditions gives support to a particle assembly mechanism.

The porosity of MSU-B boehmites arises from the voids between individual boehmite particles. As noted above, the pores of the oxide framework do not mimic the size or shape of the surfactant. So, although regular micelles may be formed, the boehmite particles may be ordered randomly about the micelles, leading to irregularly shaped pores. Again, noting the difference in these materials and silica materials prepared through supramolecular templating, there may be instances when the observed d-spacing is actually smaller than the

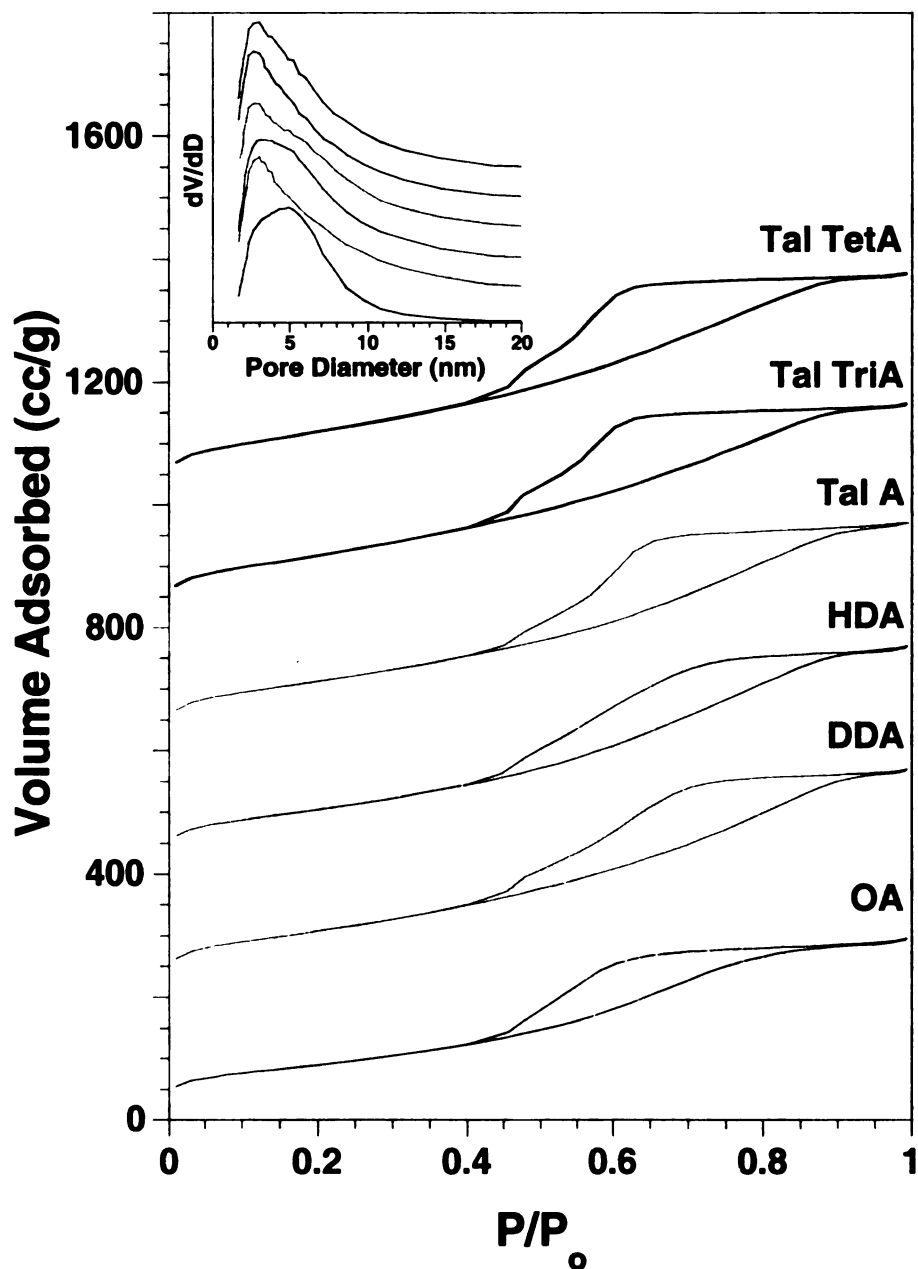


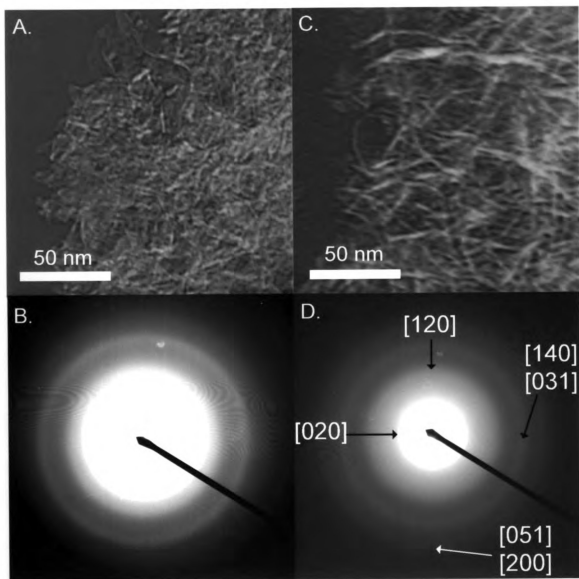
Figure 2.8. Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for MSU-B aluminas prepared from the hydrolysis of aluminum sec-butoxide in the presence of different amine surfactants as porogens. The six isotherms, offset by 200 cc/g for clarity, correspond to MSU-B aluminas described in lines 7-12 of Table 2.1. PSD curves are displayed in the same order as the isotherms.

average pore size. In materials prepared from templating synthesis, pore sizes are smaller than the d-spacings because the d-spacing is indicative of the repeat distance of both pore and framework wall. However, in MSU-B, the XRD peak is most likely due to the particle thickness and the pore size is due to void spaces, between particles. Therefore, the fact that the small angle XRD d-spacings do not correlate with the pore size is understandable.

The presence of a scaffold morphology was identified through TEM. Bright field images of representative MSU-B aluminas are shown in Figure 2.9. The open framework resulting from the random orientation of fundamental boehmite particles can be seen. It is estimated that average particle thickness in these samples is 3 – 7 nm. Electron diffraction patterns are also provided for these materials. The presence of diffuse rings confirms the polycrystalline nature of the materials. Many small crystals in all orientations give rise to the diffuse rings. This is in contrast to a single crystal that would show distinct points in the pattern. The patterns contain four rings containing the strongest reflections of boehmite.

^{27}Al NMR spectra were obtained to verify the coordination environment of the aluminum in MSU-B (Figure 2.10). ^{27}Al NMR chemical shifts are referenced to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, which is assigned a value of 0 ppm. Octahedral (6-coordinate), tetrahedral (4-coordinate), and 5-coordinate aluminum will have shifts of less than 10 ppm, 65 – 75 ppm, and approximately 35 ppm, respectively. In boehmite, all aluminum has octahedral coordination. The shift observed for MSU-B at 7 ppm is in agreement with a boehmite structure. The small peak coincident with

Figure 2.9. Bright field TEM images (A and C) and electron diffraction patterns (B and D) of MSU-B materials prepared from aluminum sec-butoxide and dodecylamine as described in Table 2.1, (A) line 8 and (B) line 3. The open framework results from the random orientations of fundamental particles. Electron diffraction patterns, (B) and (D), corresponding to bright field images (A) and (C), respectively show diffuse rings, signifying the polycrystalline nature of the material. The reflections contributing to the pattern are labeled in (D).



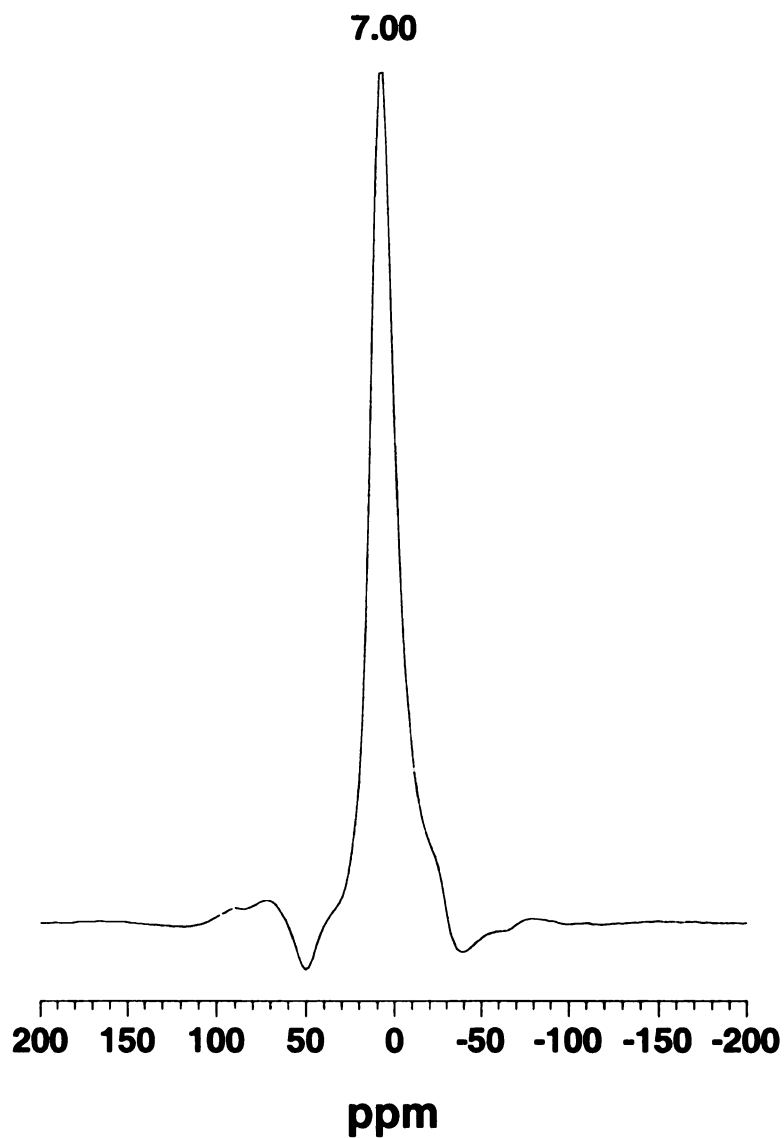


Figure 2.10. ^{27}Al NMR spectrum of MSU-B prepared from aluminum sec-butoxide and dodecylamine prepared as described in Table 2.1, line 3. The resonance at 7 ppm is consistent with the structure of boehmite, in which all aluminum ions are in octahedral environments.

the spinning sideband may signify a small amount of Al in a tetrahedral environment, possibly due to the onset of the boehmite to gamma alumina phase transition.

2.3.3. Peptization

Boehmite and pseudoboehmite can be differentiated from each other based upon their ability to be dispersed in dilute acidic solutions. The small particle size and high water content of pseudoboehmite will cause this form of boehmite to dissolve and form a sol in such solutions. This form of boehmite is said to be peptizable. Boehmite, on the other hand, does not behave in this manner. MSU-B materials were tested for peptizability to determine the identity of the oxidic framework in these materials.

Small amounts of as-synthesized MSU-S/B, calcined MSU-B, and ethanol extracted MSU-B materials were added to 0.05M HNO₃. In no instance did the materials peptize, as judged by the settling of the materials. It is possible that in the case of the as-synthesized samples, the presence of surfactant restricts access to the boehmite framework. If this is the case, then it cannot be concluded that the framework in the MSU-S/B materials is boehmite. However, after surfactant removal, neither calcined nor ethanol extracted MSU-B materials peptize, indicating that these surfactant free materials truly are boehmites.

The sample prepared without surfactant was also tested for peptizability. It was determined that the as-synthesized material is peptizable. That small particle pseudoboehmite is formed in this synthesis is not an unreasonable result when

the hypothesis that the presence of surfactant allows for particle growth is employed. After calcination, however, this product also does not peptize. Therefore it is believed that calcination leads to sintering and growth of the particles that governs the formation of boehmite as opposed to pseudoboehmite. Calcination may play a dual role in the synthesis of MSU-B. Not only does this lead to surfactant removal, but it also helps to ensure that boehmite is the phase that is formed.

2.4. Mechanistic Aspects of MSU-B Alumina Synthesis

Bagshaw and Pinnavaia first reported the synthesis of mesoporous alumina, named MSU-X alumina⁸. It was prepared using aluminum alkoxide and PEO surfactants, but under different synthetic parameters and calcination procedures than those used in the present work. In the MSU-X synthesis, the alkoxide to surfactant ratio is greater than the ratio used here and the two reagents are mixed homogeneously prior to the hydrolysis step. The amount of water used in the synthesis is considerably less as well. The addition of the water is done over a 10-minute period, after which the reaction mixture forms a gel. In the MSU-B synthesis, the alkoxide is added to an aqueous solution containing the surfactant. The rate of hydrolysis and precipitation in this procedure is faster and a precipitate rather than a gel is formed. Accordingly, the morphologies of the two aluminas afforded are different. Amorphous MSU-X exhibits a wormhole motif where the crystalline MSU-B has a scaffold morphology. It is believed that the faster hydrolysis and precipitation in the MSU-B reactions are responsible for the

difference in morphology. In the MSU-B synthesis, boehmite particles are formed first. These particles are directed to form a mesostructure and hydroxyls between individual boehmite particles are condensed upon calcination, leading to the scaffold structure. In this manner, the surfactant is not used as a rigid template, but as a generic porogen used to impart increased porosity and surface area to the alumina. Under the controlled hydrolysis procedure used in the MSU-X synthesis, alkoxide molecules have time to interact with the surfactant molecules prior to hydrolysis, allowing for the formation of the amorphous wormhole structure. In this manner, the formation of MSU-X can be considered a templating mechanism whereas the formation of MSU-B is governed by a particle assembly mechanism. Particle assembly syntheses leading to other mesostructured oxides have been reported, including SnO_2 ¹⁹, ZrO_2 ²⁰, and mixed metal oxides²¹.

In the synthesis of mesostructured $\gamma\text{-Al}_2\text{O}_3$ from aluminum salt precursors, it is believed that the alumina phase first formed has amorphous framework walls like MSU-X, which are converted to the crystalline boehmite walls of MSU-S/B upon thermal aging²². However, in the syntheses of MSU-S/B from aluminum alkoxide as reported here, no evidence exists to support such a claim. Inspection of the wide angle powder XRD patterns of the MSU-S/B shows that at least in a disordered state, formation of a boehmite phase occurs in the first minute after addition of the alkoxide to the surfactant solution. Within 4 hours, the boehmite phase is well organized and within 12 – 24 hours, the reaction and condensation is complete, as shown in Figure 2.11.

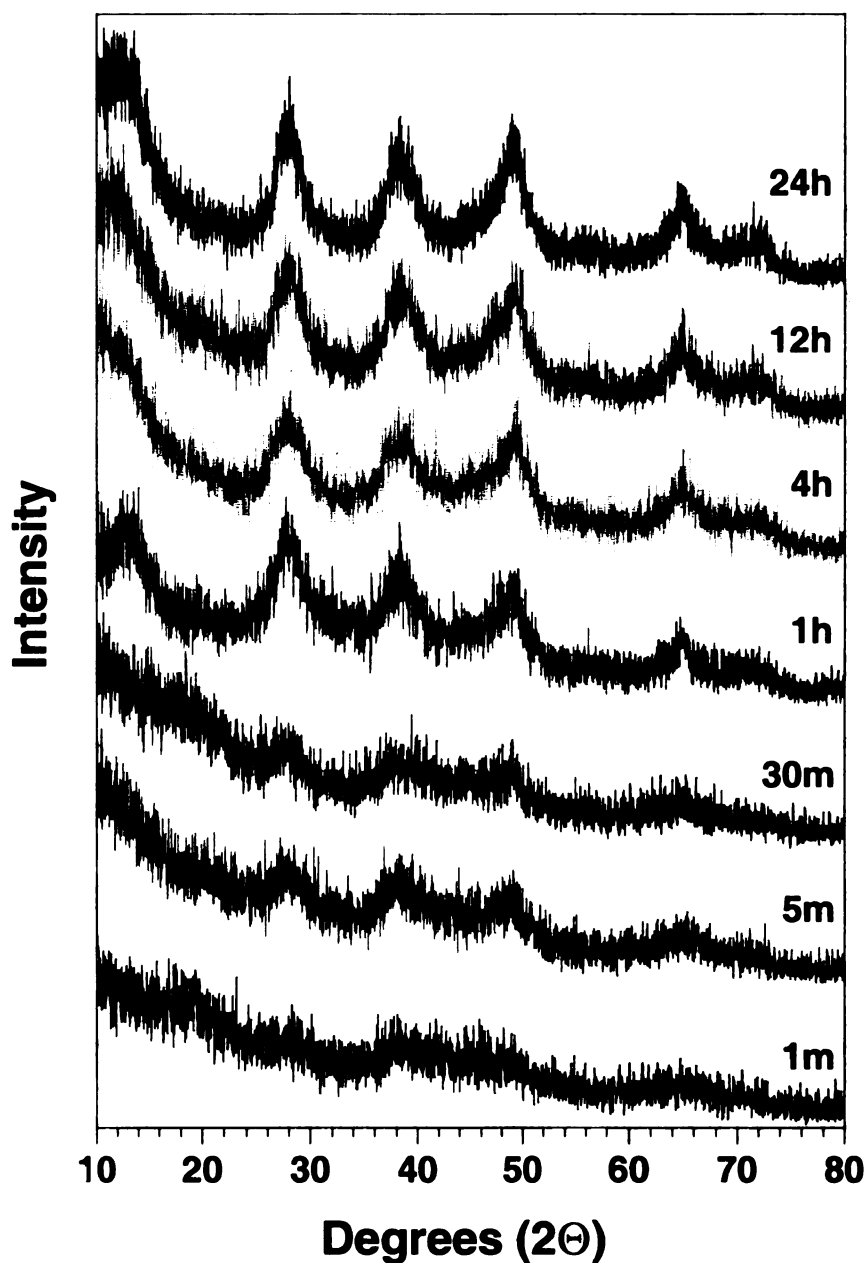


Figure 2.11. Wide angle XRD patterns of MSU-S/B prepared from aluminum sec-butoxide and dodecylamine at 20 °C showing evolution of the boehmite phase over time. The presence of weak reflections assignable to boehmite after only 1 minute show that the formation of MSU-B does not proceed through an MSU-X type of intermediate with amorphous framework walls.

2.5. Conclusions

Reported here is what is believed to be the first mesostructured boehmite material, MSU-B, prepared from the hydrolysis of aluminum sec-butoxide in the presence of amine surfactants as porogens. The key in the synthesis strategy is the formation of the MSU-S/B surfactant/boehmite precursor using surfactants that are easily vaporized at low temperature calcination. It has been shown that these materials are synthesized through a particle assembly pathway as opposed to the templating mechanisms often used in the preparation of mesostructured materials. Additionally, an MSU-X intermediate is not formed, as boehmite is precipitated immediately. This affords products having a scaffold morphology with an open framework comprised of boehmite walls. This open framework allows for the realization of materials having surface areas of up to 497 m²/g, pore sizes of up to 6.8 nm, and pore volumes of up to 0.95 cc/g. The materials are stable to calcination at 350 °C without conversion of boehmite to transition alumina phases. Although surfactant can be removed by ethanol extraction, calcination is the preferred method as it ensures that the inorganic framework is boehmitic in nature. Further evidence that the MSU-B materials consist of walls of the boehmite phase was provided from the lack of the ability to peptize these materials.

The textural properties of MSU-B materials could be controlled only slightly by altering the synthesis parameters. Increasing the mass of surfactant used in the surfactant solution leads to increased surface areas and pore volumes. Surface areas are relatively independent of the reaction temperature, but pore volumes

decrease with increasing temperature, signifying that less surfactant is incorporated into the framework at higher temperatures. At a constant aluminum to surfactant molar or mass ratio, however, increasing the surfactant size does not correlate to an increase in pore size or volume. In fact, pore volumes and pore sizes remain nearly constant over this series of experiments.

The textural properties of MSU-S/B materials are not controlled by surfactant size. Also, the mass of surfactant used in any given synthesis does not match the observed pore volume of the surfactant free product. Additionally, the peak in the low angle region of the powder XRD patterns is not reproducible. From these observations, it is concluded that MSU-S/B surfactant-boehmite compositions are formed through a particle assembly pathway rather than a supramolecular templating pathway.

2.6. Future Directions

Pseudoboehmite is actually the industrially preferred form of the aluminum oxide hydroxide because it is conveniently dispersed into a sol and easily introduced into other formulations or used in other applications. While the present work has focused on the synthesis of boehmite and avoidance of pseudoboehmite, a method to produce pseudoboehmite from a less expensive precursor would be of considerable interest. Similarly, it would be interesting to synthesize MSU-B materials from other aluminum sources as well.

Although pseudoboehmite can be formed without the aid of a surfactant, it would interesting to know if a mesostructured (pseudo)boehmite sol could be

prepared. Another application of pseudoboehmite is that of a vaccine adjuvant²³. A mesostructured sol may provide for increased loading of vaccine, effectively lowering the amount of aluminum administered per dose.

Boehmites are more often used as precursors to catalysts than as catalysts themselves. Finding suitable catalytic applications for MSU-B would be a logical direction in which to proceed. Since these materials are stable only under relatively lower temperatures, they may be of utility as catalyst supports for organic conversions under mild conditions.

There also exists another aluminum oxide hydroxide, α -AlOOH, diaspore. This polymorph is formed at high temperatures and under high pressures. If it is feasible to form a mesostructured diaspore, then this would also be of great interest. Because diaspore is structurally similar to α -Al₂O₃, corundum, it is converted directly to corundum at 550 °C. Prepared from other aluminas, temperatures in excess of 1000 °C are required for this transformation. Thus a mesostructured diaspore may lead to a mesostructured α -Al₂O₃ phase with significantly improved textural properties.

