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MECHANO CHEMISTRY FOR SOLID-STATE SYNTHESSES AND CATALYSIS

by

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B.S. University of Central Florida, 2008

A dissertation submitted in partial fulfillment of the requirements
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ABSTRACT

Traditional methods of synthesizing inorganic materials, such as hydrothermal, sol-gel, calcination and grinding steps, can typically require use of high temperatures, expensive precursors or use of solvents. Because of the energy-intensive nature or environmental impact these techniques, there is a push, especially from an industrial perspective, to move towards greener approaches. Mechanochemistry is a solvent-free alternative technique that can be used to synthesize a variety of materials under ambient conditions. Due to this, there is an increase in attention towards the use of this approach in both solid-state inorganic and organic chemistry.

This dissertation reports the mechanochemical synthesis of a few inorganic materials without the need of using high temperatures or solvents. Additionally, examples are presented in which mechanochemistry is used in conjunction with a secondary technique. This mechanical activation of the precursors lead to a decrease in calcination temperature and reactions times, as well as alteration of properties or unique reaction products. The synthesis of kaolinite, vanadia nanostructures, and spinels were carried out in this fashion. Mechanical activation of the precursors allowed for reduced hydrothermal treatment times in case of both kaolinite and vanadia nanostructures and the spinels are calcined at lower temperature for shorter periods of time. In addition, we report alternative template agents than previously reported for the formation of vanadia nanotubes, and report the formation of nanorods. Choosing the appropriate amine template can alter the structure and size of the material.

Isomorphously substituted mixed oxides, kaolinite and spinels (MgAl$_2$O$_4$ and ZnAl$_2$O$_4$) were synthesized through a mechanically assisted process. Kaolinites are treated hydrothermally
for 1 week at 250 ºC to produce an X-ray pure crystalline material. The spinels undergo calcination as low as 500 ºC to produce a nanocrystalline material. Rare-earth metals and transition metals were used as the substitutional atom. The substituted kaolinites exhibit strong order along the c axis, but less ordering along the a and b axes. Trivalent chromium and trivalent rare-earth metals, such as La, Ce, Pr, Nd, Eu, Gd, Ho, and Er, are used to replace aluminum in the structure. Likewise, divalent and trivalent transition, such as Mn, Ni, Cu and Cr, are used as the substitutional atoms in MgAl₂O₄ and ZnAl₂O₄. Cathodoluminescence studies on the substituted Spinel structure show that Mn²⁺ ions can occupy both the tetrahedral or octahedral holes to give a green and red emission, respectively. On the other hand, Cr³⁺ ions only occupy the octahedral holes to yield a red emission, similar to that in ruby. These isomorphously substituted materials may have potential applications in catalysis or glaze materials in ceramics.

Oxidized graphite, an alternative to graphite oxide and graphene, can be synthesized rapidly by mechanochemical means. Grinding urea hydrogen peroxide adduct with graphite without the need of a solvent produces a product with an oxygen content of 5-15 wt%. The byproducts of this reaction are urea and water. This material is oxidized along the edges of the sheets, allowing it to be hydrophilic while retaining the conductivity. The material can suspend in water and processing allows for films of resistivities between 50 Ω cm⁻² and 10 kΩ cm⁻². It was determined that the edges are fully oxidized to yield –COOH groups. This process offers a scalable, environmentally benign route to large quantities of oxidized graphite.

An alternative method for the synthesis of nanostructured vanadia is reported. This process involves mechanical grinding of vanadium pentoxide, V₂O₅, with an amine template,
such as diphenylamine, theophylline, rhodamine 6G and rhodamine, prior to hydrothermal
treatment. This allows for the synthesis of VO₃ nanotubes and nanorods dependent on which
template is used. Diphenylamine, theophylline, and rhodamine B produce nanorods. Use of
rhodamine 6G produces asymmetric VO₃ nanorods.

In addition to the mixed metals oxides mentioned above, sodium and calcium tantalates
are synthesized mechanically. This route does not require the need of elevated temperatures or
expensive and hazardous materials. X-ray diffraction analysis of NaTaO₃, Ca₂Ta₂O₇, Ca₄Ta₂O₉
and CaTa₂O₆ shows that these are the only phases detected after 4 h, 10 h, 27 h and 10 h of
milling, respectively. During the synthesis of Ca₂Ta₂O₇, an intermediate phase, Ca₄Ta₂O₉, forms
within 1 h, which reacts after 5 h to form the desired product. Reference Intensity Ratio analysis
shows that the material synthesized mechanically is nanocrystalline Ca₂Ta₂O₇.

Nanocrystalline ZrSi₂ can also be obtained through mechanochemical synthesis. This
method allows for size control and results in crystallites ranging from 9 to 30 nm. Dilution with
CaCl₂ enables the size control process. A linear relationship exists between the concentration of
CaCl₂ and the crystallite size. Contrary to a typical self-propagating metathesis reaction, this
process does not allow for self-propagation and requires continuous input of mechanical energy
to continue. However, this method allows for non-passivated nanoparticles of ZrSi₂, which can
be incorporated into composites as a reinforcement material for several applications.

Hard and ultra-compressible borides, such as ReB₂ and OsB₂, can be synthesized
mechanically. The traditional synthesis of ReB₂ requires excess boron due to treatment at high
temperatures. This can lead to amorphous boron aggregating at the grain boundaries, which in
turn, this would degrade the properties of the material. The mechanochemical approach requires mechanical treatment of Re and B powders in stoichiometric quantities for 80 h. Mechanical synthesis of OsB$_2$ powders requires a 1:3 ratio of Os and B powders. After 12 h of milling time, \textit{h}-OsB$_2$ begins to form, and is the major phase present after 18 h. The lattice parameters corresponding to the hexagonal OsB$_2$ were determined to be $a = b = 2.9047$ Å, $c = 7.4500$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. Treatment of the OsB$_2$ powder at 1050 °C under vacuum for 6 days did not induce a phase change, suggesting the hexagonal phase is very stable.

Mechanocatalysis of the depolymerization of cellulose and hydrogenation of olefins over BN are reported as well. Heterogeneous catalysis is difficult to apply to solids, such as cellulose. However, mechanical grinding of kaolin and cellulose allows for the catalysis to occur in the solid state. This process allows for a variety of different biomasses to be used as feedstock without inhibition. Kaolinite was found to be the best acid catalyst due to high surface acidity and its layered structure, allowing for up to 84% conversion of the cellulose to water-soluble compounds. This process allows for reduction of waste, insensitivity of feedstock, multiple product pathways and scalability.

Hydrogenation reactions are carried out using transition-metals catalysts. These metals have desirable catalytic properties not seen in main group elements, but there is growing concern over their use. A metal-free heterogeneous hydrogenation catalyst based on frustrated Lewis pairs would significantly reduce the health, environmental, and economic concerns associated with these metal-based catalysts. We report the first metal-free heterogeneous hydrogenation catalyst. Hydrogenation of trans-cinnamic acid is carried out over defect-laden \textit{h}-BN. The
reactor we use is designed to maximize the defects produced in BN sheets. The introduction of defects in BN creates frustrated Lewis pairs. DFT calculations show that the carbon double bond is weakened over boron substitution for nitrogen sites, vacancies of both boron and nitrogen, and Stone-Wales defects.

A new method for crystalline germanium deposition occurring at lower temperatures (210-260 °C) is reported. This method involves mechanical treatment of the precursors to reduce the particle size. A ground mixture of Ge and CuI are heated under vacuum to synthesize GeI₂. In situ disproportionation of this compound at 210 °C allows for the deposition of polycrystalline Ge films onto a both glass and polymer substrates. The rate of deposition is found to be 25 ng min⁻¹. The byproducts of this process are GeI₂, GeI₄ and Cu₃Ge, which are valuable precursors for the synthesis of germanium nanostructures and organogermainium compounds.

Mechanochemistry is also utilized for the synthesis of trisubstituted pnictides. Mechanochemical treatment of bromobenzene with either Na₃Sb or Na₃Bi allows for the formation of triphenylstibine or triphenylbismuthine, respectively. The synthesis of the alkali metals pnictide precursors is reported as well. The synthesis of triphenylstibine produces SbPh₃ as the major product from the reaction. The synthesis of triphenylbismuthine produces more Wurtz-type coupling products, which are due to the BiPh₃ acting as a catalyst. Tributyl and triphenyl analogues are reported as well. The trialkylated analogues for both Sb and Bi produce more Wurtz type coupling products. This would allow for a more cost effective and scalable, alternative methods than what is currently in use today.
Dedication to my mother, Consuelo, my father, Antonio, and my brother, Andres, for the love and support they have given me over the years as I pursued my goals in life.
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TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. xx

LIST OF TABLES ....................................................................................................................... xxxii

LIST OF SYMBOLS .................................................................................................................... xxxiii

LIST OF ACRONYMS .................................................................................................................. xxxv

CHAPTER 1: INTRODUCTION AND LITERATURE OVERVIEW ............................................. 1

1.1 Overview Of Mechanochemistry ....................................................................................... 1

1.2 Milling Equipment ............................................................................................................. 5

1.2.1 Shaker Mill ......................................................................................................................... 6

1.2.2 Planetary Mill .................................................................................................................... 7

1.2.3 Attrition Mill ..................................................................................................................... 8

1.2.4 Pebble Mill ....................................................................................................................... 10

1.3 Milling Parameters ........................................................................................................... 11

1.3.1 Milling Speed ................................................................................................................... 12

1.3.2 Ball to Mass of Reagents Ratio ....................................................................................... 13

1.3.3 Milling Vessel ................................................................................................................... 13

1.3.4 Grinding Material And Size ........................................................................................... 15

1.3.5 Milling Time ...................................................................................................................... 16

1.3.6 Vial Atmosphere ............................................................................................................. 17

1.3.7 Amount Of Free Volume ............................................................................................... 17

1.3.8 Temperature .................................................................................................................... 18

1.4 Scope of Work ................................................................................................................... 18
CHAPTER 2: MECHANOCHEMICALLY ENHANCED SYNTHESIS OF ISOMORPHOUSLY

SUBSTITUTED KAOLINITES .......................................................... 20

2.1 Introduction .............................................................................. 20

2.2 Experimental Section .............................................................. 22

2.2.1 Reagents ............................................................................ 22

2.2.2 Milling .............................................................................. 23

2.2.3 Precursor Synthesis ............................................................. 24

2.2.4 Cerium (III) Hydroxide Synthesis ........................................ 24

2.2.5 Hydrothermal Synthesis ...................................................... 25

2.2.6 Product Isolation ................................................................. 25

2.2.7 X-ray Diffraction ................................................................. 26

2.2.8 Attenuated Total Reflectance Spectroscopy ......................... 26

2.2.9 Elemental Analyses .............................................................. 27

2.2.10 Reflectance UV-Visible Spectroscopy ............................... 27

2.3 Results and Discussion ............................................................ 28

2.3.1 Synthetic Kaolinite ............................................................. 28

2.3.2 Chromium Substituted Kaolinites ........................................ 30

2.3.3 Rare-Earth Substituted Kaolinites ........................................ 35

2.4 Conclusion ............................................................................. 39

CHAPTER 3: A GREEN ROUTE TO OXIDIZED GRAPHITE .................. 41

3.1 Introduction ............................................................................. 41

3.2 Experimental ......................................................................... 43

3.2.1 Reagents ........................................................................... 43
3.2.2 Synthesis of Oxidized Graphite .................................................................44
3.2.3 Characterization ..........................................................................................45
3.2.4 Thermogravimetric Analysis ......................................................................46
3.2.5 Electrical Measurements ...........................................................................47
3.3 Results ..............................................................................................................47
3.4 Discussion ........................................................................................................54
3.5 Conclusions .....................................................................................................62

CHAPTER 4: MECHANOCHEMICALLY ASSISTED SYNTHESIS OF VANADIUM OXIDE NANOTUBES AND NANORODS USING CYCLIC AMINE TEMPLATES .................................................. 63

4.1 Introduction ......................................................................................................63
4.2 Experimental ..................................................................................................65
  4.2.1 Materials ..................................................................................................65
  4.2.2 Preparation ...............................................................................................65
  4.2.3 Characterization ......................................................................................66
4.3 Results and Discussion ..................................................................................66
4.4 Conclusion ......................................................................................................71

CHAPTER 5: MECHANOCHEMICAL SYNTHESIS OF CALCIUM AND SODIUM TANTALATES ............................................................................................................. 72

5.1 Introduction ......................................................................................................72
5.2 Experimental Section ....................................................................................74
  5.2.1 Reagents ..................................................................................................74
  5.2.2 Milling ......................................................................................................74
  5.2.3 X-ray Diffraction .....................................................................................75
5.3 Results and Discussion .........................................................................................................................75
  5.3.1 Formation of NaTaO$_3$ ......................................................................................................................75
  5.3.2 Kinetics of the Ca$_2$Ta$_2$O$_7$ System ..............................................................................................76
  5.3.3 Formation of Ca$_4$Ta$_2$O$_9$ and CaTa$_2$O$_6$ ...................................................................................80
  5.4 Conclusion .............................................................................................................................................82