Finally, while the target of the syntheses described in this work was mesostructured boehmite, it is possible to calcine MSU-S/B (and MSU-B) materials at elevated temperatures, converting them to mesostructured γ -Al₂O₃. This is one of the synthetic approaches discussed in the following chapter.

2.7. References

- (1) Misra, C. *American Chemical Society Monograph, Vol. 184: Industrial Alumina Chemicals*, 1986.
- (2) Stamires, D.; Brady, M. F.; Jones, W.; Kooli, F. In *U.S.*; (Akzo Nobel N.V., Neth.). Us, 2002, pp 12 pp., Cont.-in-part of U.S. Ser. No. 21,839, abandoned.
- (3) Callender, R. L.; Harlan, C. J.; Shapiro, N. M.; Jones, C. D.; Callahan, D. L.; Weisner, M. R.; MacQueen, D. B.; Cook, R.; Barron, A. R. *Chemistry of Materials* **1997**, *9*, 2418-2433.
- (4) Wefers, K.; Misra, C. "Oxides and Hydroxides of Aluminum," Alcoa Laboratories, 1987.
- (5) Yoldas, B. E. *Am. Ceram. Soc., Bull.* **1975**, *54*, 289-290.
- (6) Baker, B. R.; Pearson, R. M. *J. Catal.* **1974**, *33*, 265-278.
- (7) Guzman-Castillo, M. L.; Bokhimi, X.; Toledo-Antonio, A.; Salmones-Blasquez, J.; Hernandez-Beltran, F. *Journal of Physical Chemistry B* **2001**, *105*, 2099-2106.
- (8) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1102-1105.
- (9) Vaudry, F.; Khodabandeh, S.; Davis, M. E. *Chem. Mater.* **1996**, *8*, 1451-1464.
- (10) Yada, M.; Kijima, T. *Zeoraito* **1997**, *14*, 104-111.
- (11) Valange, S.; Guth, J. L.; Gabelica, Z. *Stud. Surf. Sci. Catal.* **1998**, *117*, 517-518.
- (12) Cabrera, S.; El Haskouri, J.; Alamo, J.; Beltran, A.; Beltran, D.; Mendioroz, S.; Marcos, M. D.; Amoros, P. *Adv. Mater. (Weinheim, Ger.)* **1999**, *11*, 379-381.
- (13) Gonzalez-Pena, V.; Diaz, I.; Marquez-Alvarez, C.; Sastre, E.; Perez-Pariente, J. *Microporous Mesoporous Mater.* **2001**, *44-45*, 203-210.
- (14) Zhang, Z.; Hicks, R. W.; Pauly, T. R.; Pinnavaia, T. J. *Journal of the American Chemical Society* **2002**, *124*, 1592-1593.

- (15) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309-319.
- (16) Barrett, E. P.; Joyner, L. G.; Halender, P. P. *Journal of the American Chemical Society* **1951**, *73*, 373.
- (17) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603-619.
- (18) Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids*; Academic Press: London, 1999.
- (19) Severin, K. G.; Abdel-Fattah, T. M.; Pinnavaia, T. J. *Chemical Communications (Cambridge)* **1998**, 1471-1472.
- (20) Pacheco, G.; Zhao, E.; Garcia, A.; Sklyarov, A.; Fripiat, J. J. *Journal of Materials Chemistry* **1998**, *8*, 219-226.
- (21) Wong, M. S.; Jeng, E. S.; Ying, J. Y. *Nano Letters* **2001**, *1*, 637-642.
- (22) Zhang, Z.; Pinnavaia, T. J. *Journal of the American Chemical Society* **2002**, *submitted*.
- (23) Hem, S. L.; White, J. L. *PHARMACEUTICAL BIOTECHNOLOGY FIELD* **1995**, *6*, 249-276.

Chapter 3

Synthesis and Characterization of Mesostructured $\gamma\text{-Al}_2\text{O}_3$

3.1. Introduction

Transition aluminas are disordered crystalline phases formed through the thermal dehydration of aluminum hydroxides and oxyhydroxides¹. These oxides are used as adsorbents and catalysts or catalyst supports in many chemical processes, including the cracking, hydrocracking, and hydrodesulfurization of petroleum feed stocks². At least seven transition aluminas have been reported. Of these, $\gamma\text{-Al}_2\text{O}_3$ is perhaps the most important for catalytic applications. The utility of $\gamma\text{-Al}_2\text{O}_3$, as well as other transition aluminas, can be traced to a favorable combination of textural properties (i.e., surface area, pore volume and pore size) and acid - base characteristics.

The structure of $\gamma\text{-Al}_2\text{O}_3$ is based on that of a tetragonally distorted defect spinel (MgAl_2O_4) structure. The unit cell of spinel contains 8 formula units. The 32 oxygen atoms are arranged in a cubic close packed lattice. In spinel, the 8 aluminum ions occupy octahedral positions and the 8 magnesium ions occupy tetrahedral positions. The presence of trivalent aluminum ions (in $\gamma\text{-Al}_2\text{O}_3$) in lieu of divalent magnesium ions (in spinel) necessitates that only $5\frac{1}{3}$ of the original 8 tetrahedral sites be occupied per unit cell in the $\gamma\text{-Al}_2\text{O}_3$ structure. Overall, the ratio of the number of aluminum ions in octahedral to tetrahedral sites is 3:1.

Recently, density functional theory calculations have revealed the presence of hydrogen in the spinel lattice of $\gamma\text{-Al}_2\text{O}_3$ ³.

The $\gamma\text{-Al}_2\text{O}_3$ phase is formed upon the dehydration of the aluminum oxidehydroxide boehmite at temperatures ranging from 400 to 700 °C. During this process, porosity is generated as water is eliminated from the structure, creating cracks and void space in the alumina. Along the progression from hydroxide phases to oxide phases, there is an initial rise in surface area and porosity. However, heating at temperatures above 500 °C leads to diminished textural properties. Conventional forms of $\gamma\text{-Al}_2\text{O}_3$ typically exhibit a BET surface area below 250 m²/g and a pore volume less than 0.50 cc/g². The properties of $\gamma\text{-Al}_2\text{O}_3$ for applications in catalysis and adsorption are determined in large part by these textural parameters.

In view of the recent advancements realized for mesostructured forms of silicas^{4,5}, similar improvements may be anticipated in the properties of mesostructured aluminas. However, comparatively limited progress has been made in this area. Since Bagshaw's initial disclosure of the supramolecular synthesis of mesostructured alumina from aluminum alkoxides and PEO surfactants⁶, others have synthesized similar materials using both ionic⁷⁻⁹ and non-ionic^{10,11} surfactants as structure directors. A common feature of all these mesostructured aluminas is the amorphous framework walls that limit their thermal and hydrothermal stability, greatly compromising their usefulness in potential catalytic applications. Recently, a mesostructured alumina containing a transition alumina phase has been reported¹². However, the true composition of

this material remains unclear without evidence of a boehmite precursor, which, as described below, is the crucial step leading to the formation of mesostructured γ -Al₂O₃.

This work reports on the synthesis, characterization, and stability of crystalline mesostructured γ -aluminas prepared from the hydrolysis of aluminum sec-butoxide in the presence of either PEO or amine surfactants as porogens. The novelty of the synthesis is the resulting formation of a mesostructured surfactant-boehmite composition, denoted MSU-S/B. Upon thermal transformation, MSU-S/B is converted to crystalline, mesostructured γ -Al₂O₃, denoted MSU- γ . It will be demonstrated that these materials are structurally stable and afford textural properties exceeding those of conventional transition aluminas.

3.2. Experimental

3.2.1. Synthesis

The assembly of the MSU-S/B surfactant-boehmite mesostructure was achieved by hydrolysis of aluminum sec-butoxide in an alcoholic aqueous solution of the desired surfactant. Syntheses could be performed over a wide range of reaction conditions. Two general routes to mesostructured γ -Al₂O₃ are identified in sections 3.2.1.1 and 3.2.1.2 below. The surfactants selected for study are as follows:

<u>Surfactant</u>	<u>Formula</u>
Pluronic P84	$(\text{EO})_{19}(\text{PO})_{39}(\text{EO})_{19}$
Pluronic P65	$(\text{EO})_{19}(\text{PO})_{30}(\text{EO})_{19}$
Pluronic L64	$(\text{EO})_{13}(\text{PO})_{30}(\text{EO})_{13}$
Pluronic L61	$(\text{EO})_2(\text{PO})_{30}(\text{EO})_2$
Tergitol 15-S-9	$\text{C}_7\text{H}_{15}\text{CH}_2((\text{EO})_9\text{OH})\text{C}_7\text{H}_{15}$
Tergitol 15-S-12	$\text{C}_7\text{H}_{15}\text{CH}_2((\text{EO})_{12}\text{OH})\text{C}_7\text{H}_{15}$

3.2.1.1. Synthesis from PEO Surfactants

A typical MSU- γ synthesis using a PEO surfactant as a porogen was carried out as follows. Pluronic P84 and aluminum sec-butoxide were dissolved in 2-butanol. To this solution water was added to hydrolyze the alkoxide. The solution was stirred on a magnetic stirrer until homogenous, sealed in a glass vessel, and placed in a 100 °C oven under static conditions for a period of ~20 hours. The resulting MSU-S/B was recovered by vacuum filtration, washed with 2-butanol and water, and air dried. Conversion to MSU- γ was achieved by calcining the as-synthesized MSU-S/B at 500 °C for 4 hours. Alternatively, during the synthesis, the water, alcohol, and surfactant could be mixed first, adding the alkoxide last. Reaction mixtures in syntheses involving lesser amounts of solvent would become quite thick. In these instances, a laboratory grade blender was used to mix the reactants.

3.2.1.2. Synthesis from Amine Surfactants and MSU-B Materials

A second method used to synthesize MSU- γ materials is to calcine either the MSU-S/B surfactant-boehmite compositions made from amine surfactants or surfactant free MSU-B boehmites, described in the previous chapter, at temperatures ~ 500 °C. Both methods afford mesostructured MSU- γ aluminas.

3.2.1.3. Synthesis of Doped MSU- γ Aluminas

MSU- γ aluminas were also doped with metal ions. In these syntheses, the desired amount of dopant was administered as a salt which was dissolved in the 2-butanol and water surfactant solution. $\text{La}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ were used to supply La and Ce, respectively, in the doping reactions. The processing of the reaction mixtures was performed as described in section 3.2.1.1 above.

3.2.2. Characterization of MSU- γ Aluminas

Powder diffraction patterns were collected on a Rigaku Rotoflex Diffractometer using Cu K_α radiation ($\lambda = 0.154$ nm). Intensity was calculated in counts per second every 0.02 degrees 2θ . Sweep rates were varied from 2 – 8 degrees $2\theta/\text{min}$.

Nitrogen adsorption – desorption isotherms were collected on a Micromeritics TriStar 3000 sorptometer at 77K. Samples were degassed at least 12 hours at 150 °C under a vacuum of 10^{-6} torr prior to analysis. Surface areas and pore sizes were determined by the BET¹³ and BJH¹⁴ methods, respectively.

TEM images were collected on a JEOL 100CX microscope with a CeB₆ filament at an accelerating voltage of 120 kV. Samples were prepared by sonicating a suspension of the powder in ethanol for 20 min. One to two drops of the suspension were then placed on a carbon coated holey film that was supported on a 3mm, 300 mesh copper grid.

²⁷Al NMR spectra were collected on a Varian 400 VRX solid – state NMR spectrometer. Samples were placed in a zirconia rotor and spun at 4 kHz with a pulse width of 0.5 μs and a pulse delay of 0.5 s. Chemical shifts were referenced to Al(H₂O)₆³⁺ which is assigned a value of 0 ppm.

Steam testing was performed by passing 20% H₂O in nitrogen over the alumina at 600 °C for 5 hours. Exposed aluminas were air dried before further analysis.

3.3 Results and Discussion

3.3.1. MSU-γ Aluminas from PEO Surfactants

3.3.1.1. General Properties of Materials

Representative wide angle powder XRD patterns of an as-synthesized MSU-S/B surfactant-boehmite composition made from aluminum sec-butoxide and P84 and the corresponding MSU-γ alumina are presented in Figure 3.1. In the case of these materials, peaks assignable to boehmite and γ-Al₂O₃ for MSU-S/B and MSU-γ, respectively, are evident. As was the case for the surfactant-free MSU-B boehmite materials described in the previous chapter, a low angle diffraction

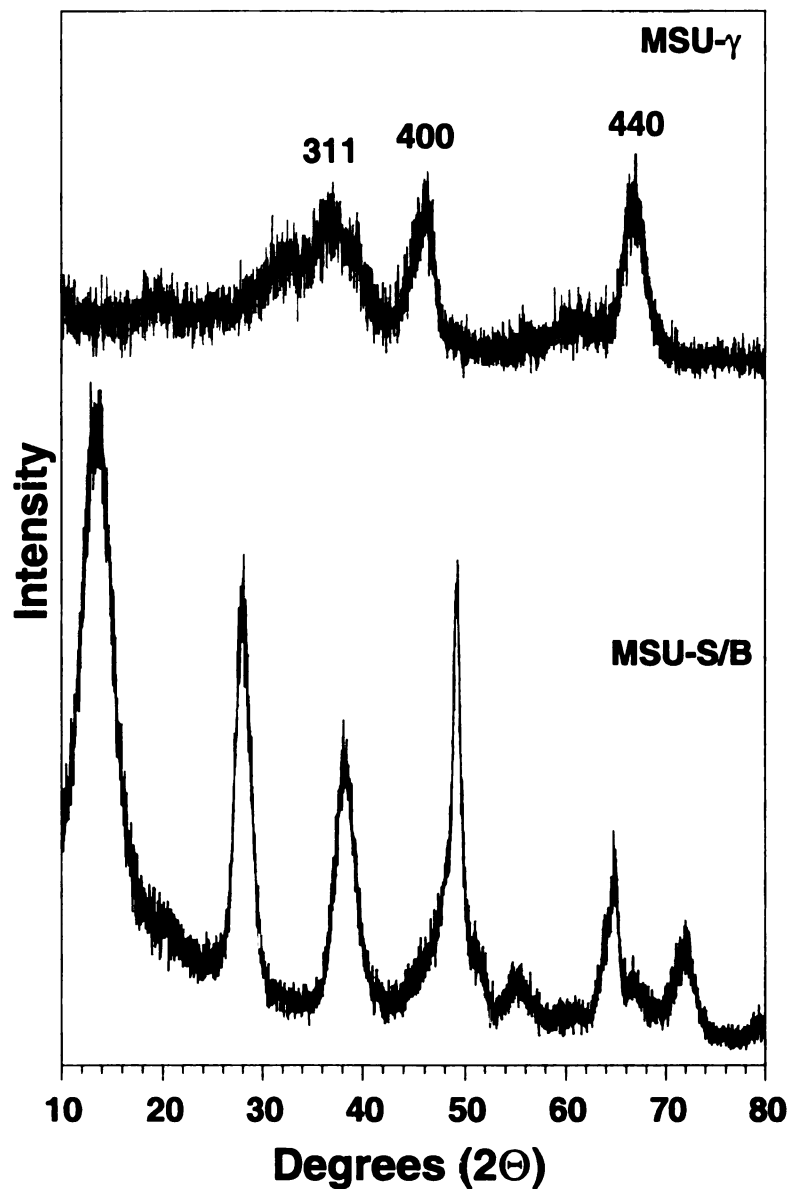


Figure 3.1. Representative wide angle powder XRD patterns of an MSU-S/B surfactant-boehmite composition made from aluminum sec-butoxide and the PEO surfactant P84 under reaction conditions described in Table 3.1, line 3 and the corresponding MSU- γ alumina prepared from calcination of the as-synthesized MSU-S/B at 500 °C for 4 hr.

peak in the XRD patterns was not always observed. However, when low angle peaks were observed, the d-spacings of these peaks have recurring values in multiples of ~ 8 Å. The most common values, 48 and 56 Å, correspond to an average of 6 to 7 building units in the particle.

Nitrogen adsorption – desorption isotherms and pore size distributions of a representative MSU- γ alumina and a similar alumina prepared without surfactant (blank) are shown in Figure 3.2. It can be seen that the pore volume and pore size are increased in the MSU- γ as compared to the material prepared in absence of surfactant. Porosity in conventional γ -Al₂O₃ is generated as cracks and voids form upon the dehydration of the oxidehydroxide precursor, so it is reasonable to expect some adsorption in the blank sample. However, use of surfactants as porogens imparts considerably larger pore volumes and sizes, as is reflected in the isotherms. Typical surface areas, pore sizes, and pore volumes for MSU- γ aluminas range from 300 – 380 m²/g, 10 – 20 nm, and 0.75 – 1.6 cc/g, respectively. These same values for the blank sample are 259 m²/g, 5 nm, and 0.47 cc/g, which are in line with those expected for textural properties of conventional γ -aluminas. The textural properties of these materials made from PEO surfactants are summarized in Table 3.1.

In addition to the XRD data, further evidence of the presence of γ -Al₂O₃ in the framework walls was provided by the ²⁷Al NMR spectrum of MSU- γ . As described in section 3.1, the unit cell of γ -Al₂O₃ contains aluminum ions in both octahedral and tetrahedral coordination, in a ratio of 3:1. Accordingly, ²⁷Al NMR spectra of γ -Al₂O₃ show peaks consistent with this distribution of aluminum ions¹⁵.

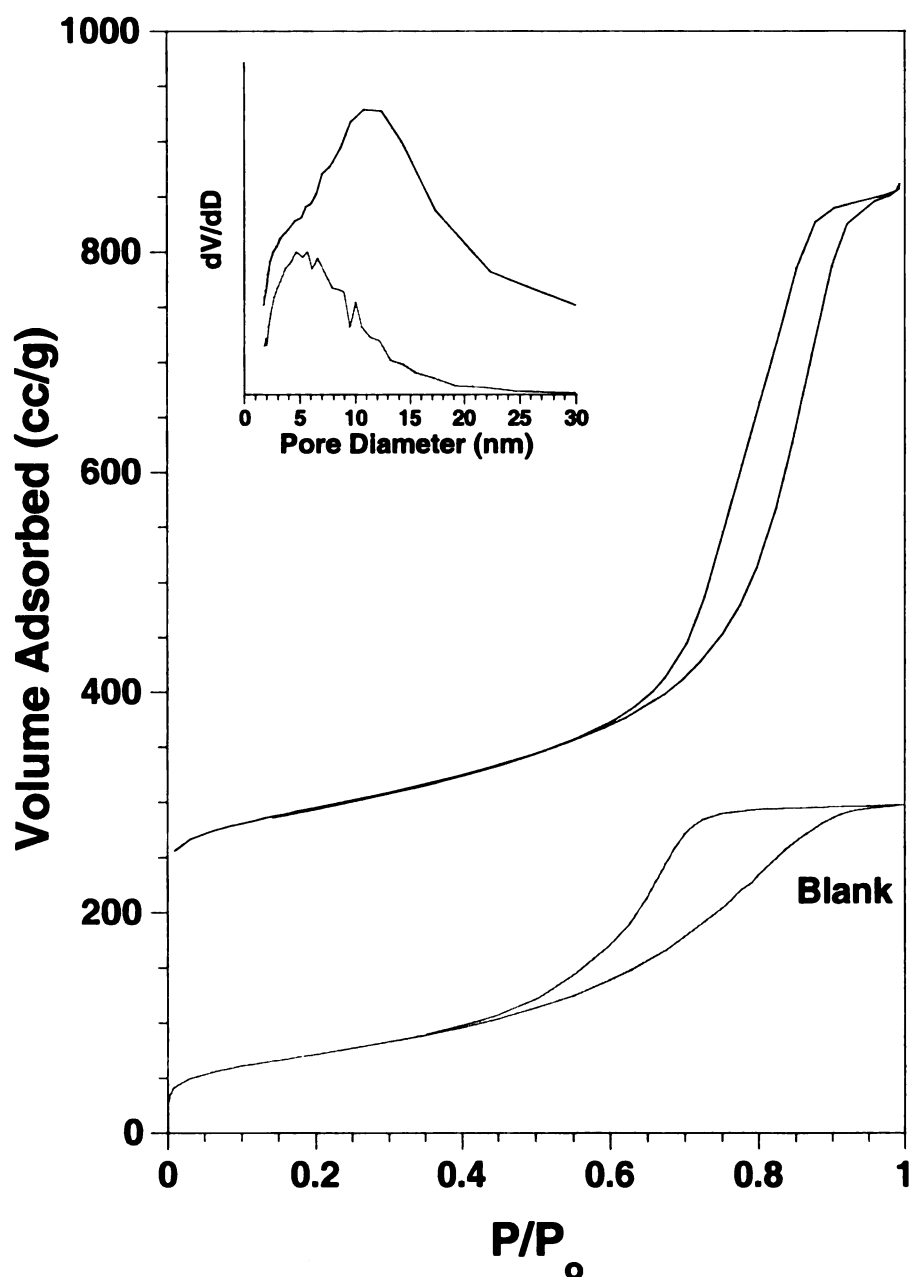


Figure 3.2. Nitrogen adsorption-desorption isotherm and BJH adsorption pore size distribution (inset) of an MSU- γ alumina prepared from aluminum sec-butoxide and the PEO surfactant P84 as described in Table 3.1, line 3. Included for comparison is the same data for an alumina prepared without surfactant as described in Table 3.1, line 20. Isotherms are offset 200 cc/g for clarity and PSD curves are displayed in the same order as the isotherms.