CHAPTER 6: SIZE CONTROLLED MECHANOCHEMICAL SYNTHESIS OF ZrSi$_2$ .......................... 84
  6.1 Introduction ...........................................................................................................................................84
  6.2 Experimental ........................................................................................................................................85
    6.2.1 Synthesis of ZrSi$_2$ Nanocrystallites ..........................................................................................85
    6.2.2 Characterization ...........................................................................................................................87
  6.3 Results and Discussion .......................................................................................................................87
  6.4 Conclusion .............................................................................................................................................91

CHAPTER 7: MECHANOCHEMICAL SYNTHESIS OF ReB$_2$ POWDER ........................................ 93
  7.1 Introduction .........................................................................................................................................93
  7.2 Experimental Section ..........................................................................................................................97
    7.2.1 Materials and Preparation ...........................................................................................................97
    7.2.2 Phase Analysis ............................................................................................................................97
    7.2.3 Microscopy ...................................................................................................................................98
    7.2.4 Compositional Analysis ..............................................................................................................98
    7.2.5 Micro-Raman Spectroscopy ........................................................................................................99
  7.3 Results and Discussion .......................................................................................................................99
  7.4 Conclusions ........................................................................................................................................109

CHAPTER 8: MECHANOCHEMICAL SYNTHESIS OF HEXAGONAL OsB$_2$ ..............................111
8.1 Introduction .......................................................................................................................... 111
8.2 Experimental ....................................................................................................................... 114
8.3 Results and Discussion ...................................................................................................... 115
8.4 Conclusion ......................................................................................................................... 123

CHAPTER 9: MECHANOCATALYSIS FOR BIOMASS-DERIVED CHEMICALS AND FUELS.....124
9.1 Introduction ......................................................................................................................... 124
9.2 Experimental ....................................................................................................................... 126
  9.2.1 Reagents............................................................................................................................ 126
  9.2.2 Mechanical Processing...................................................................................................... 127
  9.2.3 Gravimetric Analysis ...................................................................................................... 128
  9.2.4 Gas Chromatography with Mass Sensitive Detection .................................................. 128
  9.2.5 Thin Layer Chromatography ......................................................................................... 129
  9.2.6 Discrete Element Modeling ............................................................................................. 129
  9.2.7 Degree of Polymerization .............................................................................................. 129
9.3 Results .................................................................................................................................. 130
9.4 Discussion ............................................................................................................................. 133
  9.4.1 Kinetics and Depolymerization Mechanism ................................................................... 136
  9.4.2 Industrial Applicability and Economics ....................................................................... 142
9.5 Conclusion ............................................................................................................................. 145

CHAPTER 10: HETEROGENEOUS METAL-FREE HYDROGENATION OVER DEFECT LADEN
HEXAGONAL BORON NITRIDE .............................................................................................147
10.1 Introduction ......................................................................................................................... 147
10.2 Materials and Methods ...................................................................................................... 148
10.2.1 Synthesis of Defect-Laden h-BN ................................................................. 148
10.2.2 Hydrogenation ......................................................................................... 149
10.2.3 Gas Chromatography with Mass Sensitive Detection ............................ 151
10.2.4 X-ray Photoelectron Spectroscopy ........................................................ 152
10.2.5 Computational Details ........................................................................... 152
10.3 Results and Discussion .............................................................................. 153
10.3.1 Binding Energies .................................................................................... 160
10.3.2 Total Charge Density Analysis ............................................................... 164
10.4 Conclusion .................................................................................................. 166

CHAPTER 11: LOW-TEMPERATURE (210 °C) DEPOSITION OF CRYSTALLINE GERMANIUM VIA IN-SITU DISPROPORTIONATION OF GeI2 ............................................................... 167

11.1 Introduction ................................................................................................ 167
11.2 Experimental ............................................................................................. 169
11.2.1 Reagent Preparation .............................................................................. 169
11.2.2 Substrates for Germanium Deposition ............................................... 169
11.2.3 Polymer Film Preparation ..................................................................... 170
11.2.4 Reaction Vessel ..................................................................................... 171
11.2.5 Deposition Rate Measurements .......................................................... 173
11.2.6 Characterization ................................................................................... 174
11.3 Results and discussion .............................................................................. 174
11.4 Conclusion ................................................................................................ 183

CHAPTER 12: MISCELLANEOUS MECHANOCHEMICAL REACTIONS ..................... 184

12.1 Mechanochemical Synthesis of Isomorphously Substituted Spinels .......... 184
12.1.1 Introduction ......................................................................................................................... 184
12.1.2 Experimental ...................................................................................................................... 186
12.1.3 Results and Discussion ...................................................................................................... 189
12.1.4 Conclusion ......................................................................................................................... 202
12.2 Mechanochemical Synthesis of Organopnictide Compounds ............................................. 203
  12.2.1 Introduction ....................................................................................................................... 203
  12.2.2 Experimental .................................................................................................................... 204
  12.2.3 Results and Discussion ..................................................................................................... 206
  12.2.4 Conclusion ....................................................................................................................... 211

CHAPTER 13: CONCLUSION ............................................................................................................. 213

APPENDIX: COPYRIGHT PERMISSION LETTERS ........................................................................... 217

LIST OF REFERENCES .................................................................................................................... 220
LIST OF FIGURES

Figure 1: Typical examples of SPEX Certiprep a) 8000M Mixer/Mill for a single vial and b) 8000D Mixer / Mill for using two vials at once................................................................. 7

Figure 2: a) Planetary mill and b) planetary mill vial. ................................................................. 8

Figure 3: A lab scale attrition mill manufactured by Union Process. a) Attrition mill and its components, including the control box (top left) and ¼” steel ball bearings (bottom left); b) attritor between two acoustic insulation pads during a run; and c) attrition vial, rubber gasket and tree.................................................................................................................................................. 9

Figure 4: Custom designed pebble mill with rotary feedthroughs at the ends to allow for gas flow. ........................................................................................................................................ 11

Figure 5: Shaker mill vials come in a variety of materials, such as a) 440C hardened steel flat bottom vial, b) flat bottom tungsten carbide vial, and a c) hourglass-shaped Lucite vial. .......... 14

Figure 6: A few examples of ½” ball bearings available for purchase. From left to right: 440C stainless steel, polypropylene, alumina, PTFE, Torlon PAI, and tungsten carbide. ............... 16

Figure 7: XRD patterns for synthetic kaolinite precursors milled for different times and then hydrothermally treated at 170 ºC for two weeks. All patterns match kaolinite (JC-PDS 14-0164) with high crystallinity in the 00l direction for samples b) through e). .................................................. 29

Figure 8: XRD patterns for comparing natural kaolinite (a) to the mechanically ground synthetic kaolin (b) and the non-ground synthetic kaolin (c). Both synthetic products were treated hydrothermally................................................................. 30
Figure 9: XRD patterns for chromium-substituted kaolinite treated hydrothermally at 215°C for different lengths of time. All patterns match kaolinite (JC-PDS 14-0164).

Figure 10: The change in the coordination sphere of chromium from (a) all hydroxide in chromium (III) hydroxide and (b) mixed hydroxide and oxide for chromium in the kaolinite structure. This change in coordination results in a color change from green to sky-blue (not shown).

Figure 11: Reflectance data for several substituted kaolinites: a) 5 at.% Cr-substituted precursors; b) 7.5 at.% Er-substituted precursors; c) 10 at.% Gd-substituted kaolinite; d) 7.5 at.% Er-substituted kaolinite; e) 7.5 at.% Nd-substituted kaolinite; f) 5 at.% Cr-substituted kaolinite. The precursors designate mechanically ground samples that were not hydrothermally treated.

Figure 12: ATR spectra for kaolinite (dotted) and 5% chromium-substituted kaolinite (solid).

Figure 13: Powder X-ray diffraction patterns of rare-earth substituted kaolinites. All patterns match kaolinite (JC-PDS 14-0164) with high crystallinity in the 00l direction for all samples except e).

Figure 14: A TEM image of La-doped kaolinite. Structures on the order of a few hundred nanometers are evident.

Figure 15: XRD patterns for cerium-substituted kaolinite. All patterns match kaolinite (JC-PDS 14-0164) with high crystallinity in the 00l direction and no other phases observed.

Figure 16: An SEM image for 7.5% at. cerium-substituted kaolinite.

Figure 17: The mechanochemical oxidation of graphite produced a product that is mostly sheets 3-10 layers thick with a few large undelaminated pieces.
Figure 18: AFM image of oxidized graphite spin coated onto a silicon oxide substrate. The final product consists of a mixture of a) large and b) small platelets.

Figure 19: X-ray Diffractograms indicating crystallinity and structural differences between graphite oxide (C$_2$O) synthesized from Hummers’ method and oxidized graphite prepared by milling graphite with urea hydrogen peroxide adduct. The sharp peaks in the unwashed diffractogram is due to urea. Hummers’ method C$_2$O rapidly loses crystallinity on milling. The graphene structure is maintained by our method.

Figure 20: Zeta potential titration of the oxidized graphite produced in this study.

Figure 21: TGA under flowing air of grade TC306 as received.

Figure 22: TGA under flowing air of grade TC306 milled for 12 h in a SPEX mixer mill.

Figure 23: TGA under flowing air of TC306 graphite oxidized with urea hydrogen peroxide adduct in a planetary ball mill.

Figure 24: The X-ray photoelectron spectrum of graphite oxidized with urea hydrogen peroxide. The π system is intact, as indicated by the π – π * shakeup peak. Partial oxidation is indicated by the presence of a peak at 285.83 eV.

Figure 25: ATR-IR spectra of the starting materials (TC306), graphite oxide produced by the Hummers’ method, and oxidized graphite produced by this method. All the samples were dried in vacuo at 170 °C for 24 h prior to analysis. A higher concentration of –OH stretches are observed in the oxidized graphite sample.

Figure 26: Annotated ATR spectra comparing Hummers’ graphite oxide, grade TC306 graphite, and our material. All of the samples show absorption in the –OH stretch region. The C=O
stretch (dotted line) in our material is masked by the broad graphene peak. Additional C-H and C-O stretches attributable to carboxylic acids are observable in the spectrum for our material.

Figure 27: Raman spectrum of oxidized graphite deposited from methanol.

Figure 28: The 2D band fit to two Lorenzians. The distance between the two fit peaks indicate that the bulk consists of a material greater than 6 layers thick.

Figure 29: Several amine templates used in the synthesis of VO$_x$ nanostructures.

Figure 30: XRD patterns for VO$_2$ nanorods synthesized using diphenylamine as the template. All patterns match JC-PDS 65-7960.

Figure 31: XRD patterns for different precursors: a) diphenylamine, b) theophylline and f) rhodamine B yielded nanorods of VO$_2$ matching JC-PDS 65-7960; c) rhodamine 6G has a peak forming 5 ($\theta$), which indicates layering of the nanostructures; d) dodecylamine and e) di-n-decylamine also show a peak around 5 ($\theta$), indicating layering as well.

Figure 32: SEM images of VO$_x$ nanostructures using different amine templates.

Figure 33: XRD patterns for NaTaO$_3$ samples mechanically ground at different times. The black lines correspond to NaTaO$_3$ (JC-PDS 25-0863). The ◆ corresponds to unreacted Ta$_2$O$_5$ (JC-PDS 25-0922).

Figure 34: XRD patterns for Ca$_2$Ta$_2$O$_7$ mechanically ground between 1 and 10 h. The black lines correspond to Ca$_2$Ta$_2$O$_7$ (JC-PDS 44-1008), while ◆ corresponds to unreacted Ta$_2$O$_5$ (JC-PDS 25-0922) and □ correspond to Ca$_4$Ta$_2$O$_9$ (JC-PDS 31-0308).