Table 3.1. Synthetic parameters and textural properties of MSU- γ aluminas prepared from aluminum sec-butoxide and PEO surfactants.

	Surfactant	Al/Surf/s-BuOH/H ₂ O Molar Ratio ^a	S _{BET} (m ² /g)	Pore Size ^b (nm)	Pore Volume (cc/g)
1	P84	100 : 1 : 27 : 544	334	15	1.17
2	P84	75 : 1 : 27 : 544	332	17	1.23
3	P84	66 : 1 : 27 : 544	378	13	1.09
4	P84	50 : 1 : 27 : 544	365	15	1.25
5	P84	25 : 1 : 27 : 544	366	17	1.39
6	P84	66 : 1 : 249 : 544	339	10	0.76
7	P84	66 : 1 : 160 : 544	341	13	0.93
8	P84	66 : 1 : 107 : 544	381	4, 17	0.84
3	P84	66 : 1 : 27 : 544	378	13	1.09
9	P84	66 : 1 : 12 : 544	342	14	1.06
10	P84	66 : 1 : 0 : 544	325	10	0.92
3	P84	66 : 1 : 27 : 544	378	13	1.09
11	P84	66 : 1 : 46 : 933	355	11	1.14
12	P84	66 : 1 : 65 : 1322	338	11	1.04
13	P84	66 : 1 : 103 : 2100	338	12	1.12
14	P84	66 : 1 : 218 : 4433	314	9	0.85
15	15-S-9	66 : 1 : 17 : 285	367	20	1.63
16	15-S-12	66 : 1 : 14 : 232	368	20	1.66
17	L61	66 : 1 : 41 : 670	279	12	0.78
18	L64	66 : 1 : 70 : 1160	300	10	0.76
19	P65	66 : 1 : 83 : 1360	324	6	0.69
20	None	66 : 0 : 65 : 1322	259	5	0.47

^a Due to the large molar masses of PEO surfactants, molar ratios of aluminum alkoxide to PEO surfactants are much higher than when amine surfactants are used. The mass ratios, however, are comparable (section 3.3.1.2).

^b BJH pore diameter as measured by the adsorption branch

The ^{27}Al NMR spectrum of MSU- γ is provided in Figure 3.3. Two resonances are observed, one at 72 ppm and another at 6.7 ppm, corresponding to the four- and six- coordinate aluminum, respectively. From the relative intensity of these peaks, it can be seen that there is good agreement between the observed tetrahedral occupancy with the theoretical values. Furthermore, in the NMR spectra of amorphous aluminas, an additional resonance at ~35 ppm is often observed, which is attributable to 5- coordinate aluminum centers. The lack of any such resonance in the spectrum of MSU- γ is evidence that no appreciable amount of amorphous alumina exists in this material.

Perhaps the best evidence for the confirmation of a mesostructured alumina with crystalline walls is attained from TEM. Bright field and dark field images of MSU- γ prepared from P84 and aluminum sec-butoxide are shown in Figure 3.4. The same fiber like morphology evident in MSU-B is also seen here. This indicates that there is retention of morphology on going from the boehmite to the gamma phase. From the image in Figure 3.4 A, it appears that the randomly oriented fibers have a length of approximately 30 nm and an average thickness of 5 nm. The porosity of MSU- γ alumina is defined by the space between the overlapping fibers.

In part B of Figure 3.4, a lower magnification image and the corresponding selected area electron diffraction pattern is provided for an MSU- γ prepared from aluminum sec-butoxide and P84 as described in Table 3.1, line 3. The presence of the rings in the diffraction pattern, corresponding to hkl reflections of [311],

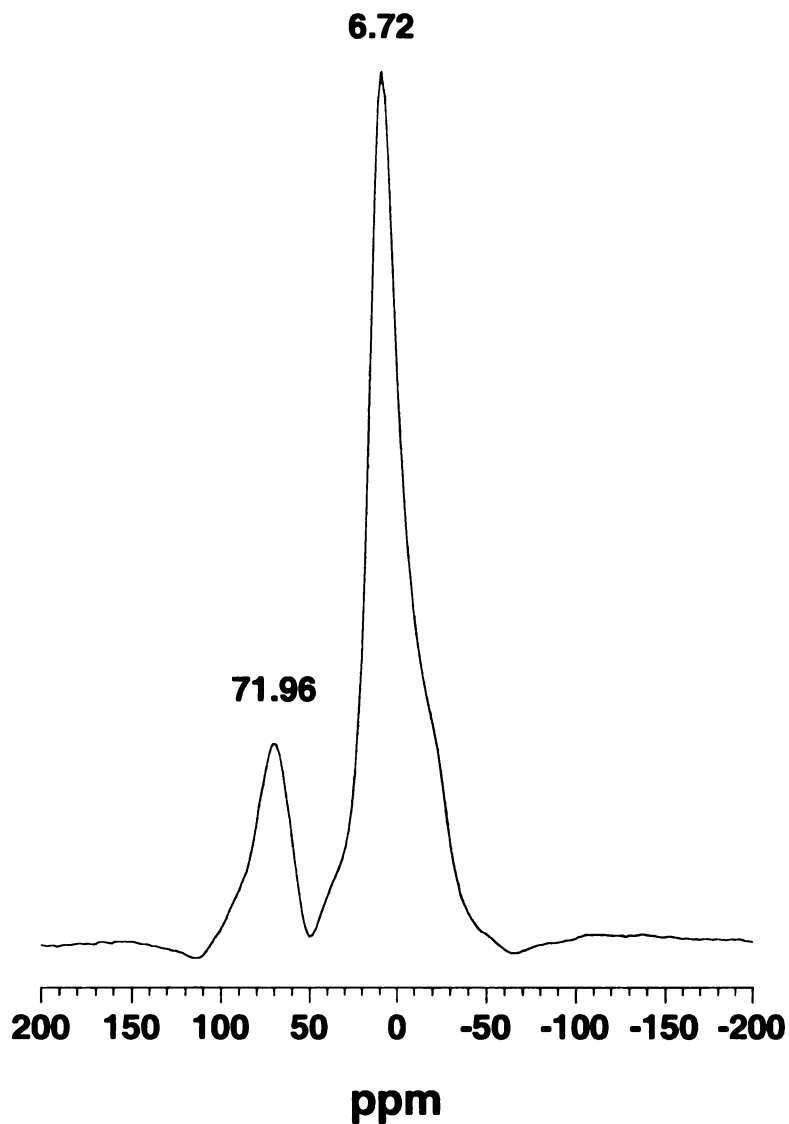
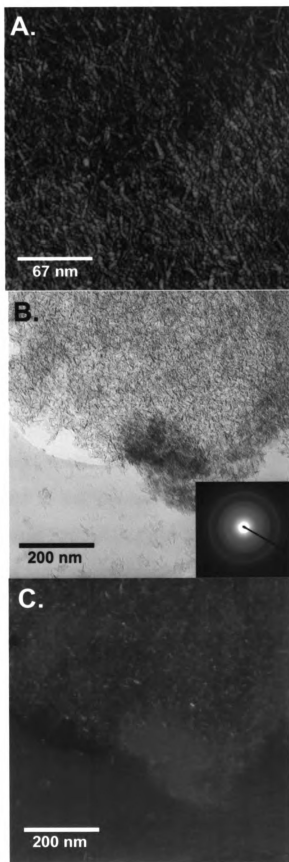


Figure 3.3. ^{27}Al NMR of calcined (500 $^{\circ}\text{C}$) MSU- γ alumina prepared from aluminum sec-butoxide and P84 as described in Table 3.1, line 3. The two resonances at 6.7 ppm and 72 ppm are assigned to aluminum in octahedral and tetrahedral coordination, respectively. The peaks are in the approximate 75:25 ratio consistent with $\gamma\text{-Al}_2\text{O}_3$.

Figure 3.4. Bright field TEM image of (A) calcined (500 °C) MSU- γ alumina prepared from aluminum sec-butoxide and P84 as described in Table 3.1, line 3. (B) Lower magnification image of the same product and the corresponding electron diffraction pattern, with diffuse rings assignable to the [311], [400], and [440] crystallographic planes. (C) Dark field image of the same particles as in (B), but formed from an $\sim 7^\circ$ arc of the [440] diffraction ring. The crystal orientations contributing to the [440] ring appear as bright spots in the image.



[400], and [440], is a direct consequence of the polycrystalline nature of the material. Their presence confirms the crystalline nature of these materials. Dark field imaging in TEM is accomplished by using only diffracted electrons to form images. Additionally, an aperture can be inserted into the electron beam to select only electrons that are diffracted by specific crystallographic planes. Part C of Figure 3.4 displays such an image, the dark field image of the same particles as in Part B, created from $\sim 7^\circ$ arc of the [440] diffraction ring of MSU- γ . The crystal orientations contributing to the [440] ring of the diffraction pattern appear as bright spots in the dark field image. The appearance of these bright spots uniformly across the image confirms that γ -Al₂O₃ nanoparticles comprise the framework walls in MSU- γ .

3.3.1.2. Variations of Synthetic Parameters

As was discussed in the previous chapter for mesoporous boehmites prepared from aluminum sec-butoxide and amine surfactants, these new MSU aluminas are synthesized through a particle assembly pathway. Consequently, controlling the textural properties of the products as is practiced with templated mesostructured materials is not straightforward. Although the pore size distributions do not respond to differences in surfactant size, the γ -Al₂O₃ compositions reported here can be made over a range of synthetic conditions while exhibiting textural properties in excess of for conventional aluminas. The textural properties are summarized in Table 3.1.

The aluminum to surfactant ratio was altered to range from ratios Al/P84 = 100 to Al/P84 = 25. It should be noted that the molar ratios of Al to surfactant employed in the syntheses leading to the formation of MSU- γ aluminas are considerably greater than in the syntheses leading to the formation of MSU-B boehmites. The molar masses of the PEO surfactants are generally much larger than those of the amine surfactants. While the reported molar ratios differ greatly, the mass ratios of the two reagents are comparable. For example, at Al/P84 = 66, the mass of aluminum sec-butoxide to the mass of P84 = 3.91. For comparison, an Al/DDA = 5 corresponds to an aluminum sec-butoxide to DDA mass ratio of 6.65.

While the textural properties of the alumina prepared at Al/Surf = 66 appear to be out of line, there is a general increase in both surface area and pore volume with decreasing Al/Surf ratios (Table 3.1, lines 1-5). There is no apparent trend in pore size. While aluminas prepared at other ratios appear better, most syntheses were carried out at an Al/Surf = 66 ratio for two reasons. First, reaction mixtures at high surfactant concentrations (low Al/Surf ratios) tend to be very thick, sticky, and difficult to process. Second, at the time of this work, the origin of the low angle diffraction peak was unclear, and aluminas exhibiting a low angle peak were expected to have more desirable textural properties than those that did not. The differences in textural properties for reaction products that exhibit a low angle XRD reflection and those that do not are not substantial. Perhaps there exists a certain ratio where there is an optimum coverage of surfactant by alumina, above which any additional alumina is not mesostructured into new

fibers, but rather goes toward increasing the thickness of existing MSU- γ fibers. Void space that would contribute to pore volume would, above this ratio, be sacrificed as alumina fibers thickened. Nevertheless, syntheses carried out at this ratio proved fruitful.

Recently, the synthesis of γ -Al₂O₃ nanofibers prepared from NaAlO₂ and PEO surfactants was reported¹⁶. Molar ratios of aluminum to surfactant in syntheses leading to the γ -Al₂O₃ fibers were ~ 2:1, much lower than the ratios employed in the current work. Although no claims of a mesostructure were made, fibers of comparable length and thickness to those reported here were obtained. Additionally, the large amount of surfactant used in the syntheses provided for the formation of an alumina with pore volumes in the range of 1.41 – 1.95 cc/g. A direct relationship between mass of surfactant used in the synthesis and pore volume of the resulting product was noted in Zhu's work. These findings are not in agreement with observed trends in the syntheses of MSU-B boehmites reported in the previous chapter and in the syntheses of MSU- γ aluminas, as described in the following paragraphs.

Solvent polarity was also adjusted to examine the effect on the textural properties of MSU- γ aluminas. From the nitrogen adsorption – desorption isotherms and pore size distributions in Figure 3.5 and the data in Table 3.1, lines 6 – 11, it can be seen that the textural properties go through a maximum for aluminas prepared at a water : 2-butanol ratio of 4 : 1 (80/20 v/v). It could be that as the polarity decreases at high a 2-butanol content, the surfactant ceases to form micelles capable of directing the structure. At the other extreme, of low 2-

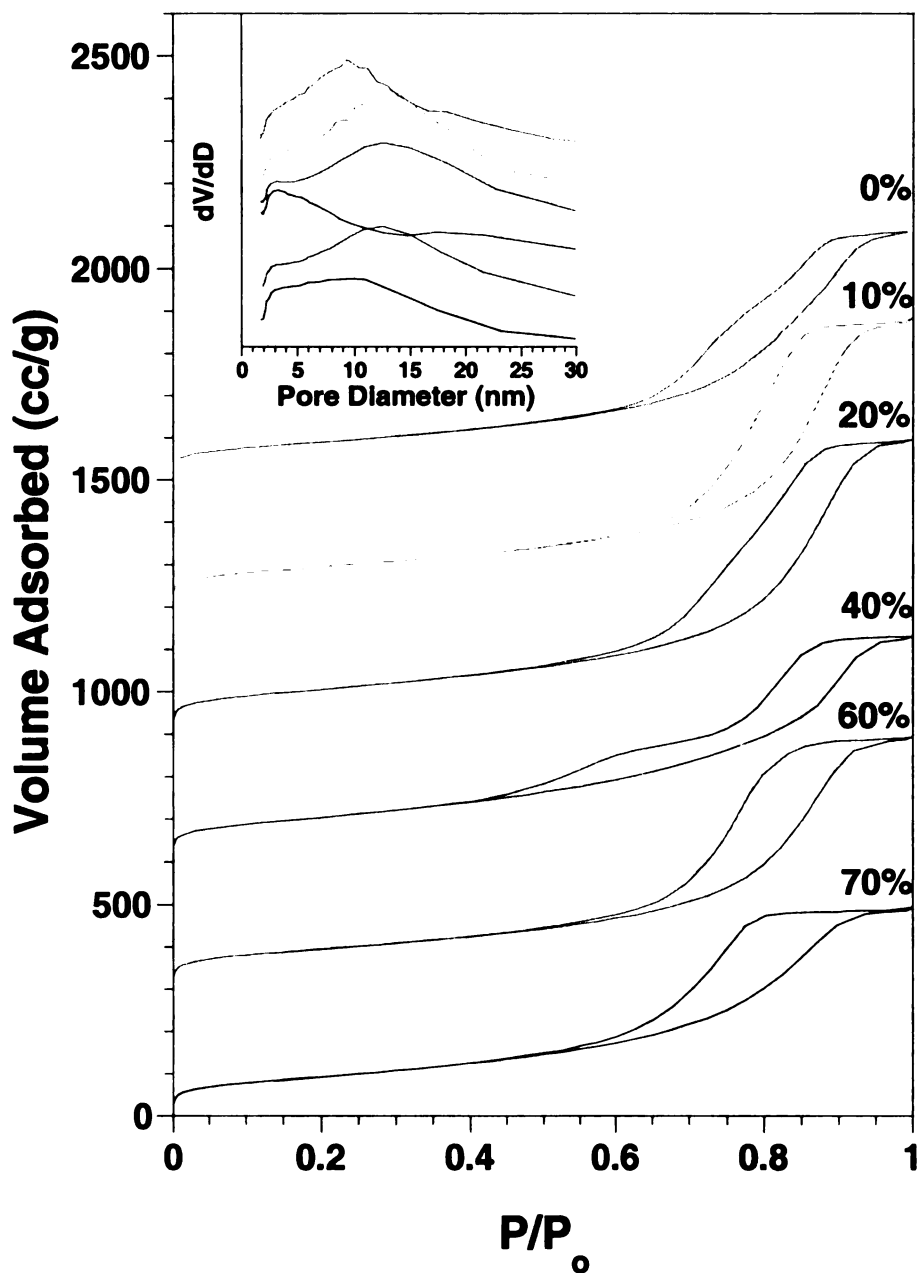


Figure 3.5. Nitrogen adsorption-desorption isotherms of MSU- γ aluminas prepared from aluminum sec-butoxide and P84 as described in Table 3.1, lines 3 and 6-10 showing the effect of solvent polarity on the textural properties. The volume percent of 2-butanol in the solvent is labeled for each isotherm. Isotherms are offset 300 cc/g for clarity. The BJH adsorption pore size distributions (inset) are in the same order as the isotherms.

butanol content, the total amount of solvent may be decreasing to point that is not conducive to mesostructure formation.

Nitrogen adsorption – desorption isotherms and pore size distributions for MSU- γ aluminas prepared from aluminum sec-butoxide and P84 solutions of varying concentration are shown in Figure 3.6. It was observed that the surface areas, pore volumes, and pore sizes decreased slightly with decreasing concentration of the surfactant employed in the synthesis. The effect of surfactant concentration is most pronounced at a concentration of 5%. Aside from ease of processing the reaction mixture, there seems to be little advantage in diluting the reaction mixture. The surfactant concentration does not appear to be a critical factor affecting the textural properties and pore structure. This is the same phenomenon that was observed in the syntheses of MSU-S/B precursors and MSU-B boehmites from aluminum sec-butoxide and amine surfactants as described in the previous chapter.

Finally, MSU- γ aluminas could be prepared with other nonionic PEO surfactants in which Figure 3.7 shows the nitrogen adsorption – desorption isotherms and the corresponding pore size distributions for these aluminas. It seems odd that the smallest molecular weight surfactants yield aluminas with the largest pore volumes and sizes. However, in no case does the amount of surfactant used in the synthesis correspond to the pore size or volume observed in the surfactant free products. Again, the lack of a direct relationship between surfactant properties and textural properties of MSU- γ aluminas is evidence of a particle assembly pathway.

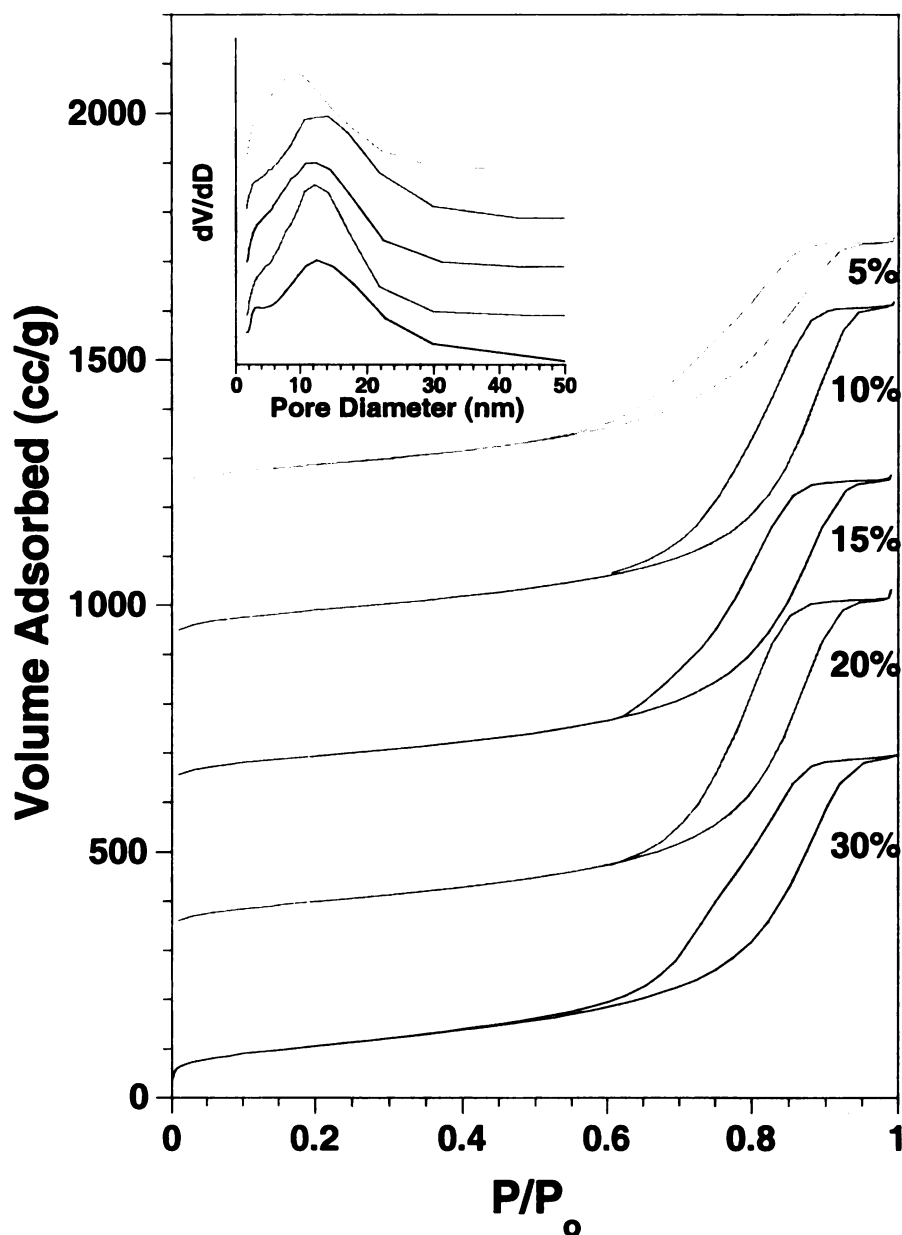


Figure 3.6. Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) for MSU- γ aluminas prepared from aluminum sec-butoxide and P84 as described in Table 3.1, lines 3 and 11-14 showing the effect of surfactant concentration (mass P84 / mass solvent) on the textural properties. The mass percent of P84 is labeled for each isotherm. Isotherms are offset 300 cc/g for clarity. The PSD curves are displayed in the same order as the corresponding isotherms.