Figure 35: Percent crystalline phase vs. time for Ta$_2$O$_5$ (solid black line), Ca$_2$Ta$_2$O$_7$ (solid gray line), and the intermediate, Ca$_4$Ta$_2$O$_9$ (dashed black line) as the reaction progressed to completion.
Figure 36: Crystallite sizes of Ta$_2$O$_5$ (solid black line), Ca$_2$Ta$_2$O$_7$ (solid gray line) and the intermediate, Ca$_4$Ta$_2$O$_9$ (dashed black line) at varying mill times. ................................................................. 79

Figure 37: XRD patterns for the formation of Ca$_4$Ta$_2$O$_9$ milled for a) 8 h; b) 14 h; c) 18.5 h; d) 24.5 h; and e) 27 h. The black lines correspond to Ca$_4$Ta$_2$O$_9$ (JC-PDS 31-0308) while O corresponds to unreacted Ta$_2$O$_5$ (JC-PDS 25-0922). ......................................................................................... 81

Figure 38: XRD Patterns for CaTa$_2$O$_6$ milled for a) 0.5 h; b) 2 h; c) 4.5 h; d) 7 h; and e) 10 h. The black lines correspond to CaTa$_2$O$_6$ (JC-PDS 39-1430) while O corresponds to unreacted Ta$_2$O$_5$ (JC-PDS 25-0922). ......................................................................................... 82

Figure 39: XRD patterns of the mechanochemically synthesized ZrSi$_2$ at different diluent loadings. By adding an inert diluent (CaCl$_2$) the crystallite size can be reduced. All patterns match ZrSi$_2$ (JC-PDS 32-1499). ................................................................................................. 88

Figure 40: Control of the average crystallite size in the mechanochemical synthesis of ZrSi$_2$. The concentration of ZrCl$_4$ is expressed in terms of moles/liter of free volume. ................................. 89

Figure 41: TEM images of ZrSi$_2$ prepared mechanochemically from a reaction diluted 50 mass% with CaCl$_2$. The material was isolated air-free using formamide: a) particles range from 100 nm to 20 nm; b) each particle is composed of crystalline regions as small as 5 nm in diameter; c) elemental analysis shows that calcium chloride was effectively removed. The remaining calcium is due to calcium oxide in the starting material. .................................................................................. 91

Figure 42: X-ray diffraction patterns of a) Re powder, b) B powder, c) ReB$_2$ mechanically alloyed powders after 30, 50 and 80 h of milling, and d) ReB$_2$ powder after 1-year storage in the plastic bag without any protective atmosphere. The observed broad peak at ~18° 2θ in b) is a common peak seen for amorphous materials................................................................. 101
Figure 43: SEM micrograph of ReB$_2$ powders after ball milling for 80 h. ........................................ 103

Figure 44: a) TEM micrograph of a particle of ReB$_2$ powder after 80 h of milling; b) electron diffraction of ReB$_2$ particle; and c) TEM micrograph of ReB$_2$ lattice fringes. ......................... 103

Figure 45: Distribution maps of a) boron, b) rhenium, and c) tungsten in ReB$_2$ particle obtained. .......................................................................................................................... 104

Figure 46: Negative secondary ion mass spectrometry (SIMS) of ReB$_2$ powders after (a,d) 0.5 h, (b,e) 40 h, and (c,f) 80 h of milling time................................................................. 105

Figure 47: Positive SIMS of ReB$_2$ powders after a) 0.5h, b) 40 h, and c) 80 h of milling time. 105

Figure 48: Raman spectra of mechanically alloyed ReB$_2$ powders after 80 h of ball milling..... 108

Figure 49: XRD patterns of a 1:3 Os and B mixture after different milling times.................... 116

Figure 50: Rietveld refinement of the OsB$_2$ XRD pattern. After mechanochemical synthesis, the hexagonal OsB$_2$ produced was annealed in vacuo at 1050 ºC for 48 h. The unindexed peak around 36º (▲) may be due to Os$_2$B$_3$. ........................................................................................................ 117

Figure 51: The crystal structure of hexagonal OsB$_2$. Osmium atoms are the larger gray spheres and boron atoms are the smaller black spheres......................................................... 118

Figure 52: The $a$ and $c$ lattice parameters of hexagonal OsB$_2$ along with the volume of the unit cell in the -223 ºC to 875 ºC temperature range................................................................. 120

Figure 53: a) An SEM micrograph and b) EDS of OsB$_2$ after 18 h of milling. ....................... 121

Figure 54: HAADF-STEM images of (a,b) OsB$_2$ powder, and (c,d) individual nanocrystallites. The corresponding fast Fourier transforms of the images are included in the insets. .............. 122
Figure 55: Solubilization of cellulose as a function of milling time in a SPEX 8000D mixer mill. Catalysts were milled with microcrystalline cellulose in a 1:1 ratio. The most rapid solubilization was measured using 1:1 aluminosilicates such as kaolinite.

Figure 56: Mechanocatalytic activity for a sample of compounds investigated. Catalysts were milled with microcrystalline cellulose in a 1:1 ratio for 2 h. Layered compounds with a surface acidity, $H_0$, $<-3.0$, as determined by dicinnamalacetone gave the best yields. The catalytic efficiency of kaolinite was improved through physical delamination and proton exchange. (*).

Figure 57: Cellulose can be mechanocatalytically converted to glucose and, with prolonged treatment, into a variety of products. The formaldehyde produced was not observed with the analytical techniques utilized.

Figure 58: The structures for the 2:1 smectite bentonite (left) and 1:1 smectite kaolinite (right). The octahedral are AlO$_6$ unites and the tetrahedral are SiO$_4$ units. The sheets in bentonite are charged due to an Al:Si imbalance. The sheets are held together by ionic forces between the sheets and a cation (dark sphere). The sheets in kaolinite are held together by hydrogen bonds from protons on the Al layer to the oxygens on the Si layer.

Figure 59: A first (left) and second (right) order plot of the hydrolysis of cellulose in a SPEX shaker mill. Both plots show strong linear relations, but the data point near the intersection of the two fit lines (inset) indicates that a second-order process is the more accurate description. The catalyst used was $H^+$ exchanged, physically delaminated kaolinite.

Figure 60: Change in the degree of polymerization for the insoluble residue of cellulose hydrolysis as a function of degree of solubilization. The dotted line represents a model where hydrolysis only occurs at the ends of the polymer chain.
Figure 61: Unlike current approaches to cellulose hydrolysis, mechanocatalytic hydrolysis is relatively insensitive to feedstock................................................................. 143

Figure 62: The energy consumed to produce 1 gram of glucose from 1 gram of cellulose treated in a shaker mill, 1 kg of cellulose treated in an attritor, and modeled consumptions for 100 kg in a large attritor. The dashed line is the energy released by burning the ethanol produced from 1 gram of glucose................................................................. 145

Figure 63: Configuration of the mechanochemical reactor. ....................................................... 150

Figure 64: A close-up of the reaction vessel. Hydrogen is introduced through the solenoid at the left. Heat is applied by the NiChrome element (top center). Temperature is monitored by two thermocouples; the larger one on the left also serves as the control thermocouple for the heating element. The reaction vessel is rotated by a drive wheel that is driven by a pulley...................... 150

Figure 65: Hydrogenation of trans-cinnamic acid over defect laden h-BN selectively reduces olefin moiety................................................................. 154

Figure 66: Absolute pressure (black trace) and gas concentration (red trace) during the hydrogenation of trans-cinnamic acid over h-BN. The initial pressure increase is due to heating from room temperature to 170 °C. The rapid pressure drops are from the pressure control in the hydrogenation apparatus. ................................................................. 156

Figure 67: An SEM image of defect-laden h-BN produced by mechanochemical intercalation and reaction with lithium metal. Clusters and single-sheets of BN can be seen, with the few-layer sheets adopting a scroll-like secondary structure................................................................. 158
Figure 68: XPS spectra of the carbon 1s region of h-BN as received (black), after inducing defects (red), and after se as a hydrogenation catalyst (blue). Carbon incorporation is evident even after thorough washing with CH₂Cl₂...

Figure 69: Top view of different defect structures in BN. These are (from top left to bottom right): 180° rotation of a BN bond (B/N), 90° rotation of a BN bond {Stone-Wales defect} (SW), nitrogen substitution for boron (N_B), boron substitution for nitrogen (B_N), carbon substitution for boron (C_B), boron vacancy (V_B), and a nitrogen vacancy (V_N). Gray, green, and pink balls represent boron, nitrogen, and carbon atoms, respectively. The light-gray backgrounds indicate the defected areas...

Figure 70: A) Charge-density redistribution after the adsorption of C₂H₄ on B_N, SW, V_B, and V_N defects in a BN substrate. Isosurfaces are drawn at 0.01 e/Bohr³. The blue and red surfaces represent, respectively, the charge-deficient and –accumulation regions (i.e. charge flows from blue to red regions). B) Side view; C) top view of the respective configurations without showing the charge density.

Figure 71: Vertical plane cross-sections, passing through the center of the two ethene carbon atoms, of the total charge density of gas-phase a) C₂H₄ and b) C₂H₆, and of c) C₂H₄/defective BN for defect types B_N, SW, V_N and V_B. Contours are drawn in a linear scale (9 contours from 0 to 0.27 e/Bohr³).

Figure 72: Side view of reactor vessel design and set up. a) End cap (6.6 cm O.D. × 13.1 cm) with valve and vacuum line inlet. b) No. 65 clamp. c) O-ring; d) Bottom (6.6 cm O.D. × 18-1/4 in.). e) Piece of steel (22.8 cm × 2.5 cm × 0.32 cm). f) Clamp used to hold substrates. g) Socket
cap screw (1-¾ in., 1/4-28) with two nuts (1/4-28) holding the clamp (2 cm to 3 cm from edge of steel). h) Borosilicate reagent cup (1.9 cm O.D. × 6.5 cm).

Figure 73: Reaction vessel after 18 h of deposition. Germanium (shiny, black mirror) has deposited onto the sides of the reactor vessel, along with crystals of GeI₂ (yellow-orange) and CuI (white). GeI₄ is deposited in the region at room temperature (left of yellow band, not visible).

Figure 74: Powder X-ray diffraction patterns for germanium deposited onto various surfaces after 18 h, before and after washing with acetonitrile. The black lines correspond to Ge (JCPDS 04-0545), which is visible for all samples. The CuI is removed by washing with acetonitrile. The broad hump around 2θ = 25° is due to the amorphous glass (or polymer) substrate.

Figure 75: SEM images of Ge deposited onto glass showing a) twinning of Ge Crystals and b) as viewed edge on.

Figure 76: SEM images of germanium deposited onto glass, viewed a) normal to and b) nearly parallel to the substrate.

Figure 77: Powder XRD pattern for the by-products of germanium deposition. a) Yellow film corresponding to GeI₂ (JCPDS 15-0833). b) Red crystals corresponding to GeI₄ (JCPDS 07-0196).

Figure 78: Powder XRD pattern of the black residue remaining in the reagent vial following deposition of germanium. The peaks matching with the black lines correspond to CuI (JC-PDS 06-0246), and “*” represents peaks associated with Cu₃Ge (JC-PDS 06-0693).
Figure 79: Plot of mass-difference versus time observed for a quartz crystal onto which Ge was deposited (gray line). The rate of deposition was obtained from the slope of line fit to the data in the period 1360 - 14500 s (dotted black line).

Figure 80: Plot of QCM temperature versus deposition time (red line). The frequency of the QCM crystal (dotted black line) shows an immediate change during deposition that corresponds to the condensation of CuI.

Figure 81: XRD patterns of MgAl$_2$O$_4$ reactions milled for 3 h and calcined at different temperatures. The powders were calcined at a) 500 °C; b) 600 °C; c) 700 °C; d) 800 °C; e) 900 °C; f) 1000 °C; g) Hand ground powder calcined at 900 °C. The black lines correspond to MgAl$_2$O$_4$ (JC-PDS 21-1152) and the blue lines correspond to MgO (JC-PDS 45-0946).

Figure 82: XRD patterns for ZnAl$_2$O$_4$ milled for a) 1h, b) 3 h, c) 4 h, d) 6 h and e) 10 h. The black lines correspond to ZnAl$_2$O$_4$ (JC-PDS 05-0669).

Figure 83: XRD patterns for the MgAl$_2$O$_4$ system using different reagents. a) MgO + Al(OH)$_3$; b) Mg(OH)$_2$ + Al(OH)$_3$; c) MgO + Al$_2$O$_3$; and d) Mg(OH)$_2$ + Al$_2$O$_3$. The blue lines correspond to MgAl$_2$O$_4$ (JC-PDS 21-1152), the black lines correspond to Mg(OH)$_2$ (JC-PDS 44-1482) and the green lines correspond to MgO (JC-PDS 45-0946).

Figure 84: XRD patterns for the ZnAl$_2$O$_4$ system using different reagents. a) Zn(OH)$_2$ + Al(OH)$_3$; b) Zn(OH)$_2$ + Al$_2$O$_3$; c) ZnO + Al$_2$O$_3$; and d) ZnO + Al(OH)$_3$. The blue lines correspond to ZnAl$_2$O$_4$ (JC-PDS 05-0669) and the black lines correspond to ZnO (JC-PDS 65-3411).

Figure 85: The crystal structures of a) Al$_2$O$_3$ and b) Al(OH)$_3$.

Figure 86: An unsubstituted spinel (MgAl$_2$O$_4$) under a) reflected light and b) electron beam.
Figure 87: A 5 at.% Mn-substituted spinel under a) reflected light, showing a beige powder; b) under an electron beam showing a green (majority) and red (minority) cathodoluminescence. 197
Figure 88: A 5 at.% Cr-substituted spinel under a) reflected light, showing a white powder; b) under an electron beam, yielding red cathodoluminescence. ........................................................................... 197
Figure 89: The cathodoluminescence spectrum for 5 at.%-Mn substituted MgAl$_2$O$_4$. The red emission is due to Mn$^{2+}$ ions occupying the tetrahedral sites, while the green emission is a result of Mn$^{2+}$ ions occupying the octahedral sites. .................................................................................. 198
Figure 90: The cathodoluminescence spectrum for 5 at.% Cr-substituted MgAl$_2$O$_4$. The red emission is a result of Cr$^{3+}$ ions occupying the octahedral sites. .......................................................... 199
Figure 91: XRD patterns for substituted MgAl$_2$O$_4$ samples corresponding to a) 5 at% Mn$^{2+}$, b) 5 at% Cr$^{3+}$ c) 5 at% Ni$^{2+}$ and substituted ZnAl$_2$O$_4$ samples corresponding to d) 5 at% Mn$^{2+}$, e) 5 at% Mn$^{2+}$ c) 5 at% Ni$^{2+}$. All traces were milled and calcined at 800ºC, except for trace d), which was not calcined. ................................................................................................................................. 200
Figure 92: a) Base glaze used as a comparison; b) 5 at.% Co-substituted spinel that was not calcined prior to firing; c) 5 at.% Co-substituted spinel that was calcined prior to firing; b) 5 at.% Ni-substituted spinel that was not calcined prior to firing; c) 5 at.% Ni-substituted spinel that was calcined prior to firing. ............................................................................................................ 201
Figure 93: X-ray diffractogram of sodium antimonide......................................................................................................................... 207
Figure 94: The chromatogram of the triphenylstibine reaction. ........................................................................................................... 208
Figure 95: The chromatogram of the triphenylbismuthine reaction. ................................................................................................. 209
Figure 96: The chromatogram for the formation of tributylstibine. ................................................................................................. 210
Figure 97: The chromatogram for the formation of tributylbismuthine. ........................................................................................... 211
LIST OF TABLES

Table 1: Mill Class Information............................................................................................................. 6
Table 2: Percent Substitution of Synthetic Clays .................................................................................. 31
Table 3: A representative sample of reactions producing oxidized graphite with mass% oxygen, initial, and final surface areas (SA)............................................................................................................................... 56
Table 4: Tube diameters and lengths of synthesized vanadium oxide nanostructures using different amine templates............................................................................................................................................... 70
Table 5: Lattice parameters of the synthesized ReB₂ after mechanical alloying for 30, 50 and 80 h.................................................................................................................................................................................. 100
Table 6: Intensity ratio of impurities to boron SIMS peaks........................................................................ 106
Table 7: The lattice parameters of hexagonal OsB₂ .................................................................................. 119
Table 8: Second-order rates observed in the catalytic depolymerization of cellulose in a SPEX shaker mill. The column labeled “time change” indicates when the rate changes. ...................... 139
Table 9: Product distribution by GC peak area of the 5 most abundant products in the hydrogenation of trans-cinnamic acid over defect-laden h-BN and recycled defect-laden h-BN. ................................................................................................................................................................................. 155
Table 10: Binding energy (in eV) of C₂H₄ on the defects of a (6x6) BN ................................................. 161
Table 11: Binding Energy for ethene on BN, hydrogen on BN, ethene on platinum group metals, hydrogen on Pt(100), hydrogen on Pd(100), and hydrogen on Ni(100) ............................................. 163
Table 12: Calculated enthalpy of reactions for Spinel and Gahnite structures ........................................ 193
LIST OF SYMBOLS

\( \lambda \) \hspace{1cm} \text{Wavelength} \\
\( \theta \) \hspace{1cm} \text{Angle} \\
\( B_N \) \hspace{1cm} \text{Boron substitution for nitrogen} \\
\( V_B \) \hspace{1cm} \text{Boron vacancies} \\
\( V_N \) \hspace{1cm} \text{Nitrogen vacancies} \\
\( E_{XC} \) \hspace{1cm} \text{Exchange-correlation energy} \\
\( E_{XGGA}^{X} \) \hspace{1cm} \text{Semi-local exchange function from the revised generalized gradient approximation} \\
\( E_{lc}^{C} \) \hspace{1cm} \text{Local correlation energy} \\
\( E_{nlc}^{C} \) \hspace{1cm} \text{Nonlocal correlation energy} \\
\( E_{BE} \) \hspace{1cm} \text{Binding energy} \\
\( E_{System} \) \hspace{1cm} \text{Total energy of the molecule on the substrate} \\
\( E_{Mol} \) \hspace{1cm} \text{Total energy of the molecule} \\
\( E_{BN} \) \hspace{1cm} \text{Total energy of the defective } h \text{-BN}
\[ \Delta n(\vec{r}) \] Charge density redistribution of the system

\[ n_{\text{System}}(\vec{r}) \] Charge density of the system

\[ n_{\text{Mol}}(\vec{r}) \] Charge density of C_2H_2 molecule

\[ n_{\text{BN}}(\vec{r}) \] Charge density of BN sheet with defect
## LIST OF ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>BPR</td>
<td>Ball-to-powder ratio</td>
</tr>
<tr>
<td>CL</td>
<td>Cathodoluminescence</td>
</tr>
<tr>
<td>CPCD</td>
<td>Confined-plume chemical deposition</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DABCO</td>
<td>1,4-dizabiocyclooctane</td>
</tr>
<tr>
<td>DEM</td>
<td>Discrete element modeling</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transform</td>
</tr>
<tr>
<td>FLP</td>
<td>Frustrated Lewis pairs</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Gas chromatography / mass spectroscopy</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized-gradient approximation</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-angle annular dark-field</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-density polyethylene</td>
</tr>
<tr>
<td>HMF</td>
<td>5-Hydroxymethylfurfural</td>
</tr>
<tr>
<td>ISE</td>
<td>Indentation size effect</td>
</tr>
<tr>
<td>PAI</td>
<td>Polyamide-imide</td>
</tr>
<tr>
<td>PAW</td>
<td>Projected augmented wave</td>
</tr>
<tr>
<td>PIXE</td>
<td>Particle-induced X-ray emission</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal microbalance</td>
</tr>
<tr>
<td>REE</td>
<td>Rare-earth elements</td>
</tr>
<tr>
<td>RIR</td>
<td>Reference intensity ratio</td>
</tr>
<tr>
<td>RPM</td>
<td>Rotations per minute</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SA</td>
<td>Surface area</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHS</td>
<td>Self-propagating high temperature synthesis</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
</tr>
<tr>
<td>SPS</td>
<td>Spark plasma sintering</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific surface area</td>
</tr>
<tr>
<td>SSM</td>
<td>Self-propagating solid-state metathesis</td>
</tr>
<tr>
<td>SSR</td>
<td>Solid-state reaction</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning tunneling electron microscopy</td>
</tr>
<tr>
<td>SW</td>
<td>Stone-Wales</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>UHPA</td>
<td>Urea hydrogen peroxide adduct</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab initio simulation package</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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</table>
XRD

X-ray diffraction
CHAPTER 1: INTRODUCTION AND LITERATURE OVERVIEW

1.1 Overview Of Mechanochemistry

Solid-state inorganic chemistry is typically performed using the “shake and bake” method, involving multiple grinding and calcination steps. This can be a lengthy and energy-intensive route to the synthesis of various inorganic systems, such as pyrochlores, spinels, and perovskites.\(^1\)\(^{-}\)\(^4\) Typical reactions times can be above 20 h at elevated temperatures exceeding 1000 °C.\(^4\)\(^{-}\)\(^6\) An alternative route to the synthesis of these materials can be achieved through mechanochemistry. Mechanochemistry is defined as “a branch of chemistry dealing with the chemical and physiological changes of substances of all states of aggregation due to influence of mechanical energy.”\(^7\) This includes mechanical activation, such as particle size reduction, and input of mechanical energy into the system to overcome the activation energy for the chemical reaction to occur.\(^8\)\(^{-}\)\(^10\)

The beginnings of mechanochemistry have been attributed to both Mathew Carey Lea and Michael Faraday. Both of these scientists published several worked that contributed to the emergence of mechanochemistry. Carey Lea was known for his work in the 19\(^{th}\) century on the decomposition of certain metal halides through mechanical forces. Upon grinding silver and mercuric halides in a mortar and pestle, he found that a small amount of the starting material decomposed. However, upon heating, these materials are known to sublime or melt, not decompose. This suggests mechanochemistry offers a different pathway than thermal processes.\(^11\) In a similar fashion, Faraday showed that upon grinding silver chloride with a
transition metal, such as Zn, Sn, Cu or Fe, silver was reduced and the corresponding salt was formed, as shown in Equation 1:

\[
2\text{AgCl} + \text{Zn} \rightarrow 2\text{Ag} + \text{ZnCl}_2 \quad (1)
\]

The reaction was simply induced the “dry way” in a mortar and pestle. In fact, this is an example of a mechanically-induced self propagating reaction. These works show promising results for solid-solid reactions, and serves as an example for the possibilities that can be obtained through mechanochemical reactions.

In addition to solid-state inorganic reactions, mechanochemistry can also be applied to organic materials. These include Dieckmann condensation reactions, Horner-Wadsworth-Emmons reaction of \( \alpha, \beta \)-unsaturated esters, reduction of aldehydes and ketones, formation of dialkyl carbonates, aldol condensation, electrophilic addition and Grignard reactions. The benefit of performing organic reactions under mechanical action – mechanochemical synthesis – is the ability to exclude the use of solvents during the process, thus resulting in a greener approach. In addition, literature has shown that alternative products may be formed, which are not typically obtained through solvent-based methods. For instance, enolate reactions will yield the thermodynamic or kinetic product based on the identity and the amount of base used. Fullerene reactions have shown to yield the dimer C\(_{120}\) that cannot be synthesized through solution-based methods. The iodochlorination of \( trans \)-stilbene does not occur in solution, whereas the reaction proceeds under mechanical action to yield 1-iodo-2-chloro-1,2-diphenylethane. Sodium tetraalkoxyborates have also been isolated, which cannot be done in
solution. It has been suggested that alternate mechanisms exist that lead to unique products that are not obtained through traditional pathways.

Solid-solid organic reactions may also follow different trends of reactivity. An example of this can be shown by Suzuki coupling of aryl halides, where the authors found that the reactivity followed the trend Br > I > Cl vs. I > Br > Cl found in solution. Moisture sensitive reactions, such as Grignard reactions, have been shown to proceed in a ball mill under air without reducing yield or selectivity. In addition, this method offers solid–solid reactions to proceed in a fast and quantitative manner, which is desirable from an industrial standpoint. Mechanochemistry offers a sustainable route to several industrially important materials, typically for pharmaceuticals, battery materials, and catalysts. Examples include mechanochemical production of β-cyclodextrin, sodium salicylate, sodium benzoate, aspirin, and preparation of LiCoO₂ cathode materials, Raney nickel catalysts, and modified TiO₂ photocatalysts.

Mechanochemistry is not limited to the synthesis of materials. Mechanical energy can also be utilized to activate catalysts, known as mechanical activation or mechanoactivation. The former refers to activation of a solid species without inducing chemical changes, whereas the latter causes chemical changes through mechanical impacts in the presence of a catalyst. Upon grinding, the impacts of the milling media cause the reactants and catalysts to undergo a series of fracturing and cold welding processes to expose new surfaces, thus increasing the surface area. However, these impacts not only expose new surfaces, but also cause plastic deformation, which induces defects in the structure. Examples of increased catalytic activity
after mechanical grinding include, but are not limited to, decomposition of methane over Ni/MgO,\textsuperscript{36} hydrogenation of unsaturated fats over Ni,\textsuperscript{37} decomposition of N\textsubscript{2}O by CuO,\textsuperscript{38} butane oxidation by CuO,\textsuperscript{39} and carbon monoxide oxidation by Mn\textsubscript{2}O\textsubscript{3}.\textsuperscript{10} Even activation of supported catalysts can be achieved, as was shown in the hydrogenation of benzene by Ni on quartz\textsuperscript{40} and ethylene polymerization and methane oxidation by Cr\textsubscript{2}O\textsubscript{3}\textsuperscript{41} and MoO\textsubscript{2}\textsuperscript{42} on silica, respectively. On the other hand, mechanocatalysis has been shown in the catalytic formation of NH\textsubscript{3},\textsuperscript{43} hydrogenation reactions over nickel,\textsuperscript{10,44} reduction of amides and nitro groups using Mg\textsubscript{2}NiH\textsubscript{4},\textsuperscript{45} selective partial oxidation of fused aromatics in the presence of YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6.5}, MnO\textsubscript{2} or V\textsubscript{2}O\textsubscript{5},\textsuperscript{45} condensation of aromatic aldehydes with thiobarbituric acid using ammonium acetate,\textsuperscript{46} Baylis-Hillman reactions using 1,4-dizabicyclooctane (DABCO),\textsuperscript{47} Pd/Cu catalyzed Sonogashira coupling reactions,\textsuperscript{48} and NaH-catalyzed Tishchenko reactions.\textsuperscript{49}

The increase in catalytic activity upon mechanical grinding is attributed mostly to the formation of defects in the structure, as well enhanced surface area. The increased concentration of defects in crystals has been shown to be responsible for higher activities of several catalysts, suggesting the defect sites are catalytically active. In particular, point defects and dislocations have been reported to be the catalytic sites in a variety of materials. It is thermodynamically favorable for a system to localize the energy in the form of defects vs. distribution over the entirety of the crystal. The annihilation of defects releases energy that can be transferred to activate the substrate and induce a chemical reaction.\textsuperscript{10,45} The increase in defect concentration is also responsible for the transformation of phases, which can allow for the formation of metastable states.\textsuperscript{45,50}
Mechanochemistry offers several benefits over traditional methods like calcination, hydrothermal reactions, and solution-based chemistry. The benefits include simultaneous grinding and application of energy, the ability to perform reactions without the use of solvents or input of heat and pressure, ease of scale-up, decrease of technological stages to simplify processes, and the ability to synthesize metastable phases.\textsuperscript{51,52} Mechanochemical processing continuously grinds the material, thus reducing particle size, and aids in overcoming the solid diffusion barrier by intimately mixing the starting materials. Performing reactions without the need of solvents is a huge benefit, as it reduces the cost of a process by eliminating a waste source. The benefits over solvent-based methods also includes shorter reaction times, lower temperatures, less workup required, and the possibility to perform one-pot syntheses, all while obtaining equivalent or higher yields.\textsuperscript{20,24} Mechanocatalysis is beneficial over traditional catalysis, as it continually exposes new catalytic surfaces and induces defects during the catalytic process and, in certain cases, does not need heat or pressure input (see Chapter 9). The use of mills (see section 1.2) can be energy intensive, but it still wins over traditional solvent-based methods and high temperature syntheses.\textsuperscript{53}

### 1.2 Milling Equipment

There are several varieties of mills to choose from when performing a mechanochemical synthesis. Each mill offers their own advantages, disadvantages, and modes of force, and select properties are listed in Table 1. The type of reaction as well as the state of the reagents will
determine the type of mill that is suitable to use. For instance, a reaction involving a liquid and a solid may proceed more effectively in an attritor or pebble mill versus a shaker mill.