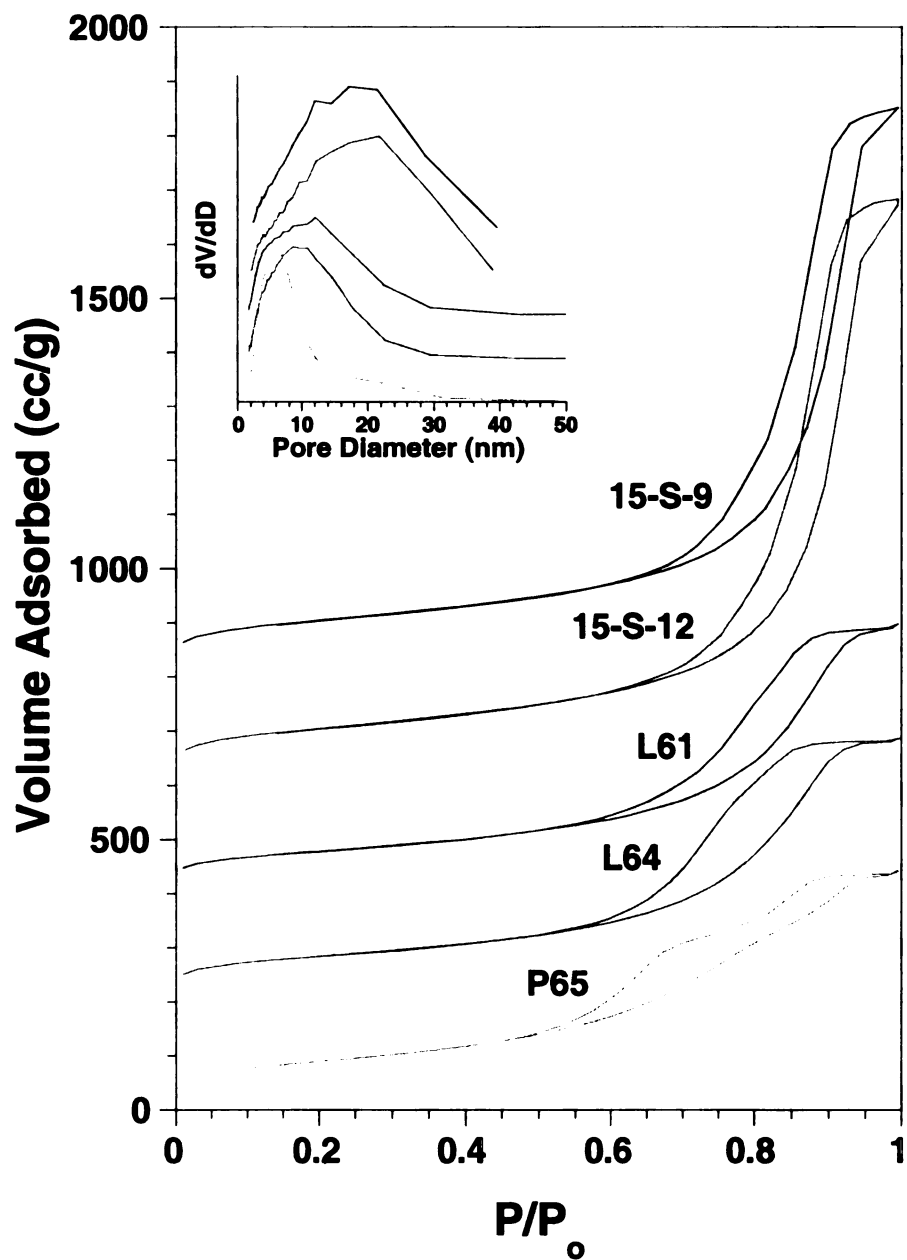


Figure 3.7. Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) for MSU- γ aluminas prepared from aluminum sec-butoxide and differing PEO surfactants as described in Table 3.1, lines 3 and 11-14. Isotherms are offset 200 cc/g for clarity. The PSD curves are displayed in the same order as the corresponding isotherms.

3.3.1.3. Effect of Calcination Procedure

As described in the previous chapter, the lower boiling points of the amine surfactants allowed for their removal from the as-synthesized MSU-S/B surfactant-boehmite compositions at mild temperatures with the retention of the boehmite phase during MSU-B synthesis. Such is not the case with the PEO surfactants. Temperatures above 400 °C are required for surfactant removal via calcination, causing the boehmite in the MSU-S/B hybrid composition to be converted to $\gamma\text{-Al}_2\text{O}_3$.

$\gamma\text{-Al}_2\text{O}_3$ is but one of at least seven identified transition aluminas. Calcination at elevated temperatures may be a general route to transition aluminas. The transformation sequence of thermal dehydration of aluminas dictates that $\delta\text{-Al}_2\text{O}_3$ is the next phase to form once $\gamma\text{-Al}_2\text{O}_3$ is heated at temperatures above ~750 °C¹. MSU-S/B aluminas prepared from PEO surfactants were calcined at 800 °C for 2hr to achieve the conversion to a mesostructured $\delta\text{-Al}_2\text{O}_3$, denoted MSU- δ . This transition alumina also has a structure based on the spinel structure and consequently, evolution from $\gamma\text{-Al}_2\text{O}_3$ to $\delta\text{-Al}_2\text{O}_3$ can be performed without significant changes in the pore structure of the alumina^{17,18}. Therefore, it is not unreasonable to expect the retention of desirable textural properties in these materials, as evidenced from the nitrogen adsorption – desorption isotherms (Figure 3.8). Due to the similarities in δ - and $\gamma\text{-Al}_2\text{O}_3$, it is somewhat difficult to distinguish between these two transition aluminas. XRD diffraction can be used to some extent to differentiate phases, but the patterns of all transition aluminas are strikingly similar. A better tool to use is ²⁷Al NMR, however in this case, site

occupancy of Al^{3+} ions is nearly identical. The inset of Figure 3.8 provides the wide angle XRD pattern of the reaction product formed through the calcination of an MSU-S/B surfactant-boehmite composition at 800 °C. The case could be made that these peaks are assignable to $\delta\text{-Al}_2\text{O}_3$. A comparison of textural properties of these two mesostructured aluminas (Table 3.2) reveals that while the pore volumes and sizes are comparable, there is a marked decrease in the surface area. This could be due to sintering of $\gamma\text{-Al}_2\text{O}_3$ fibers upon transformation to $\delta\text{-Al}_2\text{O}_3$. The ^{27}Al NMR spectra (not shown) looks nearly identical to that of the MUS- γ alumina. Due to the lack of definitive proof of $\delta\text{-Al}_2\text{O}_3$ phase formation, it could be argued that the material claimed here to be a mesostructured $\delta\text{-Al}_2\text{O}_3$ may only be a $\gamma\text{-Al}_2\text{O}_3$ whose pore structure is beginning to collapse. Regardless, this material exhibits exceptional textural properties having been calcined at 800 °C.

3.3.2. MSU- γ Prepared from Amine Surfactants

MSU- γ aluminas could also be prepared from amine surfactant-boehmite compositions synthesized as described in the previous chapter. This was achieved by directly calcining MSU-S/B surfactant-boehmite precursors, or the surfactant-free MSU-B boehmite aluminas that had been previously calcined, at temperatures sufficient to initiate conversion to $\gamma\text{-Al}_2\text{O}_3$ (>400 °C). The resulting products exhibited XRD patterns consistent with $\gamma\text{-Al}_2\text{O}_3$, signifying the crystalline nature of these materials. As expected, these materials have the same morphology as other MSU- γ aluminas. The bright field TEM image and

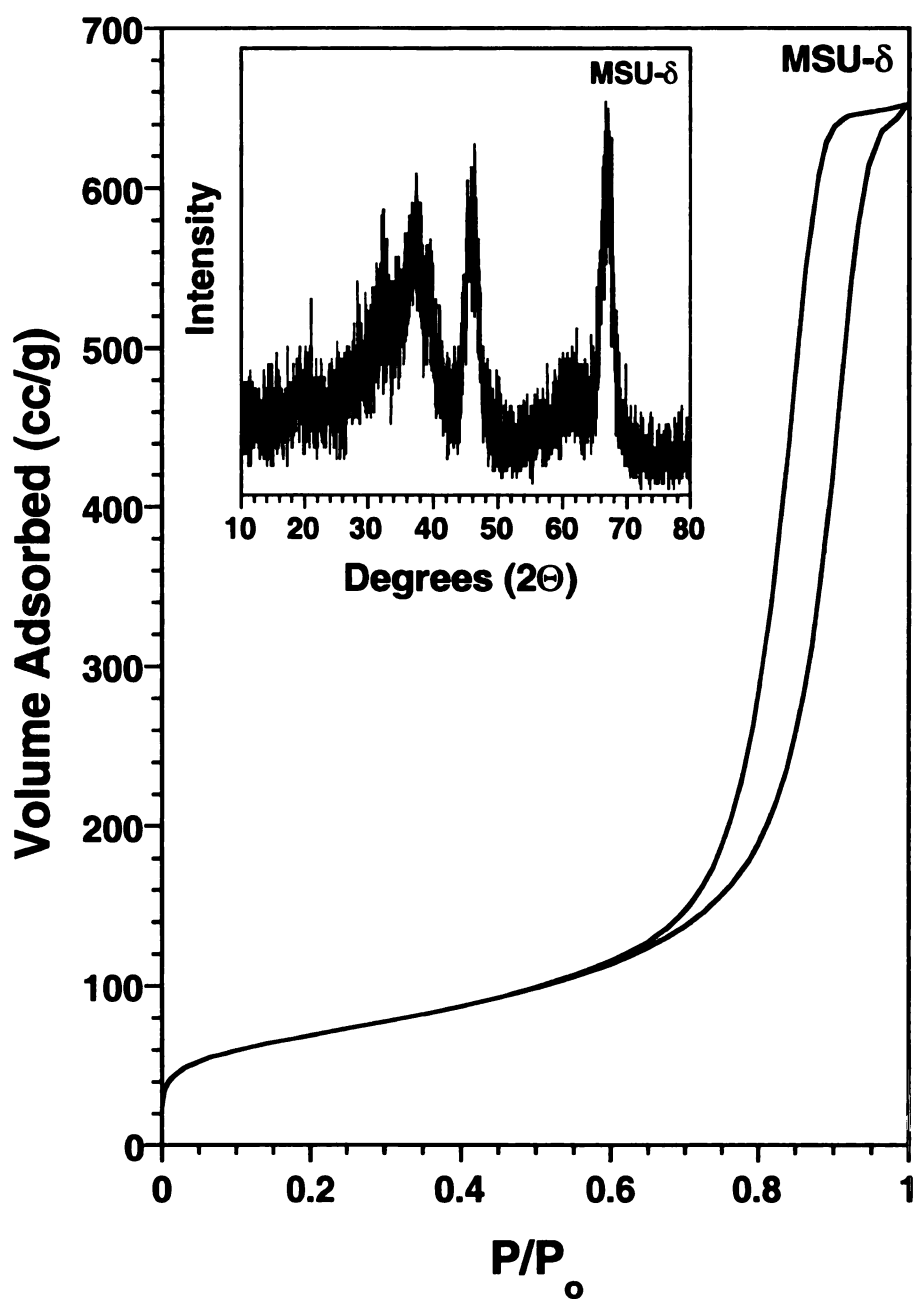


Figure 3.8. Nitrogen adsorption-desorption isotherm and wide angle powder XRD pattern (inset) of a calcined (800 °C) MSU- δ . The initial MSU-S/B surfactant-boehmite intermediate was prepared from aluminum sec-butoxide and the PEO surfactant P84 under conditions described in Table 3.1, line 13.

Table 3.2. Comparison of textural properties of calcined MSU- γ formed at 500 °C and calcined MSU- δ alumina formed at 800 °C.^a

	Calcination Temperature (°C)	Surface Area (m ² /g)	Pore Size ^b (nm)	Pore Volume (cc/g)
1	500	306	18	1.14
	800	251	16	0.98
2	500	338	12	1.04
	800	249	16	1.00

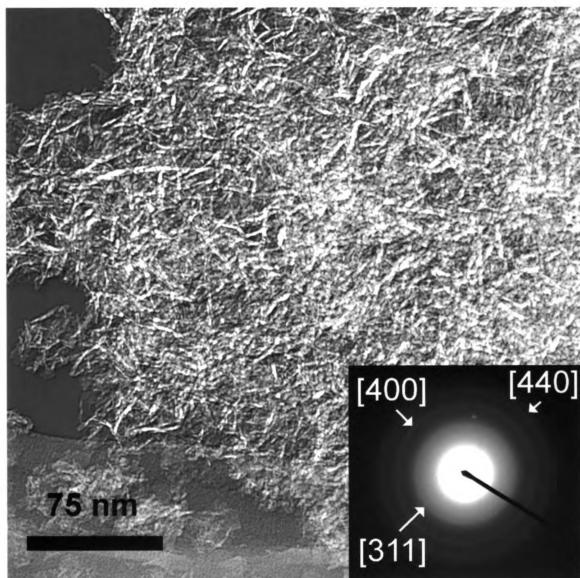
^a The initial MSU-S/B surfactant-boehmite intermediate was prepared from aluminum sec-butoxide and the PEO surfactant P84 under conditions described in Table 3.1, line 13.

^b BJH pore diameter as measured by the adsorption branch

corresponding electron diffraction pattern shown in Figure 3.9 for an MSU- γ prepared from an amine-mediated MSU-B boehmite verified that an open framework was created upon the assembly of the small crystalline particles into a mesostructure. Nitrogen adsorption – desorption isotherms (Figure 3.10) also show behavior similar to MSU- γ aluminas derived from PEO surfactants. The textural properties of these materials are summarized in Table 3.3. The pore volumes and pore sizes are approximately equal (at a given temperature) for MSU- γ aluminas prepared directly from MSU-S/B or from previously calcined MSU-B. The surface areas are greater for MSU- γ aluminas prepared through the calcination of MSU-S/B than for MSU-B precursors. Perhaps there is some structural degradation of MSU-B caused by adsorption of water onto the surface, rendering a poorer quality MSU- γ to be formed upon a second calcination. It was observed that pore volumes for MSU-B materials decreased at higher aging temperature (Table 2.1). That trend is observed here as well. Finally, it is noted that data provided in Table 3.3 for the MSU- γ aluminas from MSU-S/B and MSU-B indicate that the textural properties are enhanced compared to those in MSU- γ aluminas prepared from PEO surfactants.

Fig
boe
com
at a
tem
by c
patti
mes
and

Figure 3.9. TEM image of MSU- γ prepared through the calcination of MSU-B boehmite at 500 °C for 4 hr. The initial MSU-S/B surfactant-boehmite composition was prepared from aluminum sec-butoxide and dodecylamine (DDA) at a reaction stoichiometry of Al:DDA:EtOH:H₂O = 5:1:68.0:73.4 and a reaction temperature of 20 °C. The surfactant free MSU-B boehmite phase was obtained by calcining the MSU-S/B precursor at 325 °C for 10 hr. The electron diffraction pattern (inset) demonstrates the crystallinity of the framework of the mesostructure, as indicated by the diffuse rings attributable to the [311], [400], and [440] crystallographic planes of γ -Al₂O₃.



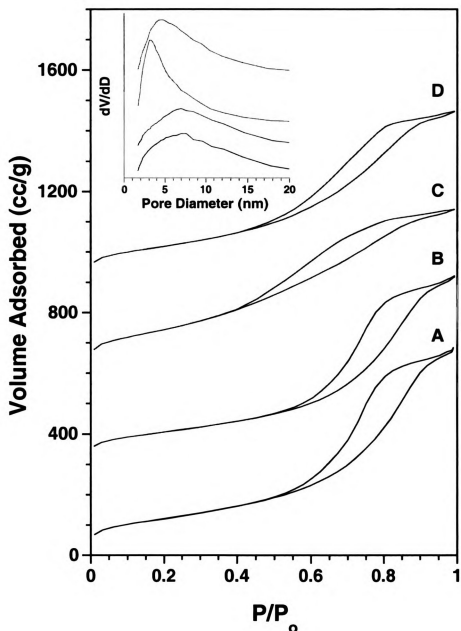


Figure 3.10. Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) for MSU- γ aluminas prepared through the calcination (500 °C) of amine-mediated MSU-S/B surfactant-boehmite precursors (samples A and C) and surfactant free MSU-B precursors (samples B and D). The Al:DDA:EtOH:H₂O reaction stoichiometry was 5:1:68.0:73.4 for all samples. Reaction temperature was 20 °C for samples A and B and 45 °C for samples C and D. Isotherms are offset 300 cc/g for clarity. The PSD curves are displayed in the same order as the corresponding isotherms.

Table 3.3. Textural properties of MSU- γ aluminas prepared through the calcination of MSU-S/B surfactant-boehmite compositions and MSU-B boehmites at 500 °C.^a

	Precursor	Surface Area (m ² /g)	Pore Size ^b (nm)	Pore Volume (cc/g)
A	MSU-S/B	440	7	1.07
B	MSU-B	385	7	0.97
C	MSU-S/B	529	3	0.86
D	MSU-B	431	4.5	0.89

^a The MSU-S/B and MSU-B precursors were prepared from aluminum sec-butoxide and dodecylamine. The Al:DDA:EtOH:H₂O reaction stoichiometry was 5:1:68.0:73.4 for all samples. Reaction temperature was 20 °C for samples A and B and 45 °C for samples C and D.

^b BJH pore diameter as measured by the adsorption branch

3.3.3 Stability of MSU- γ Aluminas

3.3.3.1 Doped MSU- γ Aluminas

It is known that the incorporation of certain elements into γ - Al_2O_3 has a stabilizing effect on the structure. While transition metals have been doped into aluminas toward this end, more commonly either lanthanum or cerium is used as the dopant. It has been demonstrated that these ions stabilize the γ - Al_2O_3 phase toward conversion to α - Al_2O_3 by forming a metal aluminate species¹⁹⁻²¹ on the surface of the alumina. Due to the nature of the spinel structure of γ - Al_2O_3 and other transition aluminas, metal ions can also stabilize alumina by filling the vacancies in the lattice^{22,23}. Most studies are aimed at delaying the temperature at which γ - Al_2O_3 is converted to α - Al_2O_3 or other transition aluminas. Many important industrial catalytic applications of alumina are performed in a steam environment, so aluminas must also be stable under these conditions if they are to function effectively. A study of the ability of lanthanum to stabilize alumina in a steam environment suggested that the lanthanide aluminate mechanism is at work here as well²⁴.

MSU-X aluminas were doped with rare earth metals to improve their thermal stability²⁵. While MSU- γ aluminas have proven to be thermally stable, improving their hydrothermal stability would increase the possibility for effective use in catalytic applications. It was also possible to dope the MSU- γ aluminas of the present work with cerium and lanthanum. As shown in Table 3.4, MSU- γ aluminas could be doped with an assortment of metal ions with the products

Table 3.4. Textural properties of doped MSU- γ aluminas prepared from aluminum sec-butoxide and P84. In each synthesis, the dopant was administered as a metal salt which was dissolved in the surfactant solution prior to addition of the aluminum sec-butoxide.

Dopant	Surface Area (m ² /g)	Pore Size ^a (nm)	Pore Volume (cc/g)
Cu	437	10	1.05
Ni	426	10	1.08
Cr	438	3-15	0.96
Co	390	3-15	0.88
Fe	380	10	0.93
Mn	392	7	0.81
Ba	322	13	0.91
La	386	7	0.68
Ce	416	9	0.99

^a BJH pore diameter as measured by the adsorption branch

exhibiting favorable textural properties. While the introduction of transition metals may introduce catalytically active sites to MSU- γ aluminas, steam testing (below) was conducted for the lanthanum and cerium doped materials, keeping with conventional methodologies.

It was concluded that in amorphous MSU-X aluminas, direct incorporation of rare earths into the framework was a feature of the formation. The method of incorporation in MSU- γ , however, may involve both the formation of an aluminate coating and the incorporation of the dopant into vacancies of the γ - Al_2O_3 lattice. Peaks assignable to a CeAlO_3 phase in the wide angle XRD pattern of 5% cerium doped MSU- γ indicates that formation of an aluminate surface species is involved during the incorporation process (Figure 3.11). However, no such peaks are evident in the pattern of the 5% lanthanum doped material, indicating that direct substitution into the spinel lattice of γ - Al_2O_3 may also be involved.

Nitrogen adsorption – desorption isotherms (Figure 3.12) indicate that the pore volume of MSU- γ is greater in the pristine sample than in either doped variation, although the pores are smaller and more uniform in the doped materials. The TEM images of these materials (Figure 3.13 A) reflect this as well; larger pores are evident in the clean sample (A) than in the lanthanum doped (C) or cerium doped (E) sample.