Table 1: Mill Class Information

<table>
<thead>
<tr>
<th>Mill Type</th>
<th>Mode of Action</th>
<th>Maximum Force (N)</th>
<th>Process Scale</th>
<th>Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shaker</td>
<td>Compression, Shear</td>
<td>3053</td>
<td>2-20 g x 2</td>
<td>Quick Testing, High Energy</td>
</tr>
<tr>
<td>Planetary</td>
<td>Centrifugal, Compression, Shear</td>
<td>n/a</td>
<td>250 g x 4</td>
<td>Larger Laboratory Scale</td>
</tr>
<tr>
<td>Attrition</td>
<td>Compression, Tumbling, Shear</td>
<td>3881</td>
<td>100 kg</td>
<td>Large Scale, Temperature and Atmosphere Control.</td>
</tr>
<tr>
<td>Pebble</td>
<td>Tumbling</td>
<td>329</td>
<td>&gt; 1000 kg</td>
<td>Large Scale, Gas Flow Operation</td>
</tr>
</tbody>
</table>

\(^a\) Forces calculated from simulations using EDEM® software.

\(^b\) The custom design has 300 mL free volume once the balls are added.

1.2.1 Shaker Mill

The most common mill used in a laboratory setting is a SPEX type shaker mill. This variety of mill can come in either a single 8000M Mixer/Mill or a double 8000D Mixer/Mill, both shown in Figure 1. The former consists of an arm made to hold one vial in a clamp, which is swung back and forth, assisted lateral motions, to give a Figure 8 motion. The latter is
equipped with two arms, thus offering the capability to support 2 vials at once. As the vial swings at approximately 1200 RPM, the balls impact the bottom and lid of the vial. These impacts provide high mechanical energy due to ball velocities reaching 5 m/s. This type of mill is used to quickly perform several reactions and test the corresponding parameters on a small scale, typically 2-20 g.

Figure 1: Typical examples of SPEX Certiprep a) 8000M Mixer/Mill for a single vial and b) 8000D Mixer / Mill for using two vials at once.

1.2.2 Planetary Mill

Planetary mills are another example of popular laboratory mills that can accommodate up to a couple hundred grams of powder. This mill variety also offers anywhere from 1-4 positions for vials. The mode of action includes centrifugal forces created from the planet-like motion of the vial rotating counter to a rotating support disk. This creates both frictional forces and impacts from the balls against the container and powder. These mills are used for ultrafine
grinding of powders, but can also be used to induce mechanochemical reactions.\textsuperscript{54,55} This class of mills is manufactured by Fritsch GmBH, as shown in Figure 2, and offers speed control.

Figure 2: a) Planetary mill and b) planetary mill vial.

1.2.3 Attrition Mill

The attrition mill, or stirred-media mill, offers the ability to perform large-scale reactions, allowing for 1-100 kg of material to be processed at once. The benefit of this mill over others is that the energy input in directly used to move the grinding media, thus direct input of mechanical energy to grind the powder or induce a chemical reaction. The motor is directly connected to a tree via the drive shaft. The tree contains several impellers located at right angles from each
other and is used to stir the ball bearings contained in the vial. The mechanical impacts are caused by the collisions of the balls against the vial walls, the tree impellers, and with each other. This induces several forces on the reagents, including impact, rotational, and shear.\textsuperscript{54} This class of mills can also be modified to allow for gas flow or operation under inert atmosphere. Union Process offers commercial horizontal attrition mills (Figure 3), whereas Zoz GmBh offers vertical mills (with respect to configuration). In addition, attritors can be run in batch or continuous mode, allow for adjustable speeds (up to 740 RPM in low setting, or up to 4000 RPM in high setting), and can be equipped with a coolant jacket, allowing for temperature control.

Figure 3: A lab scale attrition mill manufactured by Union Process. a) Attrition mill and its components, including the control box (top left) and $\frac{1}{4}$” steel ball bearings (bottom left); b) attritor between two acoustic insulation pads during a run; and c) attrition vial, rubber gasket and tree.
1.2.4 Pebble Mill

The pebble mill – also known as the roller or tumbling mill – are much larger in size than a traditional laboratory ball mill and is utilized in industry to process larger quantities of materials, on the order of hundreds of pounds\textsuperscript{54}. Examples of use of this technology include the cement industry\textsuperscript{55} as well as Asbury Carbons for particle size reduction of graphite. A cylindrical vial is rotated continuously, causing the balls to tumble on the inside. As they tumble, the balls impact the vessel walls, as well as each other, supplying mechanical energy. However, the force of these impacts is not as high in energy compared to those in a shaker or planetary mill. Because of this, pebble mills are used to help grind down materials to fine powders, rather than induce chemical transformations. A smaller version of this was custom made for the purpose of allowing gas flow, and is shown in Figure 4. This feature is more difficult to obtain using other types of mills, with the exception of the attrition mill. This custom design allows for the utilization of hydrogen flow over a substrate in the presence of a catalyst to yield the saturated organic materials (see Chapter 10).
1.3 Milling Parameters

Besides the identity of the mill used and its mode of action, there are several other parameters that must be taken into account when performing a mechanochemical reaction. These parameters include:

- Milling speed
- Ball to mass of reagents ratio
- Milling vessel
- Grinding material and size
- Milling time
- Vial atmosphere
- Amount of free volume
- Temperature

The variables listed above are not independent of each other. For instance, the optimal mill type for a specific reaction will also depend on the speed of the mill chose, as well as the ball size, ball to mass of powder ratio, etc.

1.3.1 Milling Speed

The milling speed is directly related to the energy input into the system. The kinetic energy transferred to the reagents, designated as \( KE = \frac{1}{2} m v^2 \), is based on the mass \( m \) of the milling media and the velocity \( v \) at which they are traveling. The higher the speed, the higher the energy supplied to the system. However, there exists a critical speed at which the balls are no longer freely moving inside the vessel. For example, in our custom pebble mill, if the rotational speed exceeds 300 rpm, the balls will no longer tumble inside, but slide inside the vial instead. In other mills, they can become pinned to the sides of the vessel and can no longer impart energy.\(^{51}\) Higher speeds can also lead to an increase in temperature, which may be beneficial or detrimental to the reaction (see section 1.3.8). Higher speeds may also reduce the milling time, as more energy is put into the system in a shorter amount of time. Likewise, it may take longer for a reaction to go to completion at low speed settings.
1.3.2 Ball to Mass of Reagents Ratio

The ratio of the masses of grinding media to powder, or ball-to-powder ratio (BPR), is another important parameter to consider when performing a mechanochemical reaction. There are a variety of BPR values used and they are dependent on the mill type, since there is a limited amount of volume. For instance, SPEX mills typically have a ratio of 10:1 versus upwards of 100:1 in an attrition mill. The majority of the work presented in later chapters involves a BPR of approximately 12:1 and 9:1 in a shaker and attrition mill, respectively. This ratio can be increased by using more balls of the same size, using larger balls, using a denser material (WC instead of steel) or using less of the reagents. Higher BPR values reduce processing time needed and results in a faster decrease in crystallite size. This is due to a decrease in the mean free path of the balls, resulting in more collisions per unit time. Therefore, more energy is exerted on the reagents, allowing for faster syntheses.

1.3.3 Milling Vessel

The material and design of the milling vessel can affect the reaction. Because of the grinding or impacts of the balls against the vessel walls and ends, wear may occur over great lengths of time. Wear can also occur if the material being ground is harder than the vessel and milling media. For instance, if quartz is milled in a 440C steel container, iron filings will incorporate and contaminate the powder. However, if tungsten carbide is used, this does not
occur. There are several different materials available from SPEX for the milling vessel, including hardened steel, tungsten carbide, zirconia, corundum, agate, alumina and methacrylate. A few examples of milling vessels are shown in Figure 5. Additionally, there are different types of vial designs for shaker mills, and the difference in designs can affect the kinetics of the reaction. There are flat-bottom and round-bottom vials available for purchase from SPEX. The flat-bottom offers the ability for impacts against the flat lid and bottom, but material may be trapped in the corners. On the other hand, round-bottom vials may cause the balls to roll around the bottom, inducing shear forces, instead of high-energy impacts. Because of this difference in motion, the energetics may be different and reactions may take longer to complete in a round-bottom vial. A custom hourglass-shaped vial was also made for use in our lab. This vial serves as a heat sink to help keep the reaction media cool to avoid decomposition of products from self-propagating high temperature syntheses (SHS).

Figure 5: Shaker mill vials come in a variety of materials, such as a) 440C hardened steel flat bottom vial, b) flat bottom tungsten carbide vial, and a c) hourglass-shaped Lucite vial.
1.3.4 Grinding Material And Size

The material used for the ball bearings is another important factor. The grinding media available include agate, corundum, zirconia, tungsten carbide and several varieties of steel. McMaster-Carr also offers ball bearings made of polycarbonate, acrylic, polypropylene, nylon, high-density polyethylene (HDPE), polytetrafluoroethylene (PTFE), Torlon polyamide-imide (PAI), copper and titanium. Figure 6 shows a few examples of different grinding ball materials that are commercially available. As mentioned in the previous section, it is important to choose the proper material to prevent wear and contamination. The media may also play a role in the reaction, such as use of a copper ball to catalyze Sonogashira coupling reactions.\(^{48}\)

Because the mass is directly related to energy input through collisions of the ball bearings, the mass and size of the grinding media can affect the milling time and can produce differences in the microstructure of the powder.\(^{56}\) For instance, WC is twice as dense as steel and produces a more fragmented FeCo powder due to stronger attrition effects.\(^{58}\) The size of the ball has a similar effect due to the heavier mass. Smaller balls apply softer milling conditions (lower energy) compared to larger diameter balls. This difference in energy has been shown to produce differences in the phases that are formed. If titanium and aluminum powders are milled using 15 mm dia. balls, an alloy is formed, whereas 20 mm dia. balls did not produce the alloy\(^{56}\) and 5 mm dia. balls produced an amorphous material.\(^{59}\) It has been concluded that soft-milling produces metastable phases, such as amorphous phases, whereas hard-milling allows for less metastable or equilibrium phases to form.\(^{56,59,60}\)
Most experiments are conducted using single size grinding media, but multiple sizes can also be used in the same vessel. For instance, when performing experiments in the custom pebble mill, a mixture of 6.35 mm, 12.7 mm, and 19.05 mm balls are used. The smaller ball sizes can keep material from falling between the larger balls, making the grinding process more efficient. The mixture of balls can also help dislodge any those that may have reached critical speed. In addition, it has been reported that ball bearings of a single size produce tracks and do not follow random motions. If more than one size is used, the motions of the balls would randomize through collisions with one another.\(^5\)

**Figure 6:** A few examples of ½” ball bearings available for purchase. From left to right: 440C stainless steel, polypropylene, alumina, PTFE, Torlon PAI, and tungsten carbide.

### 1.3.5 Milling Time

The milling time is one of the most important parameters to consider in a mechanochemical reaction, as it designates how long it takes for the process to be complete. It is dependent on the speed chosen, as well as the mill type and BPR ratio. Increased mill times can
also have a negative effect on the reaction. The longer the mill time, the higher the chance of contamination from the vessel or milling media. In addition, unwanted phases can form if milled too long, such as transition to the amorphous state.

1.3.6 Vial Atmosphere

As with traditional solid-state inorganic and solvent-based chemical methods, the environment can be critical. Milling is typically done under inert atmosphere, such as argon, to prevent oxidation of the starting material or product. Some reactions, such as the synthesis of kaolin (Chapter 2) or vanadia nanomaterials (Chapter 4), do not need such precautions. When a material is particularly air sensitive, both loading and unloading are performed inside a glovebox. Nitrogen and hydrogen may be unfavorable to use, as they are known to react with certain metals to produce the corresponding nitrides\textsuperscript{61,62} or hydrides,\textsuperscript{63} respectively.

1.3.7 Amount Of Free Volume

In order for impacts to be efficient, there must be sufficient amount of space for the balls to move freely in the milling vial. If the vial is filled significantly with powder and bearings, the impacts will be less energetic. On the other hand, if there is a large amount of free volume, the amount of material being produced is low. Typically, 50\% of the vial is filled with material for most mills, but attrition mills can be filled up to 80\%\textsuperscript{51}.
1.3.8 Temperature

The temperature of the vial can have a significant impact on the reaction. The temperature affects diffusion processes and defect concentrations.\textsuperscript{51} Shaker mill and attrition mill vials can reach temperatures up to 60 °C from friction and impacts of the milling media against the milling vessel. Some reactions can benefit from an increase in temperature through increased kinetics, but certain reactions may suffer from this. For example, during the synthesis of GaN, the material may decompose if a flat bottom vial vs. an hourglass vial that acts as a heat sink. If the vessel is cooled during attrition milling of cellulose in the presence of an acid catalyst, no depolymerization occurs after several hours. It has been reported that low temperatures favor formation of nanostructures or amorphization.\textsuperscript{64}

1.4 Scope of Work

As previously mentioned, mechanochemistry offers several benefits over traditional methods. In the chapters that follow, there will be several examples of mechanical synthesis and catalysis and the benefits associated with each. The majority of the work presented will be the synthesis of inorganic solid materials requiring only mechanochemical processing. A small portion will be mechanochemical activation of the reagents following calcination or hydrothermal processes, with a decrease in the temperature and time needed for their synthesis. Finally, mechanocatalysis of a few reactions will be presented, which require no solvents or use...
of high temperatures or pressure. This is a significant point to mention, as these conditions tend to be costly upon scale-up for industry.

The work presented will focus on the utilization of mechanochemistry on various reactions to improve upon them by reducing processing conditions. The studies will primarily focus on use of shaker mills; the other mills are used in certain cases and comparisons of milling technology are made. In a couple of cases, the kinetics are studied, such as in the synthesis of calcium tantalates and the catalytic depolymerization of cellulose. The milling time for several systems will be varied and the effects will be discussed. Discrete Element Modeling (DEM) will be used to gain better knowledge of the impacts during mechanical grinding and their affect on the reaction depending on which mill type is used. This research will serve as a guide to better understand the processes that can occur under mechanochemical processing and utilization of solid systems to achieve the desired materials.
CHAPTER 2: MECHANOCHEMICALLY ENHANCED SYNTHESIS OF ISOMORPHOUSLY SUBSTITUTED KAOLINITES


2.1 Introduction

Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, is a naturally occurring mineral comprised of layers that consists of a tetrahedral sheet of $\text{SiO}_2$ bound to an octahedral sheet of $\text{Al}_2\text{O}_3$. Past studies have sought to shed light on how numerous variables affect crystalline kaolinite formation in nature, and considerable efforts have been made to recreate favorable conditions in the laboratory setting to facilitate the formation of synthetic kaolinite. On rare occasions, limited isomorphous substitution of aluminum with iron, chromium, and titanium has been observed in natural kaolinite deposits. While some attempts have been made to synthesize these substituted kaolinites, the possibility of isomorphously substituting aluminum with elements not found in naturally occurring kaolinite samples remains largely unexplored.

Solid acids, such as kaolinite, can be employed in a myriad of chemical processes as they present environmentally friendly alternative to mineral acids. Examples include, polymerization,
hydrogenation, the conversion of oils to biofuels, and the depolymerization of cellulose into glucose. The catalytic activity of these materials can be ascribed to their relatively high Lewis and Brønsted acidities as well as their large pore size. Utilizing clay catalysts is advantageous because they are readily available, cost effective, and versatile.

The most commonly used method of kaolinite synthesis was first reported by Eberl and Hower (1935) and involves the co-precipitation of alumina-silica gels as precursors. This process has also been used to obtain substituted kaolinite from poorly crystalline kaolinite precursors. A variety of ions have been successfully substituted for Al\(^{3+}\) using the coprecipitation method; these ions include Fe, Cu, Ni, and Co. It is also possible to achieve formation of non-substituted kaolinite at lower temperatures. Some syntheses have been successful at room temperature and atmospheric pressure, although the resulting product was very poorly crystalline, even after a reaction period of 3 years.

Factors that influence the formation and crystallinity of kaolinite include the pH of the system, the presence of alkali ions in solution, the surface area of the starting materials, the Si/Al ratio, temperature, and the duration of hydrothermal synthesis. It has been previously determined that pH has the most significant impact on the formation of kaolinite, and that acidic conditions promote the crystal growth of kaolinite. These findings were further substantiated when it was determined that the presence of alkali ions hinders the formation of kaolinite. It has also been shown that Fe\(^{3+}\) and excess Al\(^{3+}\) can restrain the crystallization process and that the addition of Li salt into the system augments crystallization along the (00l) direction. A limited number of studies have examined the effect of starting material surface area on kaolinite
synthesis, but it has been shown that simultaneous mechanical grinding of amorphous silica and aluminum hydroxide followed by hydrothermal treatment results in a more rapid formation of crystalline kaolinite \(^{85}\).

The current study focuses on the mechanochemical preparation of kaolinite precursors, which have been partially substituted with transition metal or rare-earth metal hydroxides, followed by hydrothermal treatment. This process involves mechanically grinding the starting materials in a high-energy ball mill followed by hydrothermal treatment. We have successfully applied this technique in the synthesis of gram quantities of crystalline kaolinite at temperatures as low as 170 °C over a two-week period. Kaolinite containing isomorphously substituted Cr and La, Ce, Pr, Nd, Eu, Gd, Ho, and Er has been synthesized in as little as 1 day or one week respectively.

2.2 Experimental Section

2.2.1 Reagents

Silicic acid (Fischer Scientific) and aluminum hydroxide (J.T. Baker, 98.1%) were used as obtained. The preparation of doped kaolinite precursors required prior synthesis of the appropriate dopant hydroxide. Chromium (III) hydroxide was synthesized from chromium (III) oxide (Mallinckrodt, 99.3%) as described by Brauer \(^{87}\), while all lanthanide hydroxides were synthesized by dissolving the appropriate oxide in a strong mineral acid and neutralizing the
solution with ammonium hydroxide. The following oxides were used to prepare the corresponding lanthanide hydroxides: erbium (III) oxide (Laguna Clay Company), praseodymium (III, IV) oxide (Laguna Clay Company), neodymium trioxide (Laguna Clay Company), terbium oxide (Laguna Clay Company), lanthanum oxide (Research Chemicals, 99.999%), cerium oxide (Alfa Aesar, 99.9%), holmium oxide (MTI Corporation, 99.999%), and europium oxide (MTI Corporation, 99.995%). The resulting solids were dried at 65°C for 12 hours. Solvents were used as obtained from Fischer Scientific (Certified ACS grade): ammonium hydroxide, nitric acid, and hydrochloric acid.

2.2.2 Milling

All milling experiments were performed in 8000M and 8000D SPEX Certiprep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 mL. Viton and Buna-N quad O-rings were used to maintain a seal during milling. High kinetic energy milling was performed with three 0.5” stainless steel balls weighting approximately 8 g each. Milling was carried out for 1 to 6 hours in 30-minute increments, followed by 30 minutes of cooling to reduce wear on the mill’s motor.
2.2.3 Precursor Synthesis

Kaolinite precursors for unsubstituted kaolin were attained via mechanochemical synthesis by milling stoichiometric amounts of aluminum hydroxide and silicic acid. Substituted kaolinite precursors were prepared by replacing a fraction of aluminum hydroxide with a given dopant hydroxide to attain dopant/Al atomic ratios ranging from 1:199 to 1:9; the resulting mixture was milled with a stoichiometric amount of silicic acid. Cerium (III) hydroxide is particularly difficult to prepare, therefore a detailed synthesis is described later on. All reactions were scaled to a total reagent mass of 2 grams and milled for 1 to 6 hours.

2.2.4 Cerium (III) Hydroxide Synthesis

Approximately 25 g of Cerium (III) chloride heptahydrate (Alfa Aesar, 99%) were dissolved in 150 mL of boiled deionized water. A second solution was prepared by dissolving 8 g of sodium hydroxide in 100 mL of boiled deionized water (Acros Organics, 98.5%). The two solutions were rapidly mixed in a 500 mL Erlenmeyer flask and sealed with a septum. Argon gas was passed through the solution and into a bubbler to remove any oxygen. The resulting precipitate was allowed to settle overnight. A cannula was used to replace water in the flask with fresh hot water to remove any free hydroxides resulting in a neutral pH. The solution was quickly transferred to a sublimation tube attached to a Schlenk line and placed under vacuum. A
secondary trap immersed in an isopropanol bath was attached to the vacuum line to capture water. After 5 days in vacuo the tube was heated to 50 °C to encourage further drying.

2.2.5 Hydrothermal Synthesis

The attained precursors were placed in 25 mL of deionized water and stirred for 30 minutes. The pH was measured using a Mettler Toledo 320 pH meter and adjusted to 5 using dilute solutions of HCl and NH₄OH. The resulting suspension was placed in a polytetrafluoroethylene liner, sealed in an autoclave, and placed in an oven at temperatures between 170 and 250 °C for 1 to 3 weeks. Initial synthesis of unsubstituted kaolinite was carried out at 170 °C, while chromium-substituted kaolinites and rare-earth substituted kaolinites were prepared at temperatures of 215 and 250 °C respectively.

2.2.6 Product Isolation

The treated clays were separated by vacuum filtration. A 250-mL filter flask along with a COORS USA 60240 Büchner funnel attached to a silicone stopper, and Whatman® 5 filter paper were used. The product was rinsed several times from the autoclave liner using deionized water and allowed to dry overnight in the oven at 80 °C.
2.2.7 X-ray Diffraction

Powder X-ray diffraction (XRD) was taken using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu Kα λ = 1.5418 Å). Spectra were collected from 5 to 80 degrees 2θ using 0.010-degree steps and 0.3 seconds of dwell time. The dried products were ground in a mortar & pestle to homogenize the samples, which were then thinly spread out on glass slides.

2.2.8 Attenuated Total Reflectance Spectroscopy

Attenuated total reflectance (ATR) spectroscopy was performed using a Bruker Vortex 70 ATR equipped with a Helios FTIR micro sampling accessory. Approximately 0.1 g of synthesized clay was placed onto a KBr salt plate. A background spectrum was taken using the same KBr salt plate and subtracted from the sample spectrum. Chromium doped clay spectra were collected from 3900 cm\(^{-1}\) to 3000 cm\(^{-1}\) in reflectance mode, performing 512 scans at a resolution of 1 cm\(^{-1}\).
2.2.9 Elemental Analyses

Several hundred milligrams of each sample were pressed into a self-supporting smooth disk using a pellet press. The SEM-EDS analysis was performed with replicate spot analysis using a Hitachi TM-3000 and Quantax 70 software. The 15 keV beam was used at a magnification of approximately 1500x. The PIXE elemental analysis was performed with approximately 1 - 2 nA of 3.4 MeV protons focused to a millimeter-sized beam spot for a total integrated charge of about 0.5 μC. The data were analyzed by thick-target GUPIXWin software. Both elemental analyses were normalized to the silicon concentration for consistency, with the lightest elements characterized best by SEM/EDS and the heavier elements (including the REE's) characterized best by PIXE. This work was done at the Hope College Ion Beam Analysis Laboratory.

2.2.10 Reflectance UV-Visible Spectroscopy

Reflectance UV-Visible spectroscopy was performed on a Ocean Optics USB2000 Miniature Fiber Optic Spectrometer. The sample was placed in direct line to the tungsten lamp and at a 45º angle to the fiber optic cable. The integration time, scans to average and boxcar width were set to 100 ms, 10 scans, and 5 respectively. Samples were compacted with a Carver press into uniform 0.5” diameter pellets under 5 tons of force. A reflectance standard was
prepared from MgO. All of the reflectance data was normalized to the reflectance data obtained from MgO (nominally 100%).