3.3.3.2. Steam Testing of MSU- γ Aluminas

These three aluminas were tested for hydrothermal stability by exposing each to a 20% steam atmosphere at 600 °C for 5 hr. Interestingly, the pristine MSU- γ

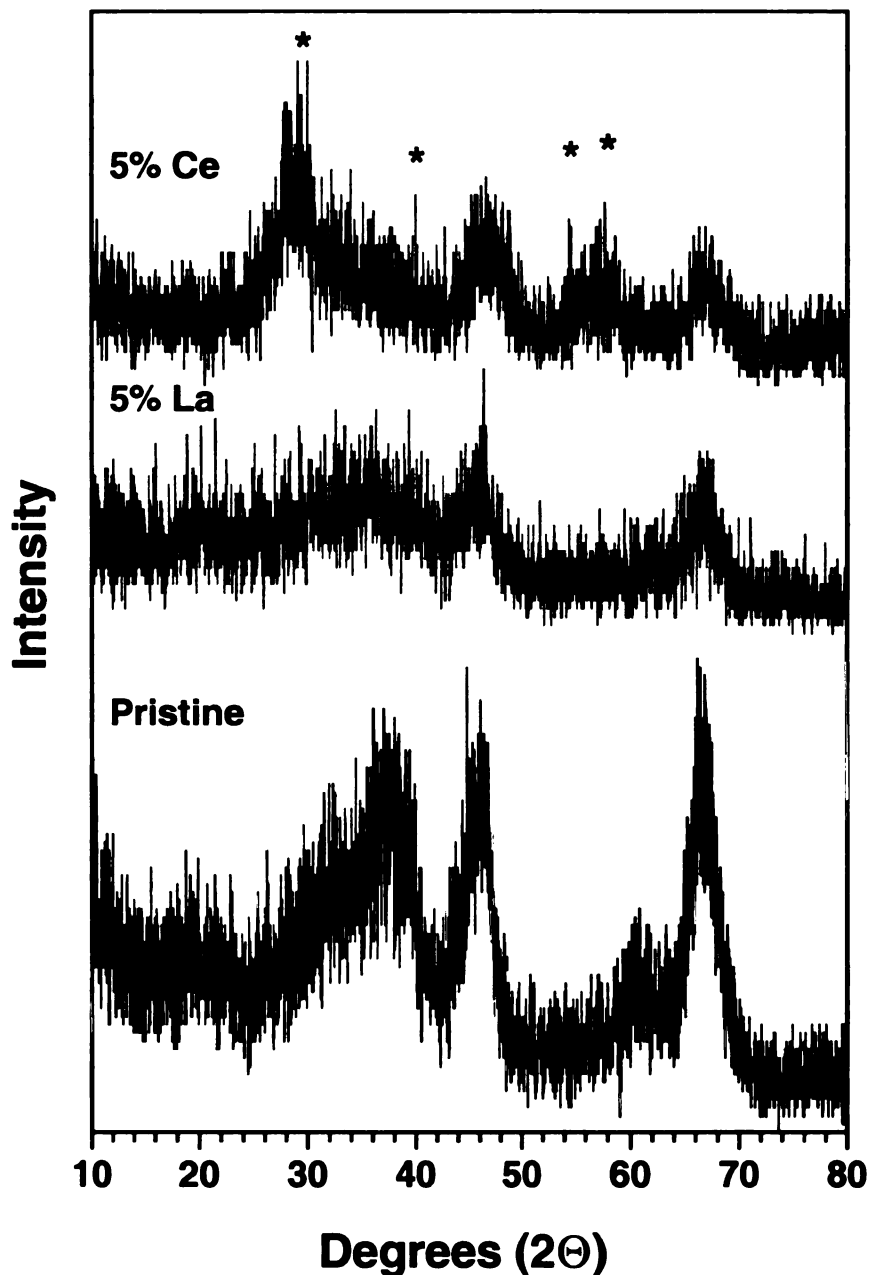


Figure 3.11. Wide angle powder XRD patterns of MSU- γ aluminas prepared from aluminum sec-butoxide and P84: pristine and doped with either lanthanum or cerium. Peaks marked with an asterisk are attributable to a cerium aluminate phase, CeAlO_3 . The doped MSU- γ aluminas were prepared through the calcination (500 °C) of doped MSU-S/B precursors prepared as described in Table 3.1, line 13.

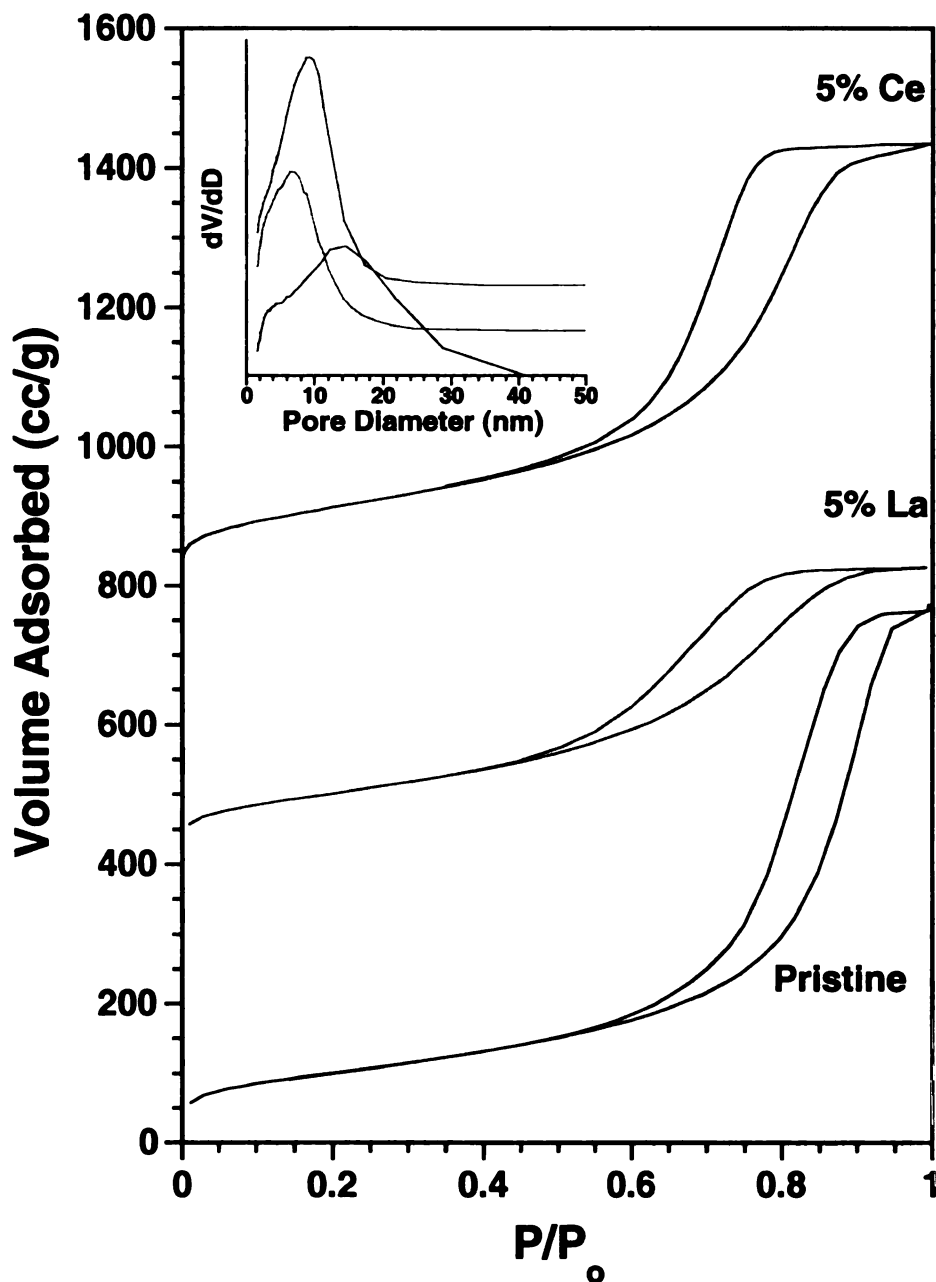


Figure 3.12. Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) of MSU- γ aluminas: pristine and doped with either lanthanum or cerium. The doped MSU- γ aluminas were prepared through the calcination (500 °C) of doped MSU-S/B precursors prepared as described in Table 3.1, line 13. Isotherms are offset 400 cc/g for clarity. The PSD curves are in the same order as the corresponding isotherms.

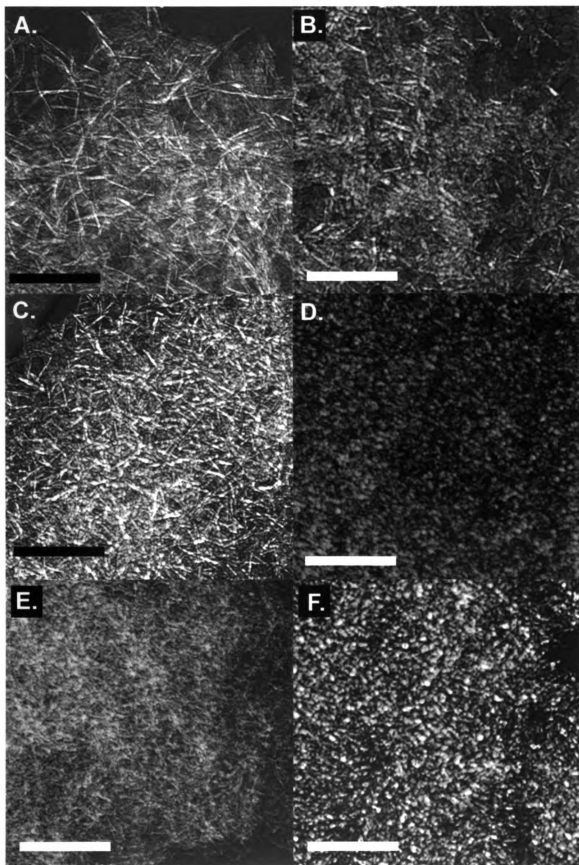
alumina appears to have the best hydrothermal stability. It retains 85% of the original surface area while the lanthanum doped and cerium doped MSU- γ aluminas retain only 57% and 55%, respectively.

A major concern under these conditions is the sintering of the nanoparticles. A comparison of TEM images of the three samples before steaming (Figure 3.13) reveals that there is more void space between fundamental building units of the framework in the undoped alumina(A). It may be that the greater distance between particles keeps them from sintering. The particles of 5% La doped (C) and Ce doped (E) aluminas may be more easily sintered as they are initially in closer proximity. The TEM images of the steamed aluminas (B,D,F) support this view. While still lath-like in morphology, the particles appear shorter and thicker in all cases, but more so for the doped aluminas than for the clean sample.

Sintering leads to loss of surface area, which is observed in all cases. It is possible that doping of aluminas leads to the formation of micropores in the structures, which contribute greatly to the surface area. Upon steaming and subsequent sintering, micropores are lost as larger pores are formed. It is noted that the average pore sizes in the doped aluminas increase after steaming (Figure 3.14).

The γ - Al_2O_3 phase is preserved for all materials. Electron diffraction patterns reveal the diffuse rings, confirming crystallinity of the frameworks. However, this structural integrity of the γ - Al_2O_3 phase is greatest in the pure alumina as judged by XRD patterns (Figure 3.15). While all samples exhibit peaks consistent with γ -

Figure 3.13. TEM images of MSU- γ aluminas prior to (A,C,E) and after steaming (B,D,F) at 600 °C for 5 hr in a 20% steam atmosphere. Images A and B are for pristine MSU- γ . Images C, D and E, F are for MSU- γ doped with 5% La³⁺ and 5% Ce³⁺, respectively. The MSU- γ aluminas were prepared as described in the caption to Figure 3.11. The scale bar represents 100 nm in all figures.



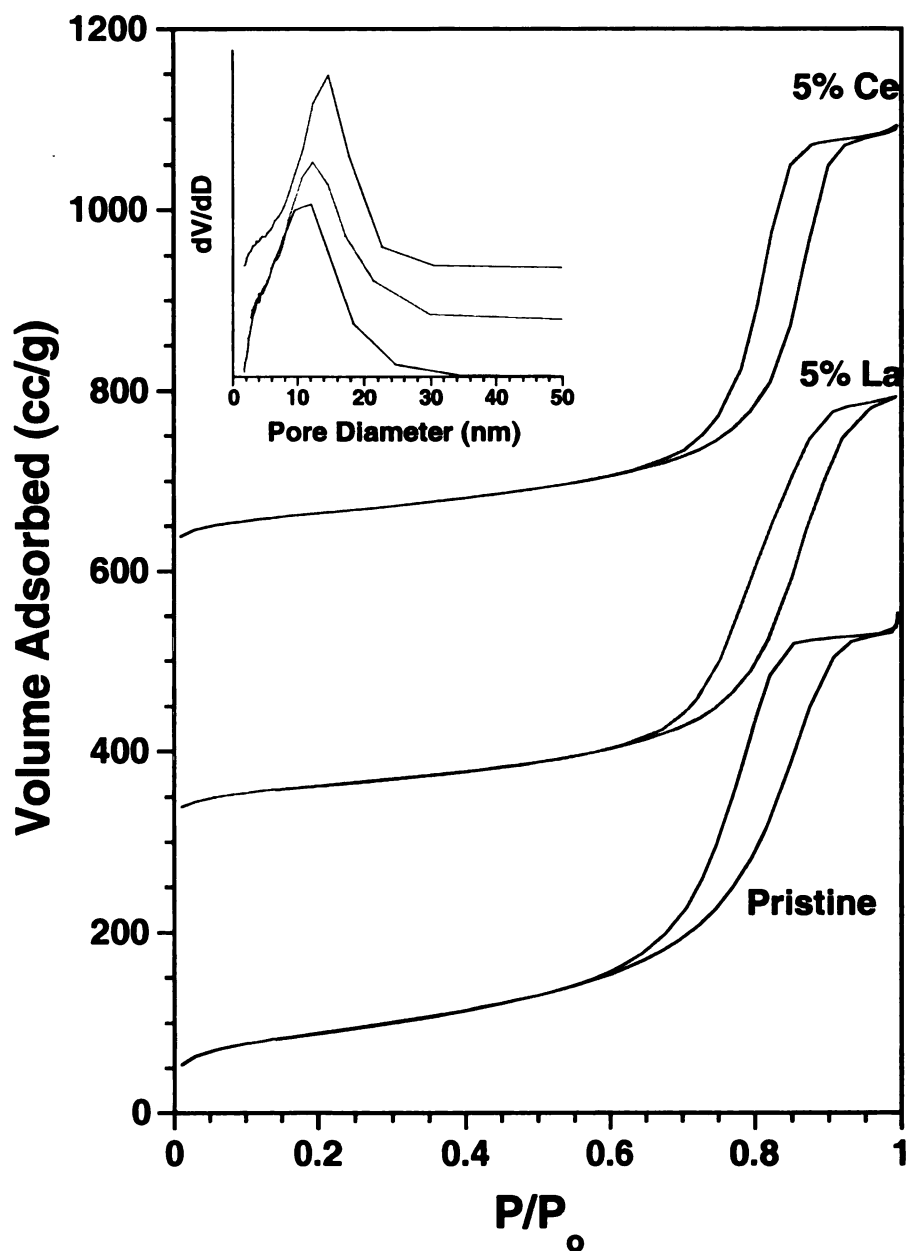


Figure 3.14. Nitrogen adsorption-desorption isotherms and BJH adsorption pore size distributions (inset) of pristine and doped MSU- γ aluminas after steaming for 5 hr at 600 °C in a 20% steam atmosphere. Samples were prepared as described in the caption to Figure 3.11. Isotherms are offset 300 cc/g for clarity. The PSD curves are in the same order as the corresponding isotherm.

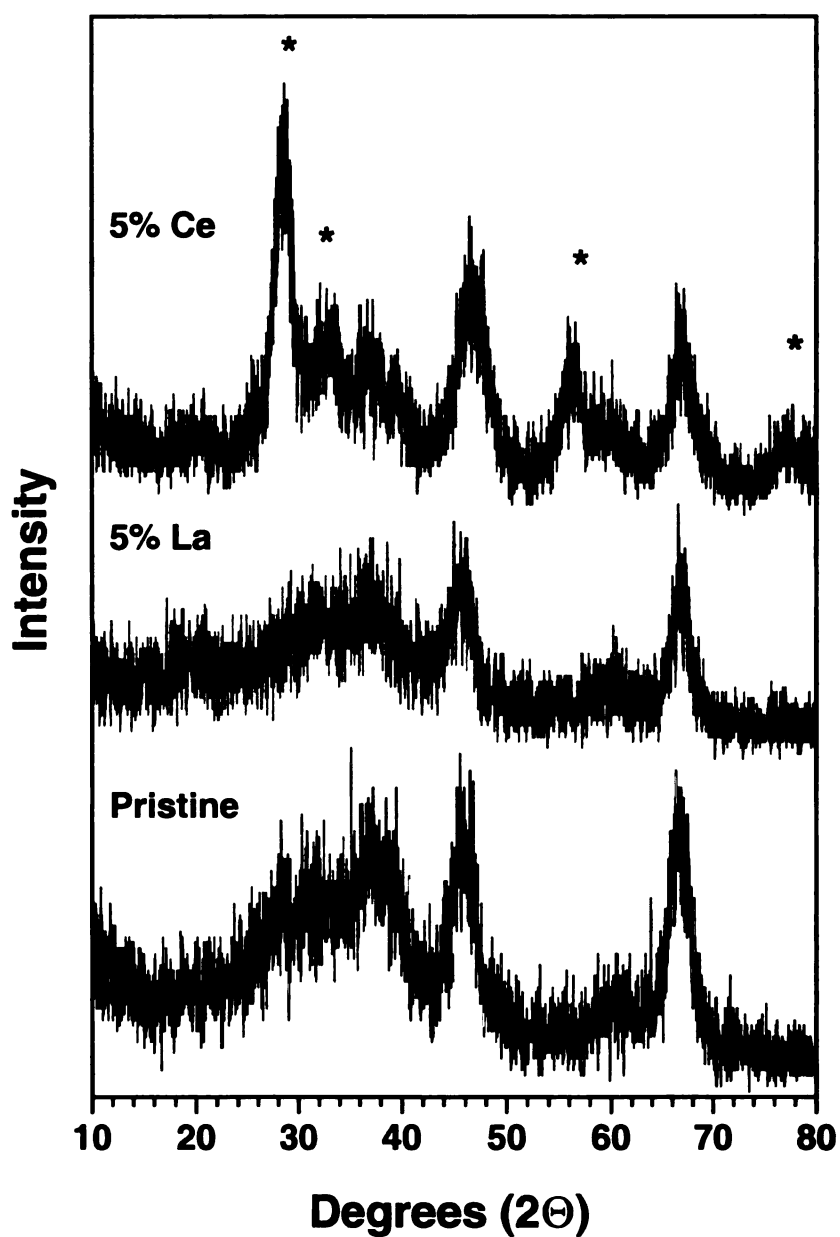


Figure 3.15. Wide angle powder XRD patterns of pristine and doped MSU- γ aluminas after steaming for 5 hr at 600 °C in a 20% steam atmosphere. Peaks marked with an asterisk are attributed to CeAlO_3 , cerium aluminate. Samples were prepared as described in the caption to Figure 3.11.

Al_2O_3 , the peak intensity is greatest in the pristine alumina. Peaks assignable to the CeAlO_3 phase are again evident for the cerium doped sample.

Traditionally, lanthanides are stabilizers of aluminas toward conversion to $\alpha\text{-Al}_2\text{O}_3$. In the case of MSU- γ aluminas, they may also provide stabilization toward $\alpha\text{-Al}_2\text{O}_3$, but the textural properties are compromised in comparison to the pristine alumina. Perhaps compared against a pure alumina synthesized without the aid of a surfactant, the lanthanides would improve hydrothermal stability. Ironically, as the pore structure is relatively unchanged after steaming, the most open framework appears to be the most stable. The results of the study are summarized in Table 3.5.

3.4. Conclusions

Synthesis of the first mesostructured $\gamma\text{-Al}_2\text{O}_3$ has been accomplished through a particle assembly pathway from the hydrolysis of aluminum alkoxide in the presence of electrically neutral nonionic PEO and amine surfactants as porogens. The formation of an MSU-S/B precursor is key in attaining these mesostructures. It has been demonstrated that these aluminas possess textural properties superior to those of conventional aluminas, exhibiting surface areas, pore sizes, and pore volumes in excess of $400 \text{ m}^2/\text{g}$, 15 nm , and 1.00 cc/g , respectively. The lack of a correlation between the size, mass, or molar mass of surfactant employed in the synthesis with the textural properties of the surfactant

Table 3.5. Textural properties of MSU- γ aluminas prior to and after treatment at 600 °C in a 20% steam atmosphere for 5 hr.^a

Sample	Condition	Surface Area (m ² /g)	Pore Size ^b (nm)	Pore Volume (cc/g)
Pristine	Fresh	371	13	1.11
	Steamed	316	12	0.85
5% La	Fresh	386	7	0.68
	Steamed	220	12	0.77
5% Ce	Fresh	416	9	0.99
	Steamed	228	14	0.77

^a The samples were prepared as described in the caption to Figure 3.11.

^b BJH pore diameter as measured by the adsorption branch

free products is evidence that these materials are not assembled through a supramolecular templating pathway. The open framework resulting from the assembly of fundamental alumina fibers was verified through TEM imaging.

MSU- γ aluminas can be doped with transition metals and lanthanides without compromising the structure or surface area of the MSU- γ alumina. Additionally, these materials show exceptional thermal and hydrothermal stability, up to 600 °C for 5 hr in a 20% steam environment. These properties make MSU- γ excellent candidates for catalysts or catalyst supports.

3.5. Future Directions

While one example of a mesostructured higher temperature transition alumina was shown here, it would be of interest to synthesize more of these phases. Pore structures in these materials seem to remain intact at high temperatures, leading one to inquire into the possibility of making a mesostructured α -Al₂O₃, or at least an α -Al₂O₃ that demonstrates marked improvements in textural properties.

As was the case for mesostructured boehmite, finding a suitable catalytic application for MSU- γ is also of interest. However, noting that γ -Al₂O₃ is perhaps the world's most widely used catalyst support, the possibilities for making an impact in this area are enormous. One such endeavor is the topic of the next chapter.

3.6. References

- (1) Wefers, K.; Misra, C. "Oxides and Hydroxides of Aluminum," Alcoa Laboratories, 1987.
- (2) Misra, C. *American Chemical Society Monograph, Vol. 184: Industrial Alumina Chemicals*, 1986.
- (3) Sohlberg, K.; Pennycook, S. J.; Pantelides, S. T. *Journal of the American Chemical Society* **1999**, *121*, 7493-7499.
- (4) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature (London)* **1992**, *359*, 710-712.
- (5) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; et al. *J. Am. Chem. Soc.* **1992**, *114*, 10834-10843.
- (6) Bagshaw, S. A.; Pinnavaia, T. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1102-1105.
- (7) Vaudry, F.; Khodabandeh, S.; Davis, M. E. *Chem. Mater.* **1996**, *8*, 1451-1464.
- (8) Yada, M.; Machida, M.; Kijima, T. *Chem. Commun. (Cambridge)* **1996**, 769-770.
- (9) Valange, S.; Guth, J. L.; Kolenda, F.; Lacombe, S.; Gabelica, Z. *Microporous Mesoporous Mater.* **2000**, *35-36*, 597-607.
- (10) Cabrera, S.; El Haskouri, J.; Alamo, J.; Beltran, A.; Beltran, D.; Mendioroz, S.; Marcos, M. D.; Amoros, P. *Adv. Mater. (Weinheim, Ger.)* **1999**, *11*, 379-381.
- (11) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 2813-2826.
- (12) Gonzalez-Pena, V.; Diaz, I.; Marquez-Alvarez, C.; Sastre, E.; Perez-Pariente, J. *Microporous Mesoporous Mater.* **2001**, *44-45*, 203-210.
- (13) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309-319.
- (14) Barrett, E. P.; Joyner, L. G.; Halender, P. P. *Journal of the American Chemical Society* **1951**, *73*, 373.

- (15) John, C. S.; Alma, N. C. M.; Hays, G. R. *Appl. Catal.* **1983**, *6*, 341-346.
- (16) Zhu, H. Y.; Riches, J. D.; Barry, J. C. *Chemistry of Materials* **2002**, *14*, 2086-2093.
- (17) Wolverton, C.; Hass, K. C. *Physical Review B: Condensed Matter and Materials Physics* **2001**, *63*, 024102/024101-024102/024116.
- (18) Krokidis, X.; Raybaud, P.; Gobichon, A.-E.; Rebours, B.; Euzen, P.; Toulhoat, H. *Journal of Physical Chemistry B* **2001**, *105*, 5121-5130.
- (19) Schaper, H.; Doesburg, E. B. M.; Van Reijen, L. L. *Appl. Catal.* **1983**, *7*, 211-220.
- (20) Beguin, B.; Garbowski, E.; Primet, M. *Appl. Catal.* **1991**, *75*, 119-132.
- (21) Oudet, F.; Courtine, P.; Vejux, A. *J. Catal.* **1988**, *114*, 112-120.
- (22) Mizukami, F.; Maeda, K.; Watanabe, M.; Masuda, K.; Sano, T.; Kuno, K. *Stud. Surf. Sci. Catal.* **1991**, *71*, 557-568.
- (23) Braun, S.; Appel, L. G.; Zinner, L. B.; Schmal, M. *Br. Ceram. Trans.* **1999**, *98*, 77-80.
- (24) Schaper, H.; Amesz, D. J.; Doesburg, E. B. M.; Van Reijen, L. L. *Appl. Catal.* **1984**, *9*, 129-132.
- (25) Zhang, W.; Pinnavaia, T. J. *Chem. Commun. (Cambridge)* **1998**, 1185-1186.

Chapter 4

Hydrodesulfurization Over MSU- γ Supported Catalysts

4.1. Introduction

The hydrodesulfurization (HDS) reaction presents a challenge in the oil refinement process. HDS is the removal of sulfur from sulfur-containing organic molecules by treatment with H_2 at elevated temperatures and pressures. HDS has been performed in refineries since the 1950's. Since that time, however, improvement of the process has been constantly targeted. When burned, fuels that are high in sulfur release SO_x pollutants into the atmosphere, contributing to smog and acid rain. In addition, the presence of sulfur in automobile exhaust reduces the effectiveness of catalytic converters. Sulfur, if not removed, also has a detrimental effect on downstream catalysts used in the refinement process. Providing more motivation, the EPA has currently set up guidelines to restrict the amount of sulfur allowed in diesel products to 15 ppm by the year 2010¹. This corresponds to a 97% reduction over a ten year period. Complicating matters is that relatively clean crude oil stocks have been consumed, leaving only heavier crudes laden with an increased amount of sulfur. Clearly, advances in HDS technology must be made to satisfy both economic and environmental concerns.

Transition metal sulfides (TMS) have proven to be effective catalysts for HDS. Within this group of compounds, there are select metals whose sulfides are particularly active. The position of the metal in the periodic table and the

morphology of the metal sulfide play a role in determining the relative catalytic activity in the HDS reaction. A number of review articles discuss periodic trends of TMS in HDS catalysis²⁻⁸. Ruthenium disulfide is perhaps the most active TMS. However, molybdenum disulfide is the catalyst of choice for commercial use. The lower activity of MoS₂ is compensated by its reduced cost. In addition, the activity of TMS can be promoted by the presence of another metal sulfide, commonly those of cobalt and nickel. The role of the promoter is not entirely clear, but it has been demonstrated that they increase catalytic activity by increasing the electron density on the primary metal or lowering the Mo-S bond strength⁹, allowing for the creation of more active sites once sulfur atoms are removed by hydrogen.

Catalytically active sites on MoS₂ are characterized by sulfur vacancies, or coordinatively unsaturated metal ions, at the edge planes of the TMS. Utilizing a support can help to disperse the catalyst and expose more of these edge planes. Studies of catalytic activity have been performed for many different supports ranging from carbon¹⁰⁻¹², mesoporous synthetic clays^{13,14} and aluminosilicates¹⁵⁻¹⁷, and zeolites¹⁸. Still, alumina is the most common support employed for HDS catalysts. Alumina is stable under the conditions encountered during the reaction. It is inert; hence it does not interfere with the HDS reaction. Aluminas are inexpensive, are readily available, and exhibit desirable surface and textural properties. Many aluminas are porous, allowing for better dispersal of catalyst and increased access to the catalytically active sites. The transition alumina γ -Al₂O₃ is one such alumina with the features described above; it is the most

common support used in HDS chemistry. In fact, many commercial catalysts are mixtures of molybdenum and cobalt sulfides on a γ -Al₂O₃ support.

The use of mesoporous supports may lead to improved pathways to sulfur removal. The increased surface area and pore volume in these materials should allow for better dispersal of the catalytic phases and better access to the active sites on these catalysts. Additionally, the pore sizes in these supports can accommodate larger sulfur containing substrate molecules such as dibenzothiophene-based molecules, which mimic more closely the sulfur bearing contaminants in real oil stocks. To this end, mesostructured MSU- γ aluminas have been used in the present work as catalyst supports in HDS reactions. MSU- γ aluminas exhibiting different particle morphologies have been recently synthesized¹⁹. Aluminas with scaffold or lath morphology could be attained from different aluminum containing precursors. Here, the difference in morphology is used as a basis for comparison of performance in HDS reactions.

4.2. Experimental

4.2.1. Sample Preparation

The MSU- γ aluminas of scaffold morphology were synthesized as described in the previous chapter. MSU- γ with lath morphology was prepared similarly, but from hydrolysis by ammonia of either aluminum cations or the Al₁₃ oligomeric cation. The MSU- γ aluminas used in this study were prepared as follows.

4.2.1.1. MSU- γ Exhibiting Scaffold Morphology

A 10% mass solution of Pluronic P84, a nonionic PEO surfactant, was dissolved in 2-butanol and water (20/80 v/v) under stirring on a magnetic stirrer. To this solution, aluminum sec-butoxide was added and stirred until homogenous, to achieve an overall reaction stoichiometry Al:P84:s-BuOH:H₂O of 66:1:103:2100. The reaction mixture was removed from stirring and allowed to age at 100 °C for 20 hr in a sealed vessel to yield the MSU-S/B surfactant-boehmite precursor. This intermediate was recovered by vacuum filtration, washed with water and 2-butanol, and air dried. The surfactant free MSU- γ alumina was obtained through calcination of the MSU-S/B material at 500 °C for 4 hr.

4.2.1.2. MSU- γ Exhibiting Lath Morphology

The assembly of a MSU-S/B mesostructure was achieved by aging an aqueous mixture of a $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]Cl_7$ and P84 at 80 °C for 6 - 10 h and then hydrolyzing the mixture with concentrated NH₄OH. The precipitate formed upon hydrolysis was aged at 80 °C for 6 h, then at 100 °C for 24h, and air dried. The resulting mixture of MSU-S/B and NH₄Cl was calcined at 325 °C for 3h, then at 550 °C for 4h, to form the surfactant free MSU- γ alumina.

4.2.1.3. Catalyst Loading

The MSU- γ alumina supports were loaded with catalyst by incipient wetness impregnation of molybdenum and cobalt salts followed by thermal degradation to

the oxides. The supports were loaded with the volume of solution necessary to fill 90% of the available pore volume. For example, to achieve a 6% loading of Mo on an alumina having pore volume of 1.0 cc/g, 0.90 mL (per gram of Al_2O_3) of a solution of ammonium heptamolybdate tetrahydrate would be required. The amount of salt dissolved in this solution is determined by the desired loading. In this case, a 6% Mo loading would require that 0.06 gram of Mo per gram of Al_2O_3 , or 0.110 gram of the Mo salt, be impregnated. The requisite volume of this solution was added dropwise to the MSU- γ alumina, with intermittent agitation by either manual or mechanical shaking, to provide even wetting. The Mo impregnated alumina was calcined at 400 °C for 2 hr to decompose the salt to the oxide.

The pore volume of this intermediate material was obtained through nitrogen adsorption. The cobalt loading was determined to provide a 3:1 molar ratio of Mo:Co. Cobalt (II) nitrate hexahydrate was impregnated onto the support in the same manner as described for the Mo loading. Another calcination at 400 °C for 2 hr yielded the catalyst in its non-active, oxidic form.

Conversion to the catalytically active sulfidic form was achieved by heating the materials to 400 °C for 1 hr in a tube furnace while a stream of 10% H_2S in nitrogen was passed over the material. In each case, this resulted in the formation of a black powder that was readied for use by pressing into a pellet.

In this study, the lath and scaffold aluminas were separately loaded with 6%, 9%, and 12% Mo by mass. These samples are denoted by their morphology and loading. For example, the scaffold alumina with a 9% Mo loading is referred to as

Scaffold-9. The loading of the commercial Crosfield 465 catalyst was in the range of 10-20% Mo by mass. It was sulfided as received.

4.2.2. Reactor Design and Experimental Conditions

The HDS pilot plant used in this study is housed in the Chemical Technology Division of Argonne National Laboratory, Argonne, IL. The automated, continuous-flow unit is made primarily of 316 stainless steel tubing. Liquid feed in all experiments was 0.8 wt% S as dibenzothiophene (DBT) in hexadecane. This feed is representative of the kind of sulfur present in a middle distillate oil. The gas feed is a hydrogen and nitrogen mixture. Both the liquid and gas feeds are separately pumped through the system, eventually mixing together prior to entering the preheater furnace. At this point, the liquid is vaporized and all feed exits the preheater in the gas state. The feed is next passed through the reactor furnace and over the catalyst bed. The bed contains approximately 1g of catalyst diluted with 2g SiC, resting between plugs of glass wool. The reaction products are swept out of the reactor and separated. Liquid products are condensed and collected while gas products, mainly H_2S , are passed through a NaOH scrubber solution before being vented. A schematic of the system is provided in Figure 4.1.

The typical reaction conditions were as follows. All liquid lines were heated to 35 °C to prevent the hexadecane from plugging the line. The preheater furnace was set to 350 °C and the reactor furnace to 400 °C. The nitrogen flow was set at 200 cc/min and hydrogen at 500 cc/min. The system was purged and the liquid

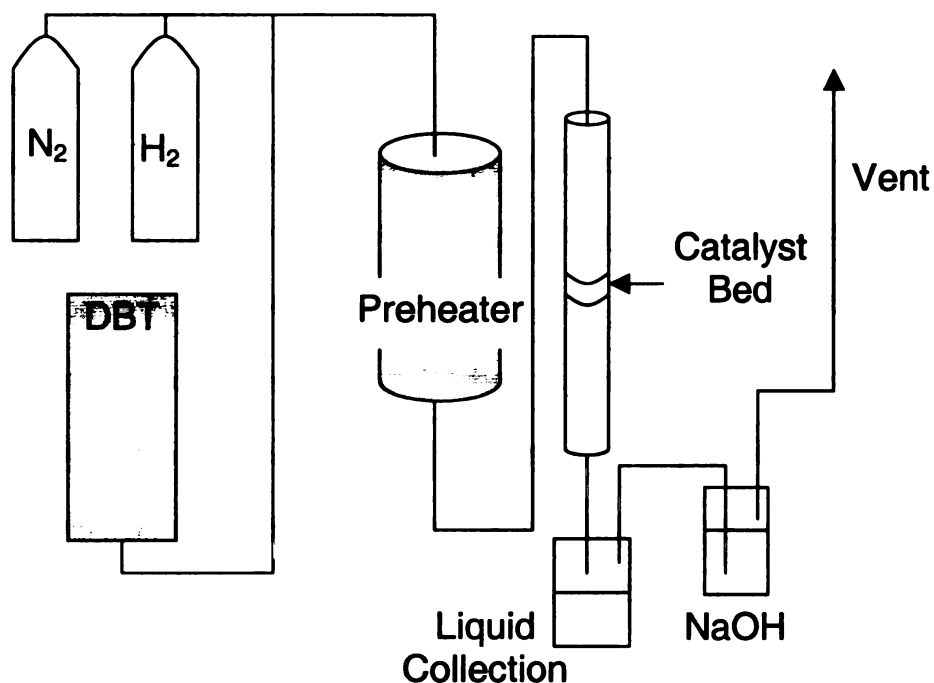


Figure 4.1. Schematic of the HDS reactor employed in the study. The liquid feed of dibenzothiophene in hexadecane was introduced to the gas feed, a mixture of hydrogen and nitrogen. The two feeds are passed through the preheater (set to 350 °C), where all feed is vaporized. Then the feed reactants are passed over the catalyst bed at 400 °C. Liquid products are condensed and collected while gas products are scrubbed in 2M NaOH prior to venting.

feed was introduced. The system pressure was set to 400 psi and was controlled by a back pressure regulator. Liquid products were collected at desired intervals.

4.2.3. Characterization

Catalysts were characterized by powder x-ray diffraction (XRD), nitrogen adsorption, and transmission electron microscopy (TEM). XRD patterns were obtained on a Rigaku Rotoflex diffractometer with Cu K α radiation of 1.54 Å. Nitrogen adsorption – desorption isotherms were collected on a Micromeritics TriStar 3000 sorptometer at 77K. Samples were degassed at least 12 hours at 150 °C under a vacuum of 10⁻⁶ torr prior to analysis. Surface areas and pore sizes were determined by the BET²⁰ and BJH²¹ methods, respectively. TEM images were collected on a JEOL 100CX microscope with a CeB₆ filament at an accelerating voltage of 120 kV. Samples were prepared by sonicating a suspension of the powder in ethanol for 20 min. One to two drops of the suspension were then placed on a carbon coated holey film that was supported on a 3 mm, 300 mesh copper grid.

Liquid collections from the HDS reactor were diluted in hexane for GC-MS analysis. The products were separated on a DB5-MS column and analyzed using an HP 5890 GC-MS Series II Plus. The conversion was determined as the percentage of DBT converted to products. The selectivity was defined as the percentage of product that is biphenyl.

4.3. Results and Discussion

4.3.1. Catalytic Reactions

In all cases, the product mixture of the HDS reactions contained biphenyl, cyclohexylbenzene (CHB), 4H-DBT (the ring hydrogenated product of DBT), and unreacted DBT. Reaction pathways are provided in Figure 4.2. From the conversion and selectivity data presented in Table 4.1, it can be seen that conversions roughly increase with metal loading. It is interesting that for both aluminas, the 9% loaded samples show a drop in conversion from that of the 6% loaded samples. As expected, conversions are highest for the 12% loaded samples, with a maximum of 87% for the scaffold-12 catalyst. Comparing selectivities, those of the scaffold catalysts are consistently higher than those of the lath catalysts. As the 12% loaded samples showed the highest conversions and were the most selective, these catalysts were studied in more detail. It should be noted, however, that both MSU- γ catalyst at all loadings show results comparable or superior to those obtained from the commercial catalyst tested under similar conditions. The Crosfield catalyst had a conversion of 77% and a selectivity for biphenyl of 61%, for a percent yield of biphenyl of 47%. The MSU- γ lath-12 and scaffold-12 catalyst led to biphenyl yields as high as 49% and 84%, respectively.

Table 4.1. Results of HDS reactions over MSU- γ catalysts exhibiting distinctly different morphologies.

Sample ^a	Time (hr)	DBT Conversion ^b %	Biphenyl Selectivity ^c %	Biphenyl Yield %
Lath -6	1	53	43	23
	2	79	62	49
	3	69	62	43
Lath -9	1	62	58	36
	2	66	58	38
	3	64	60	38
Lath-12	1	72	63	45
	2	78	61	48
	3	77	64	49
Scaffold-6	1	59	52	31
	2	76	73	55
	3	74	89	66
Scaffold-9	1	61	94	57
	2	67	89	60
	3	67	93	62
Scaffold-12	1	73	99	72
	2	87	93	81
	3	86	98	84

^a The number refers to the loading of Mo, expressed as a mass percentage of material

^b percentage of initial DBT converted

^c percentage of biphenyl in product

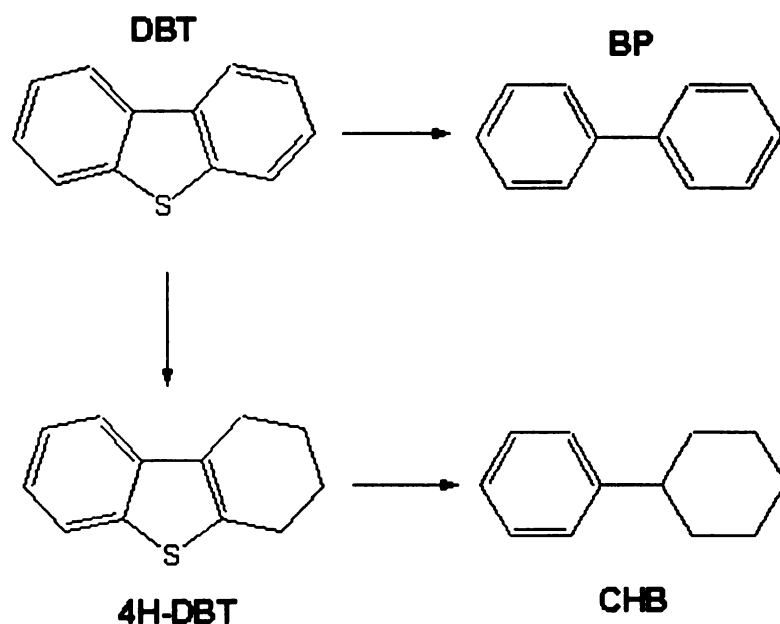


Figure 4.2. Reaction pathways of DBT in HDS reactions. The upper pathway involves direct desulfurization leading to the formation of biphenyl (BP). The lower pathway involves a hydrogenation step prior to desulfurization, leading to the formation of cyclohexylbenzene (CHB).

4.3.2. Structural and Textural Properties of MSU- γ Catalysts

Structural and textural properties were measured at several stages throughout the catalyst preparation and testing processes. Powder XRD patterns and nitrogen adsorption – desorption isotherms were obtained for each catalyst after each of the following: alumina synthesis, metal loading, sulfiding, and catalytic testing. The catalysts at each of these stages are referred to as pristine, loaded, sulfided, and spent, respectively. The properties of a commercial catalyst, Crosfield 465, are included for comparison.

The wide angle powder XRD patterns for the lath-12, scaffold-12, and Crosfield catalysts are provided in Figures 4.3 – 4.5, respectively. The structural integrity of the MSU- γ aluminas remained intact over the duration of the processing and HDS reaction; the γ -Al₂O₃ phase is evident in each pattern. The Crosfield 465 catalyst shows different behavior. After sulfiding, the alumina peaks become increasingly broad, possibility due to the formation of mixed phases, or more likely, due to coating of the alumina surface by highly dispersed MoS₂, leading to a decrease in the γ -Al₂O₃ peak intensities. Restacking of the MoS₂ may occur in the spent catalyst, exposing the γ -Al₂O₃ support. The pattern of the spent catalyst shows peaks that are assignable to both the γ -Al₂O₃ and poorly crystalline MoS₂ phases. The absence of reflections consistent with MoS₂ in any of the MSU- γ catalysts' diffraction patterns indicates that the active catalytic phase is present in small domains and is well dispersed on the supports. Similar behavior (not shown) is observed in the lower metal content samples as well.