2.3 Results and Discussion

2.3.1 Synthetic Kaolinite

Processing time was varied from 1 to 6 hours to optimize the reaction to achieve the best crystallinity. Figure 7 summarizes the results. The XRD patterns for samples prepared using different mill times show a single phase that matches kaolinite. By growing these kaolinites at a low temperature (170 °C) we were able to gauge the effect milling time has on product crystallinity. The data shows an increase in crystallinity over the first three hours of mechanical processing prior to hydrothermal treatment for two weeks. Grinding for longer than 3 hours did not significantly increase the crystallinity of the synthetic clays. Consequently, three hours of milling was used as the standard processing time. Figure 8 shows the comparison between natural kaolinite and the difference between the mechanically ground precursors with the non-ground precursors with subsequent hydrothermal treatment. As shown, the product synthesized with mechanochemical assistance matches closely to natural kaolinite, whereas the non-ground product does not.
Figure 7: XRD patterns for synthetic kaolinite precursors milled for different times and then hydrothermally treated at 170 °C for two weeks. All patterns match kaolinite (JC-PDS 14-0164) with high crystallinity in the 00l direction for samples b) through e).
Figure 8: XRD patterns for comparing natural kaolinite (a) to the mechanically ground synthetic kaolin (b) and the non-ground synthetic kaolin (c). Both synthetic products were treated hydrothermally.

2.3.2 Chromium Substituted Kaolinites

Chromium substituted kaolinite was prepared by replacing some of the Al(OH)$_3$ precursor with Cr(OH)$_3$ and milled followed hydrothermal treated for one week at 215 °C. We increased the growth temperature so that crystalline product could be produced in 1 week instead of 2 weeks at 170 °C. Final products with a nominal composition of Al$_{2-n}$Cr$_n$Si$_2$O$_7$ where
n=0.01, 0.1, and 0.375 for substitution levels of 0.5, 5 and 7.5 at. % respectively were prepared.

Table 2 shows the percent of actual substitution into the kaolin structure determined by PIXE.

### Table 2: Percent Substitution of Synthetic Clays

<table>
<thead>
<tr>
<th>Element Substituted</th>
<th>Calculated Substitution (%)</th>
<th>Actual Substitution (%)</th>
<th>Color Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Substitution</td>
<td>-</td>
<td>-</td>
<td>Off-White</td>
</tr>
<tr>
<td>Cr</td>
<td>2.50</td>
<td>1.31</td>
<td>Pale Light Blue</td>
</tr>
<tr>
<td>Cr</td>
<td>10.00</td>
<td>8.70</td>
<td>Light Blue</td>
</tr>
<tr>
<td>Nd</td>
<td>0.50</td>
<td>0.23</td>
<td>White</td>
</tr>
<tr>
<td>Nd</td>
<td>7.50</td>
<td>4.11</td>
<td>Red-Brown</td>
</tr>
<tr>
<td>Er</td>
<td>0.50</td>
<td>0.24</td>
<td>White</td>
</tr>
<tr>
<td>Er</td>
<td>7.50</td>
<td>4.08</td>
<td>Dull Gray</td>
</tr>
<tr>
<td>Eu</td>
<td>0.50</td>
<td>0.34</td>
<td>White</td>
</tr>
<tr>
<td>Eu</td>
<td>7.50</td>
<td>3.53</td>
<td>Salmon Pink</td>
</tr>
<tr>
<td>Pr</td>
<td>0.50</td>
<td>0.25</td>
<td>Off-White</td>
</tr>
<tr>
<td>Pr</td>
<td>7.50</td>
<td>3.68</td>
<td>Off-White</td>
</tr>
<tr>
<td>Ce</td>
<td>0.50</td>
<td>0.18</td>
<td>Off-White</td>
</tr>
<tr>
<td>Ce</td>
<td>7.50</td>
<td>3.09</td>
<td>Gray</td>
</tr>
<tr>
<td>Ho</td>
<td>0.50</td>
<td>0.29</td>
<td>Cream</td>
</tr>
<tr>
<td>Ho</td>
<td>7.50</td>
<td>4.42</td>
<td>Cream</td>
</tr>
<tr>
<td>Gd</td>
<td>5.00</td>
<td>2.69</td>
<td>White</td>
</tr>
<tr>
<td>Gd</td>
<td>10.00</td>
<td>5.32</td>
<td>Off-White</td>
</tr>
</tbody>
</table>
A time study examining the correlation between the duration of hydrothermal treatment and substituted kaolinite crystallinity was carried out by preparing four 5% at. chromium substituted kaolinite precursor samples and treating them for 1 – 4 days at 215 °C. The XRD data compiled in Figure 9 summarizes the results and shows that crystalline substituted kaolinite can be obtained in as little as 2 days of hydrothermal treatment. However, crystallinity does continue to increase with the duration of hydrothermal treatment. Consequently, all precursors were treated for one week to ensure the formation of crystalline product for analysis.

![Figure 9: XRD patterns for chromium-substituted kaolinite treated hydrothermally at 215 °C for different lengths of time. All patterns match kaolinite (JC-PDS 14-0164).](image)
It should be noted that hydrothermal treatment resulted in a color change due to a change in the surrounding environment of the chromium atoms. Before hydrothermal treatment, the chromium-doped material is green. This is due to octahedrally coordinated chromium atoms surrounded by hydroxyl ligands (Figure 10a). After hydrothermal treatment, the crystalline chromium-substituted kaolinite structure is sky-blue. This is due to chromium atoms that are still octahedrally coordinated with oxygen and hydroxy ligands (Figure 10b). This in agreement with the Reflectance measurements (Figure 11), which show the Cr-substituted kaolinites are reflecting mainly in the blue-green region. Figure 12 shows the ATR spectrum for the synthetic kaolinite and Cr-doped kaolinite. The replacement of aluminum cations with chromium cations causes two Al(OH)Cr bands to appear around 3580 cm\(^{-1}\) and 3560 cm\(^{-1}\).

Figure 10: The change in the coordination sphere of chromium from (a) all hydroxide in chromium (III) hydroxide and (b) mixed hydroxide and oxide for chromium in the kaolinite structure. This change in coordination results in a color change from green to sky-blue (not shown).
Figure 11: Reflectance data for several substituted kaolinites: a) 5 at.% Cr-substituted precursors; b) 7.5 at.% Er-substituted precursors; c) 10 at.% Gd-substituted kaolinite; d) 7.5 at.% Er-substituted kaolinite; e) 7.5 at.% Nd-substituted kaolinite; f) 5 at.% Cr-substituted kaolinite. The precursors designate mechanically ground samples that were not hydrothermally treated.

Figure 12: ATR spectra for kaolinite (dotted) and 5% chromium-substituted kaolinite (solid).
2.3.3 Rare-Earth Substituted Kaolinites

Our synthetic approach allowed us to successfully incorporate La, Ce, Pr, Nd, Eu, Gd, Ho, and Er by preparing the precursors mechanically and growth under hydrothermal conditions. We increased the growth temperature to 250 °C to produce products with good crystallinity in one week. Figure 13 shows the XRD patterns for the various rare earth substituted kaolinite samples. All of these patterns are similar and show a single phase matching that of kaolinite. The synthesized kaolinites show a high degree of crystallinity in the 00l direction. But much lower crystallinity in the hk0 directions. The gadolinium sample was prepared at a 10% substitution level. At that level it was impossible to increase the crystallinity beyond that depicted in Figure 13. This may indicate poor ordering due to the random substitution of dopant in the aluminum sites. Transmission electron microscopy (TEM) was used to examine the morphology of a lanthanum-doped kaolinite as a representative sample (Figure 14). The actual percent of rare-earth elements substituted into kaolin in listed in Table 2 in all cases we see less substitution than was expected. It is not a saturation effect since the substitution level is approximately half that expected regardless of the degree of substitution. This suggests that the lanthanides may be slowly incorporated into the structure from a soluble species. Reflectance measurements on the rare-earth substituted clays, shown in Figure 11, were also taken, which agree with the colors listed in Table 2. For simplicity, the 10% Gd-substituted kaolinite is representative of the white products, as they were similar. The reflectance spectrum for the ground 7.5 at.% Nd-substituted precursor was similar to the corresponding kaolinite product, so
it was not included. In addition, the neodymium-substituted samples have a similar spectrum compared to that neodymium quartz glass \(^{89}\).

![Figure 13: Powder X-ray diffraction patterns of rare-earth substituted kaolinites. All patterns match kaolinite (JC-PDS 14-0164) with high crystallinity in the 00l direction for all samples except e).](image-url)
The challenge to synthetic process was the synthesis of cerium (III) hydroxide and its stability in air. Upon contact with air, cerium (III), a light purple powder, will convert to cerium (IV), a yellow powder, over a few hours. In order to prevent this, the synthesis of the hydroxide must be performed oxygen-free using Schlenk flask techniques. In addition, all reactions involving the compound must be loaded in a glovebox to avoid any exposure to oxygen. However, once substituted into the kaolinite structure, the cerium species are no longer air sensitive. Exposure to air no longer causes the color of the powder to change, indicating that cerium has replaced aluminum sites in the structure. Figure 15 shows the successful synthesis of cerium-substituted kaolinite with substitution levels of 0.5 and 7.5 at%. The XRD data shows a
single phase matching kaolinite. In addition, there are no excess peaks due to cerium oxide, which is indicative of successful incorporation of cerium into the kaolinite structure.

Figure 15: XRD patterns for cerium-substituted kaolinite. All patterns match kaolinite (JC-PDS 14-0164) with high crystallinity in the 00l direction and no other phases observed.

Scanning electron microscope images were analyzed to confirm that only a single phase is present. Figure 16 shows the SEM image, which shows a single phase of rosette platelets. If the cerium was converted to ceria, a cubic phase would be present along with the kaolinite phase.
The absence of this secondary phase is in agreement with the XRD and provides further evidence that cerium was indeed substituted into aluminum sites within the kaolinite structure.

Figure 16: An SEM image for 7.5% at. cerium-substituted kaolinite.

2.4 Conclusion

Unsubstituted and substituted kaolinites were synthesized successfully via mechanochemical methods. The precursors were milled for 3 h in order to obtain sufficient crystallinity. Further grinding did not significantly increase crystallinity. Isomorphously substituted Kaolinite with suitable crystallinity was synthesized in as little as 2 days. In addition,
if mechanical grinding was not performed prior to hydrothermal treatment, the resulting product did not match kaolinite. Several rare-earth elements, as well as chromium, were isomorphously substituted into the aluminum sites. Cerium was the only element that proved difficult to substitute into the structure due to its air sensitivity, a problem that can be circumvented by using standard Schlenk techniques and synthesizing the precursor under inert conditions. Because of their acidity, kaolinite has been used as an alternative to mineral acids in a variety of reactions. These include depolymerization reactions, roles as cracking catalysts, and conversion of oils to biofuels. The ability to incorporate rare-earth metals and transition metal cations into the kaolinite structure has the possibility to unlock new catalytic properties for these materials.
CHAPTER 3: A GREEN ROUTE TO OXIDIZED GRAPHITE

3.1 Introduction

Graphite is an allotrope of carbon in which the atoms are arranged in large sheets of fused six membered rings. Graphite has many useful properties including a low coefficient of friction, good electrical conductivity, and high thermal conductivity.\textsuperscript{90} It does not however interact well with water, being insoluble and difficult to suspend. Graphite oxide on the other hand contains oxygen attached to the layers as both epoxy bridges and hydroxyl groups.\textsuperscript{91-93} Its properties vary from graphite in that it is an electrical insulator, thermally decomposes, and is significantly more hydrophilic, allowing complete exfoliation upon suspension in water.\textsuperscript{91,93-95} This last property makes graphite oxide a valuable precursor in the mass production of single sheets of graphite known as graphene. After exfoliation, the sheets of graphene oxide can be chemically reduced into graphene.\textsuperscript{96} Being able to produce graphene at the commercial scale is a very important because of the utility of graphene for developing number of novel device technologies.\textsuperscript{97}

Graphite oxide was synthesized as early as 1860 by Brodie, and is commonly synthesized today by the Hummers method. Unfortunately these methods require large amounts of concentrated acid, powerful oxidizing agents, and result in the generation of toxic\textsuperscript{98} and potentially explosive\textsuperscript{99} byproducts. It is highly desirable to develop a more efficient synthetic method. Recent studies have focused on incremental improvements to the Hummers method.\textsuperscript{100,101} All of these methods utilize an initial oxidation step with concentrated H\textsubscript{2}SO\textsubscript{4} and
KMnO₄. The material is typically isolated by precipitation with acetone followed by filtration. One gram of graphite oxide prepared by these methods also produces 75 mL of strongly acidic waste and an additional 244 mL of less concentrated waste.

Multilayer graphene has been produced by milling with a surfactant¹⁰² and with melamine.¹⁰³ However, surfactants can be difficult to remove and melamine is toxic. Here we report a radically different environmentally friendly technique for mass-producing a partially oxidized graphite oxide or oxidized graphite. Our study focuses on the potential of high-energy ball milling to provide a significantly different route for this synthesis. By directly milling graphite powder with a solid oxidizing agent, we can oxidize the graphite without the need for concentrated acid, or in fact any type of solvent. Additionally, mechanical processing can be energy efficient.²⁰ We investigated several solid oxidizing agents and found urea hydrogen peroxide adduct to be the most effective for our purposes. Urea hydrogen peroxide has some history of use for solvent free and non-aqueous reactions as it provides an anhydrous, solid delivery system for H₂O₂.¹⁰⁴,¹⁰⁵ It is also valuable for its comparatively mild nature compared to the oxidizing agents used for current synthetic methods. Our study focused on oxidizing graphite with urea hydrogen peroxide adduct (UHPA) to obtain a material with varying degrees of oxidation.