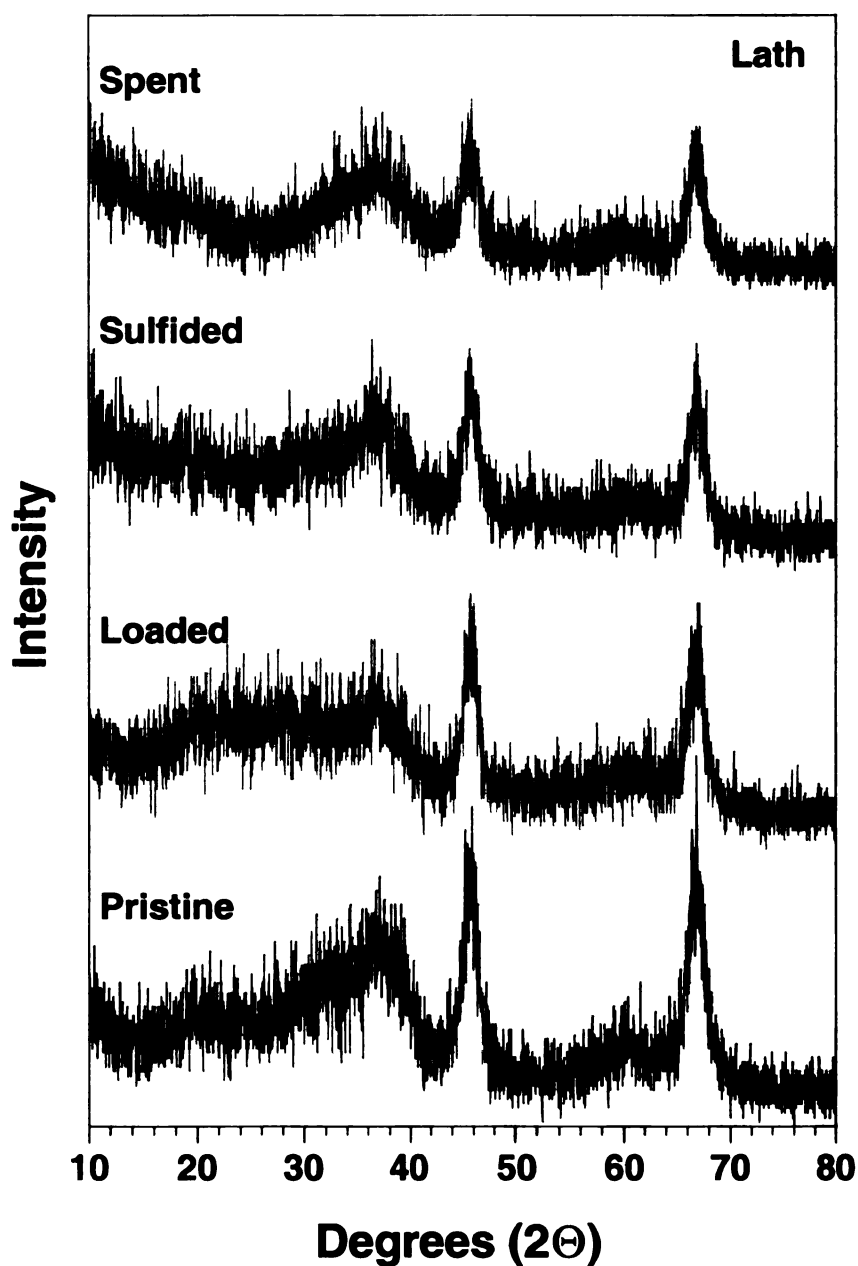


Figure 4.3. Wide angle XRD patterns for lath-12 MSU- γ alumina taken at various stages of the catalytic testing process. The γ - Al_2O_3 phase is evident throughout the process and the lack of peaks assignable to MoS_2 indicate that the active catalyst is present in small domains and is well dispersed on the support.

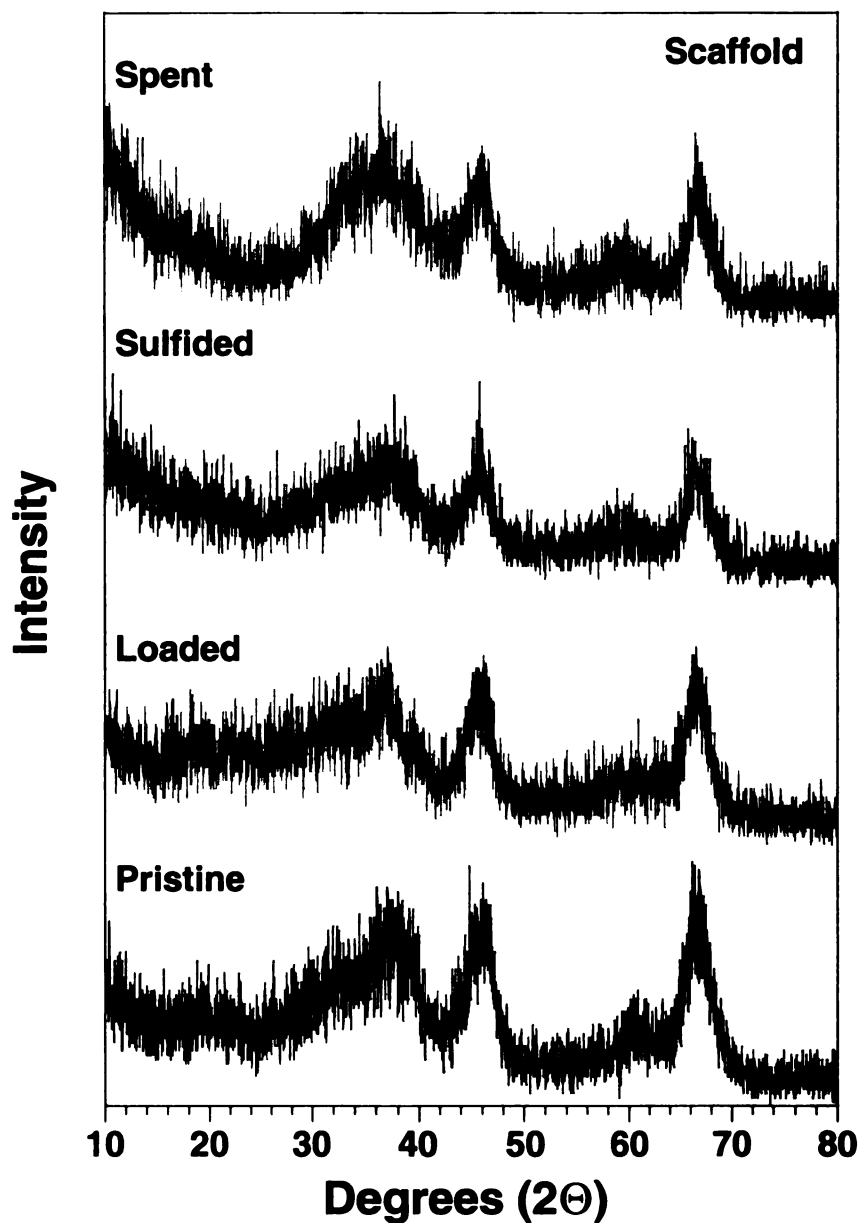


Figure 4.4. Wide angle XRD patterns for scaffold-12 MSU- γ aluminas taken at various stages of the catalytic testing process. The γ - Al_2O_3 phase is evident throughout the process and the lack of peaks assignable to MoS_2 indicate that the active catalyst is present in small domains and is well dispersed on the support.

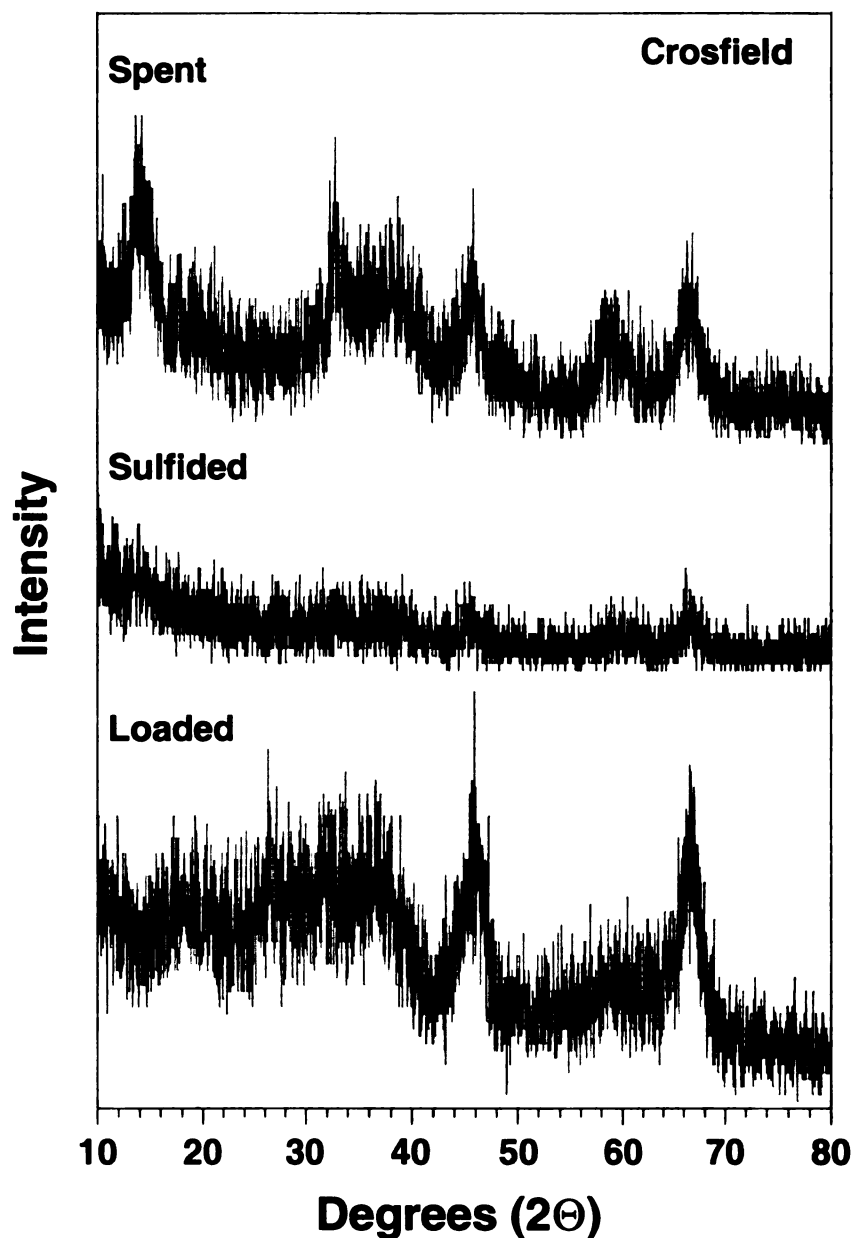


Figure 4.5. Wide angle XRD patterns for the commercial Crosfield catalyst, taken at various stages of the catalytic testing process. The decrease in intensity of the peaks assignable to $\gamma\text{-Al}_2\text{O}_3$ in the pattern of the sulfided sample may be due to the coating of the alumina surface by small domains of MoS_2 . Peaks from $\gamma\text{-Al}_2\text{O}_3$ and MoS_2 in the pattern of the spent sample indicate that MoS_2 particles may aggregate sufficiently to cause scattering and expose the surface of the support.

Upon inspection of the nitrogen adsorption – desorption isotherms of the 12% Mo loaded samples, Figures 4.6 and 4.7, it is clear that the metal loading, sulfiding, and catalytic testing have a deleterious effect upon the pore structure and textural properties of these catalysts. As the active catalytic phase is introduced onto the support, the pore size, pore volume, and surface area will naturally decrease. As shown in Table 4.2, in the lath-12 series, the pore volume is reduced to 25% of its original value after use in the HDS reaction. The scaffold-12 catalysts are the most resistant to the conditions imposed by this process as they retain approximately 45% of their original pore volumes. The effect is more pronounced at higher metal loading in each sample. A similar trend is observed in the surface areas of these materials. Again, the scaffold-12 alumina exhibits the highest degree of structural integrity, retaining approximately 65% of its original surface area while the lath-12 retains only 15%.

In the case of the lath aluminas, at any point after loading the metal, the pores appear to collapse, leaving only a small amount of porosity. The pore size distributions are so broad that it is not possible to determine a mean pore size for the catalyst at any point after loading (inset, Figure 4.6). In the scaffold-12 catalysts, the pore size distribution shifts to a smaller average pore size throughout the process (inset, Figure 4.7). Comparing the MSU- γ catalysts to the commercial catalyst, the scaffold-12 catalyst exhibits adsorption behavior most similar to the Crosfield catalyst (Figure 4.8). The textural properties of the lath, scaffold, and commercial catalyst are summarized in Table 4.2.

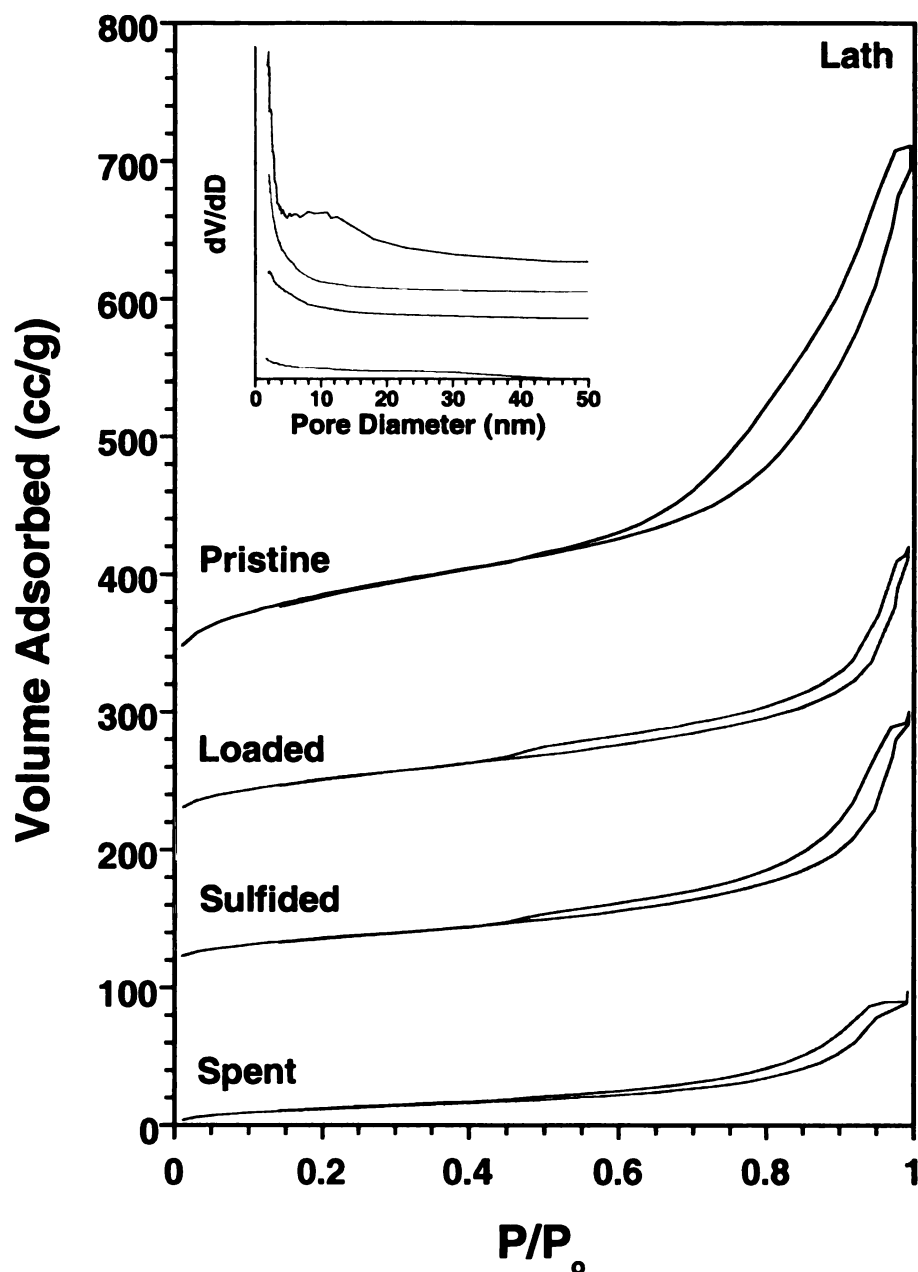


Figure 4.6. Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for lath-12 MSU- γ catalysts taken at various stages of the catalytic testing process. The pore volume steadily decreases as the catalyst is loaded, sulfided, and spent. Isotherms are offset 100 cc/g for clarity and PSD curves are displayed in the same order as the corresponding isotherms.

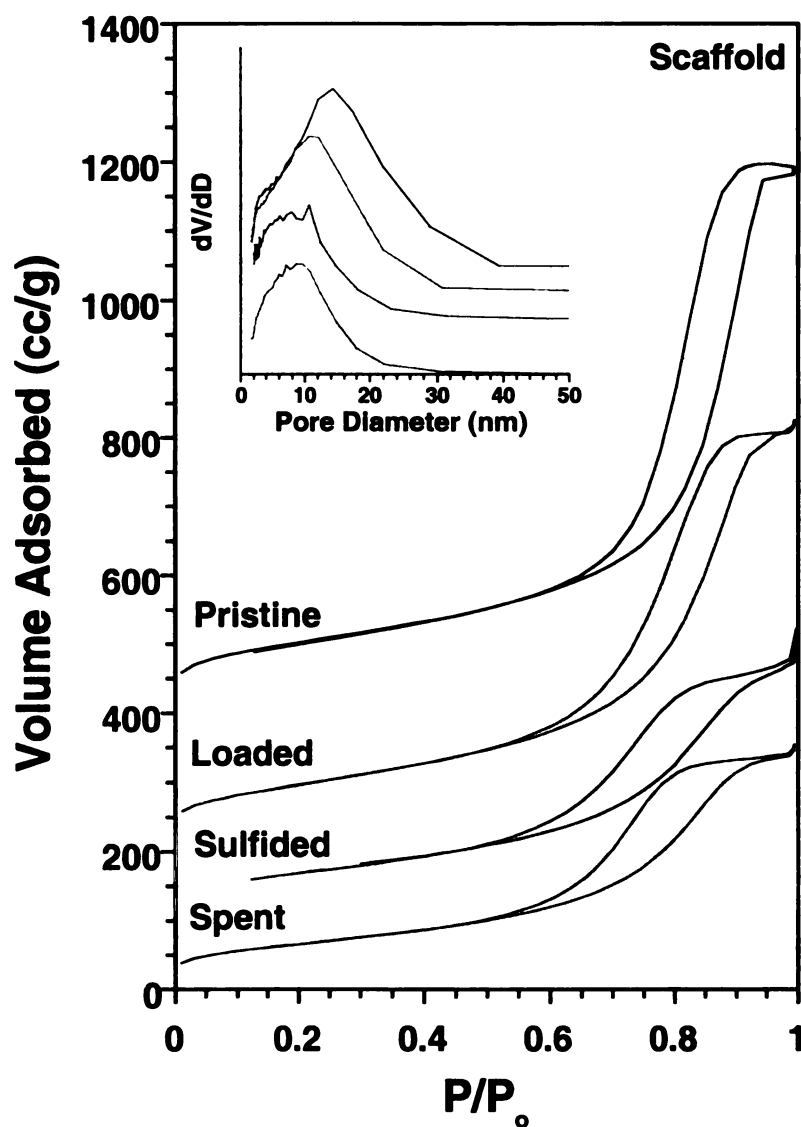


Figure 4.7. Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for scaffold-12 MSU- γ catalysts taken at various stages of the catalytic testing process. The pore volume decreases slightly as the catalyst is loaded, sulfided, and spent while the pore size is increased and the distribution broadened over the same conditions. Isotherms are offset 0, 100, 100, and 200 cc/g from bottom to top for clarity and PSD curves are displayed in the same order as the corresponding isotherms.

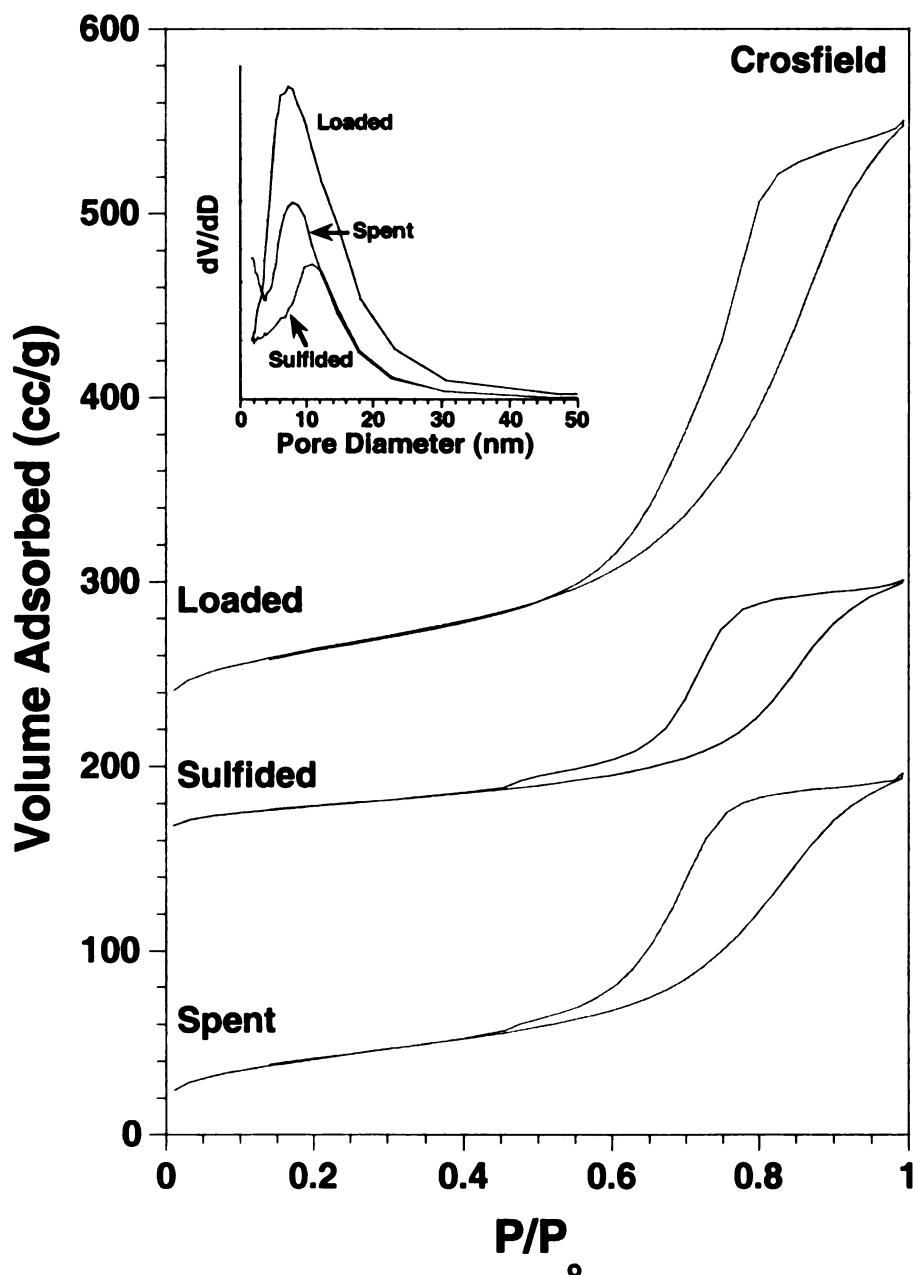


Figure 4.8. Nitrogen adsorption – desorption isotherms and BJH adsorption pore size distributions (inset) for the commercial Crosfield catalyst taken at various stages of the catalytic testing process. The pore volume decreases slightly as the catalyst is sulfided and spent. However, the pore size and distribution remain relatively unaffected over the same conditions. Isotherms are offset 100 cc/g for clarity and PSD curves are displayed in the same order as the corresponding isotherms.

Table 4.2. Textural properties of MSU- γ alumina HDS catalysts.

Sample	Condition	Pore Volume (cc/g)	BET Surface Area (m ² /g)	BJH Pore Size – Ads. (nm)
Lath-6	Pristine	0.60	309	10.0
	Loaded	0.56	234	--
	Sulfided	0.35	158	--
	Spent	0.28	140	--
Lath-9	Pristine	0.60	309	10.0
	Loaded	0.39	213	--
	Sulfided	0.35	159	--
	Spent	0.21	76	--
Lath-12	Pristine	0.60	309	10.0
	Loaded	0.33	182	--
	Sulfided	0.31	127	--
	Spent	0.15	47	--
Scaffold-6	Pristine	1.23	368	13.0
	Loaded	0.97	354	11.0
	Sulfided	0.77	270	11.0
	Spent	0.51	223	8.0
Scaffold-9	Pristine	1.23	368	13.0
	Loaded	0.58	335	4.0
	Sulfided	0.48	271	4.0
	Spent	0.44	249	4.0
Scaffold-12	Pristine	1.23	368	13.0
	Loaded	0.98	350	12.0
	Sulfided	0.58	261	9.0
	Spent	0.56	238	9.0
Crosfield	Loaded	0.55	223	7.5
	Sulfided	0.24	100	11.0
	Spent	0.31	147	8.0

It is understandable that the scaffold and commercial catalyst have similar adsorption behavior as they exhibit similarities in morphology as well. Figures 4.9 through 4.11 provide a series of TEM images comparing the particle morphology of the loaded catalysts with that of the spent catalysts. The morphology of the scaffold-12 and commercial catalysts is largely unaffected after use in the HDS reaction. However, the long range order in the lath-12 catalyst has been destroyed to some extent. The insets in each case show an approximately 30 nm by 30 nm area. It can be seen that the local pore structure in each catalyst remains nearly unchanged. The decrease in pore volume, as determined from the isotherms, is reflected in these images.

4.3.3. Relationships Between Catalyst Structure and Performance

While both MSU- γ catalysts were effective in HDS reactions, the scaffold aluminas do show better performance than the lath aluminas. This can be explained by the differences in morphology of the alumina support. The pores in the lath aluminas are slit-like and run in the direction of the fundamental particles comprising the framework. Contrast that to the scaffold aluminas, where the pores are void spaces between randomly oriented fundamental particles. This leads to two different MoS₂ particle sizes when supported on the aluminas.

The layered structure of MoS₂ is highly anisotropic. The sheets of MoS₂ can extend a thousand-fold the distance in the stack direction, leading to the formation of a large, but catalytically inactive, basal plane. It has been realized that only the edge planes of the material contain the catalytically active sites.

Figure 4.9. Bright field TEM images of the scaffold-12 MSU- γ catalyst (A) after loading and (B) after using in an HDS reaction for 3 hr at 400 °C and 400 psi. The scale bar represents 100 nm. The inset is an approximately 30 nm x 30 nm area of the catalyst. That the framework of the alumina is largely unaffected by the conditions of the HDS reaction provides evidence of its stability.

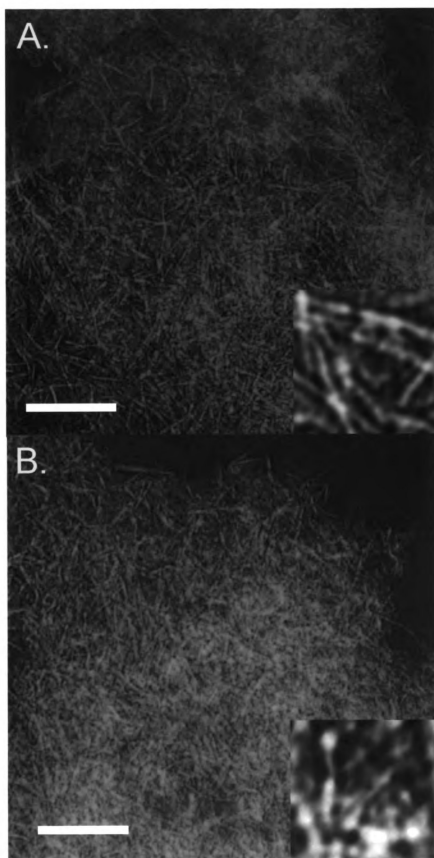


Figure 4.10. Bright field TEM images of the lath-12 MSU- γ catalyst (A) after loading and (B) after using in an HDS reaction for 3 hr at 400 °C and 400 psi. The scale bar represents 100 nm. The inset is an approximately 30 nm x 30 nm area of the catalyst. The local pore structure (inset) is compromised to some degree, as is shown by the decreased void space in (B) as compared with (A). The long range order of the alumina laths is lost after use in the HDS reaction.

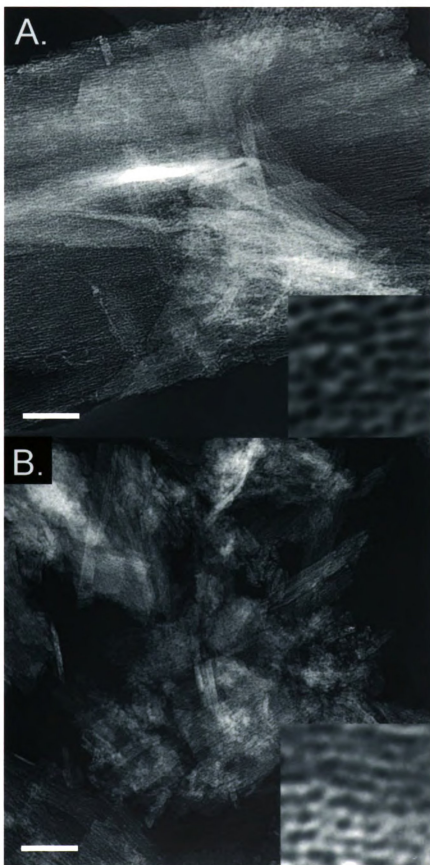
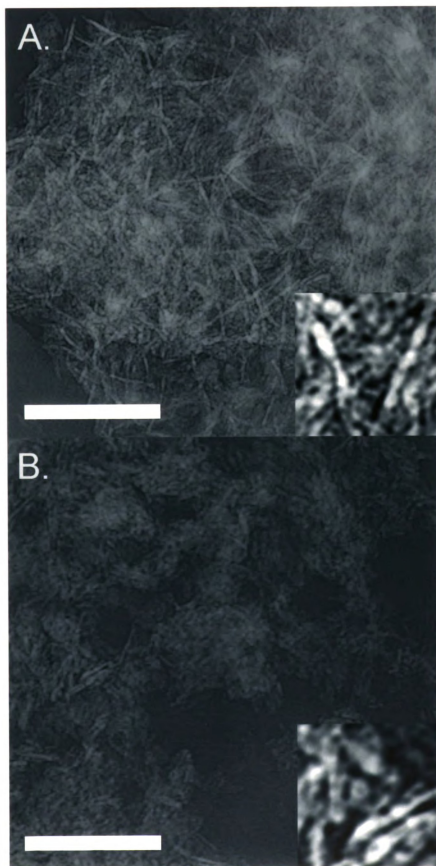


Figure 4.11. Bright field TEM images of the commercial Crosfield catalyst (A) after loading and (B) after using in an HDS reaction for 3 hr at 400 °C and 400 psi. The scale bar represents 100 nm. The inset is an approximately 30 nm x 30 nm area of the catalyst. Although the local pore structure (inset) appears to withstand the conditions encountered in the HDS reaction, it appears that there is some aggregation of the fundamental particles after use.



While the basal plane contributes greatly to the surface area of the catalyst, the surface area does not correlate with activity in HDS²². The edge planes contain the sulfur vacancies that are the active sites in HDS.

Comparing the structures, there is a good match in morphology between the pore structure in the MSU- γ lath catalyst and MoS₂. Still, the pores will limit the extent of the growth of MoS₂ in the direction perpendicular to the planes, leading to the formation of truncated slabs of the active sulfide on the MSU- γ laths. This leads to highly dispersed, small domains of MoS₂.

The pore structure of the MSU- γ scaffolds is not as ordered as in the MSU- γ laths. Additionally, the fibers of alumina constituting the framework do not provide a good area for MoS₂ to grow into large sheets. Consequently, the growth of MoS₂ should be greater in the layer stacking direction on MSU- γ scaffolds than on MSU- γ laths. For the same molybdenum loading, a more highly stacked MoS₂ particle will provide a greater number of edge sites than will a lesser stacked particle. This is one contributing factor to the greater conversion on MSU- γ scaffolds than on MSU- γ laths. Secondly, due to the nature of the open framework in the scaffold catalyst, access to these catalytically active edge sites may be increased as well.

While the conversions on MSU- γ catalysts are comparable, the selectivities are much better for the scaffolds than for the laths. The differences in selectivity are addressed by the rim – edge model of the MoS₂ catalyst^{23,24}. If the MoS₂ particle is viewed as a stack of discs, then the edge sites are divided into two categories, distinguished by their location within the stack (Figure 4.12). Sites on

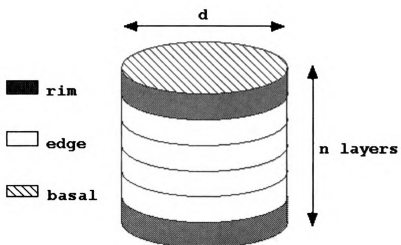
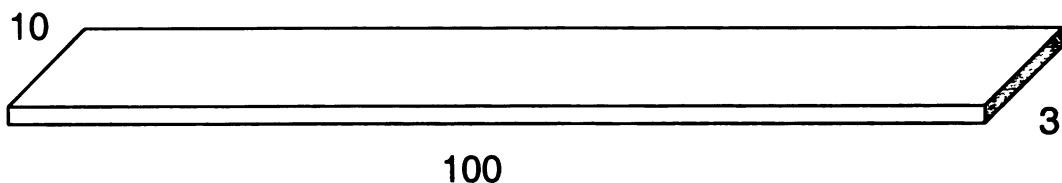


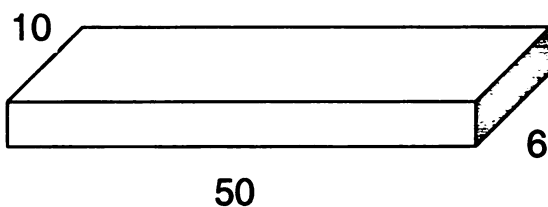
Figure 4.12. The Daage-Chianelli rim-edge model of the MoS₂ catalyst particle. Sulfur removal takes place on rim and edge sites while hydrogenation of the aromatic ring is restricted to rim sites only²⁴.

the top and bottom discs are designated rim sites and all others as edge sites. The taller the stack, the higher the edge / rim ratio. In the development of this model, Daage and Chianelli found that hydrogenation rates were inversely proportional to the stack height. It was therefore concluded that hydrogenation takes place only on the rim sites where sulfur removal (HDS) occurs on both sites.

On MSU- γ catalysts, a greater stack height on the scaffold catalysts is in accord with the increased selectivity. Having shorter but wider particles of MoS₂ on the lath catalysts also agrees with the model. While it is argued above that merely increasing the stack height will lead to a higher conversion due to an increased number of edge sites, it is clear that particle size effects have a greater influence on selectivity than conversion. As an example, consider the blocks in Figure 4.13 to represent MoS₂ particles. Keeping the overall amount of MoS₂ the same, but chopping the slab in half and stacking the two pieces on top of each other, a larger number of edge sites are created. The more pronounced effect is that the ratio of rim sites to rim plus edge sites is decreased. This is in line with the data; selectivities are much better on scaffolds than on laths, while conversions are comparable at a given loading.



Total Edge Sites: 660
 $\text{Rim} / (\text{Rim} + \text{Edge}) = 0.66$



Total Edge Sites: 720
 $\text{Rim} / (\text{Rim} + \text{Edge}) = 0.33$

Figure 4.13. Influence of morphology on the ratio of rim sites to total sites available on the edges of MoS₂ particles. While increasing the stack height leads to a slight increase in the overall number of edge sites, the more pronounced effect is the decrease in the relative number of rim sites.

4.4. Conclusions

MSU- γ aluminas were used effectively as catalyst supports for HDS catalysis. These crystalline mesostructured aluminas are capable of dispersing up to a 12% loading of molybdenum and able to withstand the harsh conditions encountered during the reaction. MSU- γ aluminas with lath morphology had conversions and selectivities comparable to a commercial catalyst while the aluminas with scaffold morphology had conversions and selectivities superior to the commercial catalyst. The MSU- γ alumina supports may lead to more economical catalysts, as greater conversions and selectivities are obtained with lesser quantity of active catalyst.

The difference in performance of the two MSU- γ aluminas is attributed to morphological matching with the catalytically active MoS₂ phase. The laths promote growth of MoS₂ in a sheet-like morphology while scaffolds lead to increased stacking in a direction perpendicular to the layers of MoS₂. Additionally, the open framework and larger pore volume of the scaffold alumina as compared to the lath alumina may provide easier access to catalytically active edge sites of MoS₂. Viewed in the rim-edge model of MoS₂ catalysts, these results are reasonable.

4.5. Future Directions

This initial venture into utilization of MSU- γ aluminas in HDS reactions was fruitful, but there are some aspects that can be explored further. Can MSU- γ aluminas be loaded with an increased mass of molybdenum? Some industrial

catalysts contain upwards of 20% molybdenum. The method of incorporation employed in this study was incipient wetness impregnation. Supports are loaded based upon their pore volume. The limiting factor is the solubility of the metal salt in the volume available with which to work. The higher pore volume of the scaffold materials may be better able to accommodate a higher loading. Otherwise, an alternative method will be needed.

HDS reactions were limited to 3 hour runs. What is the longevity of the MSU- γ catalyst? Can it remain on stream for extended periods of time? The average life of industrial catalysts may be approaching two years. Are MSU- γ catalysts poisoned after a certain time? If so, can they be recycled or regenerated?

How do MSU- γ catalysts perform with other substrates? As oil crudes become increasingly dirtier, larger molecules with sterically hindered sulfur atoms, such as 4,6-dimethyldibenzothiophene become more prevalent. The larger molecules present the toughest challenge in HDS. How do MSU- γ aluminas perform with real oil feeds?

There are reports in the literature employing lanthanide doped aluminas as supports for catalysts²⁵. Noting that similar doping of MSU- γ aluminas actually decreased the hydrothermal stability of the materials, it is possible that such an experiment would be of little value here.

Finally, there has been a report of a new HDS catalyst claiming to have superior activity as compared to any catalyst currently in existence. This new catalyst, marketed under the name Nebula, was developed jointly by Akzo-Nobel, ExxonMobil, and Nippon Ketjen²⁴. Nebula catalysts are not based upon an

alumina support as many of its predecessors are. These catalysts are already being used in European refineries to produce low sulfur diesel fuels. Consequently, there may be a shift in direction in research and development of HDS catalysts. What fate that holds for alumina based catalysts is yet to be determined.

4.6. References

- (1) In *New York Times*: New York, NY, 2000.
- (2) Chianelli, R. R. *NATO ASI Ser., Ser. C* **1983**, *105*, 361-378.
- (3) Topsoe, H.; Clausen, B. S. *Catal. Rev. - Sci. Eng.* **1984**, *26*, 395-420.
- (4) Chianelli, R. R. *ACS Symp. Ser.* **1985**, *279*, 221-234.
- (5) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev. - Sci. Eng.* **1989**, *31*, 1-41.
- (6) Harris, S.; Chianelli, R. R. *Theor. Aspects Heterog. Catal.* **1990**, 206-255.
- (7) Chianelli, R. R.; Daage, M.; Ledoux, M. J. *Adv. Catal.* **1994**, *40*, 177-232.
- (8) Hensen, E. J. M.; De Beer, V. H. J.; Van Santen, R. A. *NATO ASI Ser., Ser. 3* **1998**, *60*, 169-188.
- (9) Nielsen, L. P.; Christensen, S. V.; Topsoe, H.; Clausen, B. S. *Catalysis Letters* **2000**, *67*, 81-85.
- (10) Hensen, E. J. M.; Brans, H. J. A.; Lardinois, G. M. H. J.; De Beer, V. H. J.; Van Veen, J. A. R.; Van Santen, R. A. *J. Catal.* **2000**, *192*, 98-107.
- (11) Farag, H.; Whitehurst, D. D.; Sakanishi, K.; Mochida, I. *Catal. Today* **1999**, *50*, 9-17.
- (12) Ledoux, M. J.; Michaux, O.; Agostini, G.; Panissod, P. *J. Catal.* **1986**, *102*, 275-288.
- (13) Carrado, K. A.; Xu, L.; Marshall, C. L.; Wei, D.; Seifert, S.; Bloomquist, C. A. *Stud. Surf. Sci. Catal.* **2000**, *129*, 417-424.
- (14) Carrado, K. A.; Marshall, C. L.; Brenner, J. R.; Song, K. *Microporous Mesoporous Mater.* **1998**, *20*, 17-26.
- (15) Yue, Y.; Sun, Y.; Gao, Z. *Catalysis Letters* **1997**, *47*, 167-171.
- (16) Song, C.; Reddy, K. M. *Appl. Catal., A* **1999**, *176*, 1-10.
- (17) Ramirez, J.; Contreras, R.; Castillo, P.; Klimova, T.; Zarate, R.; Luna, R. *Appl. Catal., A* **2000**, *197*, 69-78.
- (18) Okamoto, Y. *Catalysis Today* **1997**, *39*, 45-59.

- (19) Zhang, Z.; Hicks, R. W.; Pauly, T. R.; Pinnavaia, T. J. *Journal of the American Chemical Society* **2002**, *124*, 1592-1593.
- (20) Tauster, S. J.; Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1980**, *63*, 515-519.
- (21) Daage, M.; Chianelli, R. R.; Ruppert, A. F. *Stud. Surf. Sci. Catal.* **1993**, *75*, 571-584.
- (22) Daage, M.; Chianelli, R. R. *J. Catal.* **1994**, *149*, 414-427.
- (23) Miciukiewicz, J.; Laniecki, M.; Domka, F. *Catalysis Letters* **1998**, *51*, 65-68.
- (24) Internet publication currently available on the ExxonMobil website:
http://www.exxonmobil.com/refiningtechnologies/pdf/h7_nebula.pdf

Chapter 5

Concluding Remarks

A Commentary

As mentioned in the introduction, there has been little progress made in the development of mesostructured aluminas relative to other metal oxides. At the start of this work, all known mesostructured aluminas were amorphous in nature. This work has demonstrated a considerable achievement in reporting at least two new crystalline forms of mesostructured alumina. Alumina has uses in numerous applications as a catalyst support or as a component in catalyst system. HDS was just one arena in which the utility of these new materials could have been demonstrated. The improvement in textural properties, along with the stability of these materials, provides great potential to MSU- γ aluminas for use in a variety of catalytic applications.

To fully reach this potential, eventually the syntheses reported here will need to be commercialized. That leads to one important drawback regarding these materials. They are made from relatively expensive precursors of polyalkylene oxides and aluminum alkoxide. Will other applications prove it necessary to scale up this production of this material? Are the increased costs balanced by increased performance? These are questions that will be addressed at some time in the future.

On a personal note, this project has been very challenging. There were times that I wondered if anything would come out of it. Of course, in the end it has been

very rewarding. I am satisfied with the contributions that I have made to build upon existing knowledge. It has only been ten years since Mobil's initial disclosure of the M41S family of materials. So while the entire field of mesostructured materials is relatively new, the subset of mesostructured aluminas is in infancy.

I'm excited that I have had the opportunity to create some of the pioneering work in this field. MSU and the Pinnavaia group have been at the forefront of this from the beginning. The first mesostructured alumina and now the first crystalline mesostructured aluminas have developed in these labs. Finally, I am proud to be in the lineage of scientists that have contributed to this project. It started with Steve Bagshaw, continued with Peter Tanev, Wenzhong Zhang, myself, and is now left in the capable hands of Zhaorong Zhang (and future additions to the Pinnavaia group). There is still progress to be made in this field and I look forward to the future contributions from this group.

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 02327 1012