Aside from the potential to generate completely oxidized graphite, producing partially oxidized graphite has its own value. Partial oxidation can allow graphite to retain some of its desirable properties while taking on certain properties of graphite oxide. Multilayer graphite oxide has a number of applications. It has been found to be a good sorbent for heavy metals,¹⁰⁶
it can be used a lubricious additive for water-based lubricants, and it can enhance cellular growth. The edge functionalization can be used to chemically bind magnetite for magnetic composites and it can be a useful handle for click chemistry. Partially oxidized graphite is more easily reduced to graphene and the multilayer graphene produced by this method would have uses in corrosion inhibition and as a catalyst support.

3.2 Experimental

3.2.1 Reagents

Graphite (Ashbury carbons grade TC306, 99.92%; grade 146, 96.86%; grade 3806, 98%; grade TC301, 99.84%; grade 3243, 99%; grade 2299, 97.5; grade 4827, 99.66%; and grade TC307, 99.92%), carbon black (Ashbury carbons grade 5991R, 99.89%) and urea hydrogen peroxide adduct (Alfa Aesar, 97% and Acros Organics, 35 wt% hydrogen peroxide) were the primary reagents for the preparation of oxidized graphite. Also investigated as solid oxidizing agents were KMnO₄ (J.T. Baker Chemical Co.), ZnO₂ (Alfa Aesar 50%), and CaO₂ (Alfa Aesar 65%). Acetone (Mallinckrodt 99.5%), methanol (Mallinckrodt 99.8%), and absolute ethanol (Pharmco-AAPER) were all utilized in processing the reaction mixture between steps. High surface area carbons were prepared by milling in a SPEX mill for 12 hours. The details of milling are described in the next section.
3.2.2 Synthesis of Oxidized Graphite

Small-scale milling experiments were performed in 8000M and 8000D SPEX Certiprep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 mL. Buna-N quad O-rings were used to maintain a seal during milling. High kinetic energy milling was performed with three 0.5” stainless steel balls weighing approximately 8 g each. Milling was carried out in 30-minute increments, followed by 30 minutes of cooling to reduce wear on the mill’s motor. Oxidized graphite was prepared by milling graphite with a single portion of urea hydrogen peroxide adduct to produce a product with 15 mass% oxygen. This was achieved by milling graphite (1.0000 g) with urea hydrogen peroxide adduct (1.0385 g). The final product was suspended in water and placed in dialysis tubing in a 10 liter recirculating deionized water bath to remove any remaining urea, the water was changed every day. After three days the sample was removed and dried by evaporation under the flow of a fume hood.

At any phase of the milling process, it is possible to remove a small amount of the reaction mixture and test it for the presence of peroxide by mixing it with water and adding a few drops of prepared luminol solution. If no fluorescence is observed all of the urea hydrogen peroxide adduct has reacted and further milling serves only to decompose the product. If fluorescence is observed unreacted urea hydrogen peroxide adduct is still present in the reaction mixture, and further milling is still required.
Large Scale milling experiments were performed in a Fritsch Pulverisette 6 planetary ball mill. Milling vials were constructed of X10CrNiS18-9 stainless steel with an approximate volume of 250 mL. A Viton gasket was used to maintain a seal during milling. Milling was performed with 45 0.5” stainless steel balls weighing 8 g each. Milling was carried out in 60-minute intervals with 30 minutes of cooling between each interval for a total of 12 hours of milling. Typically, graphite (TC306, 7.5147g) was milled in one portion with urea hydrogen peroxide adduct (30.0284 g). Once all the milling was complete, the reaction mixture was suspended in water, and placed in a custom flow dialyzer. The dialyzer consisted of a pump circulating a 10 liter bath of deionized water and a peristaltic pump moving 800 mL of product/water suspension through a dialysis tube suspended in the water bath. The deionized water was changed once a day. After three days, no urea was present in the product. The product suspension was transferred to a glass tray and dried under the flow of a fume hood.

3.2.3 Characterization

Powder X-ray diffraction (XRD) was taken using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu K\textsubscript{α} \(\lambda = 1.5418\) Å). Diffractograms were collected from 5 to 80 degrees 2θ using 0.010-degree steps and 0.3 seconds of dwell time. Atomic Force Microscopy (AFM) was performed on a Digital Instruments Multimode Microscope operated in air. For elemental analysis, dry urea-free samples were analyzed for C, H, N, and O content by Micro-Analysis, Inc., Wilmington, DE, www.microana.com. Surface
area measurements were performed by Asbury Carbons, Asbury, NJ. X-ray photoelectron spectra were recorded on a Physical Electronics 5400 photoelectron spectrometer with a magnesium source. ATR-IR: Attenuated total reflectance Infrared (ATR-IR) spectra were recorded on an ATI Mattson Infinity Series FTIR spectrometer equipped with a Spectra-Tech IR Plan Advantage Microscope in reflectance mode. The samples were dried under dynamic vacuum at 170 °C for 24 h, transferred to a desiccator, and only removed for the brief (15 minutes) time needed to acquire the ATR data. Raman spectra were recorded on a Horiba Yvon LabRam ARAMIS automated, confocal Raman microscope with a spatial resolution of roughly 400 nm, wavelength of 532 nm, and swift detector for 3D mapping. A Zeta-Potential titration was performed by suspending 1 drop of a 1 ppt oxidized graphite suspension in 1 mL of solution with a known pH (from 2 to 10). The zeta potential was measured on a Malvern Nanosizer 90.

3.2.4 Thermogravimetric Analysis

Thermogravimetric analyses (TGA) were performed on a TA Instruments 2050 TGA. Samples were heated to 850 °C under flowing air and under flowing nitrogen with a heating rate of 15 °C min⁻¹.
3.2.5 Electrical Measurements

Films were prepared by starting with a dilute suspension (1 ppt) of the oxidized graphite in water and dropping onto a 3.1 mm x 25 mm gap between two layers of palladium deposited on a glass slide. The water was allowed to slowly evaporate. Electrical measurements were performed with a Zentech LCZ meter. Alternatively, dilute suspensions (1 ppt) of oxidized graphite in water were sprayed onto lightly heated hydrophilized glass with an internal mix airbrush. The hydrophilized was supplied by Saint-Gobain glass (Bioclean®).

3.3 Results

The oxidants KMnO₄, NaNO₃, Na₂CO₃•1.5H₂O₂, urea•H₂O₂, ZnO₂, and CaO₂ were examined as potential oxygen sources for the mechanochemical synthesis of C₂O. Oxidation was not observed with NaNO₃, Na₂CO₃•1.5H₂O₂ ZnO₂, and CaO₂. Explosive oxidation resulted when KMnO₄ was used. Within fifteen minutes of milling, a vigorous reaction ensued and copious quantities of gas were generated. Very little product was recovered after these reactions with most of the product being blown into the mill due to seal failure on the milling vials. The urea hydrogen peroxide adduct induced partial oxidation. Initial experiments involved reacting a total of 3.902 grams of the adduct with 1.000 grams of graphite in three equal portions. After each addition of reactant and subsequent milling, the reaction by-products (urea and water) were removed by washing with a solvent, centrifuging, and drying. Once completely dry, the solid was transferred back into the vial, where it was milled with the next portion of the adduct.
Analysis of a representative sample, after isolation, found that it contained 80.07% C, 0.79% H, 1.12% N, and 11.99% O and 6.03% H$_2$O. This indicates that most of the urea was removed. Subsequent analyses were restricted to oxygen content.

We have been able to produce oxidized graphites with oxygen contents from 2 to 17 mass% (Table 1). Reactions in a mixer mill typically produced about 0.9 grams of product with yields of 83%. Reactions performed in a planetary mill produced around 5 grams of materials with yields of 69%. Oxygen levels higher than 15 mass% were not typical and oxidation beyond that achieved after the first addition of the peroxide adduct were not observed. In order to investigate the role of the carbon source in the level of oxidation achievable, the process was streamlined by milling with enough adduct to produce a product with a nominal oxygen content of 15 mass%. Reactant surface area was investigated by using high surface area starting materials and generating high surface area carbon through milling in a SPEX mill for 12 hours.

Products with equivalent compositions ranging from C$_{71.1}$O to C$_{6.4}$O were produced. This partially oxidized material retains much of the electrical conductivity of graphite and is hydrophilic. There are large graphene particles with height exceeding 50 nm in the isolated product, but smaller particles are also found with the size distribution as indicated in Figure 17. The diameter of the particles ranges from 25 to 300 nm (Figure 18). X-ray diffraction confirmed that the material produced is graphite-like and not graphite oxide (Figure 19). Before washing, the product was a mixture of urea and graphite. The adduct has a different XRD pattern from urea and no UHPA was detected in the reaction mixture after milling (Figure 19).
Figure 17: The mechanochemical oxidation of graphite produced a product that is mostly sheets 3-10 layers thick with a few large undelaminated pieces.

Figure 18: AFM image of oxidized graphite spin coated onto a silicon oxide substrate. The final product consists of a mixture of a) large and b) small platelets.
Figure 19: X-ray Diffractograms indicating crystallinity and structural differences between graphite oxide (C$_2$O) synthesized from Hummers’ method and oxidized graphite prepared by milling graphite with urea hydrogen peroxide adduct. The sharp peaks in the unwashed diffractogram is due to urea. Hummers’ method C$_2$O rapidly loses crystallinity on milling. The graphene structure is maintained by our method.

The products of the reaction that has an oxygen content higher than 5% formed stable suspensions in water and would not suspend in solvents with lower dielectric constants such as acetone or ethanol. The oxidized graphite could be precipitated by lowering the pH of the solution below 3, raising it above 12, or through the addition of 3 volumes of acetone. The colloid could be reformed from precipitate that was produced through acidification or the addition of acetone. It could not be reformed from precipitate produced by raising the pH above 12. The stability of the colloid was measured by performing a zeta potential titration. It was
found that the surface charge on the colloid was negative (Figure 20) and that the colloid was stable between pHs of 3 and 10.

Figure 20: Zeta potential titration of the oxidized graphite produced in this study.

Large-scale syntheses were performed by milling in a planetary ball mill. A microphone was used to monitor the sound of the mill every 5 minutes during the 18 hours required for a synthesis. Ball motion was detected during the first three hours of milling. No ball motion was detected between hours 4 and 11 and motion resumed during hour 12 of processing. Upon completion of milling, the container was pressurized with gas generated by the reaction. A sample of this gas was extracted and analyzed by GC/MS. It was found to be enriched in O$_2$ and CO$_2$ (18.7% N$_2$, 59.4% O$_2$, 0.3% Ar, and 21.6% CO$_2$)
Thermogravimetric analysis of the starting graphite grade TC306-unground, grade TC306-ground, and the material produced by oxidation in a ball mill showed that each had adsorbed water. Water content was determined by measuring the mass loss at 170 ºC. The water content of the unground graphite was 4.217%, the ground graphite was 3.414%, and the oxidized material was 5.615%. The oxidation onset temperature of the unground graphite was 667.0 ºC, the ground graphite was 487.8 ºC, and the oxidized material was 449.0 ºC. The oxidized material showed a significant mass loss between 170 ºC and 449 ºC (9.931%). The TGA results are shown in Figures 21, 22 and 23.

Figure 21: TGA under flowing air of grade TC306 as received
Figure 22: TGA under flowing air of grade TC306 milled for 12 h in a SPEX mixer mill.

Figure 23: TGA under flowing air of TC306 graphite oxidized with urea hydrogen peroxide adduct in a planetary ball mill.
Optically transparent films (20% transmittance) of oxidized graphite were fabricated by spray coating a 1 ppt water solution onto hydrophilic glass. The films had a resistivity of 10 kΩ/cm²; thicker, optically opaque films can be produced with resistivities near 50 Ω/cm².

3.4 Discussion

Solid KMnO₄ rapidly oxidizes graphite when mechanical force is applied. This rapid oxidation produces heat - which accelerates the reaction, and pressure - which leads to seal failure of the reaction container. Potassium permanganate is known to thermally decompose at 250 ºC into K₂MnO₄, MnO₂, and O₂.¹¹⁴ A green, water-soluble residue left in the vials confirmed the production of K₂MnO₄. In light of this route and the fact that manganese impurities in C₂O can lead to undesirable properties,¹¹⁵ we examined mild, easy to remove oxidants. In a SPEX mill, attrition is achieved though a shaking motion. Two much liquid results in the production of a viscous “mud” hindering further processing. Therefore, solid oxidants are preferred. Our initial choices were: CaO₂, ZnO₂, Na₂CO₃•1.5H₂O₂, and urea•H₂O₂. These solids all possess the ability to lose oxygen under fairly mild conditions. Of these four candidates, urea•H₂O₂ has been shown to release oxygen under the application of mechanical force.¹¹⁶ A by-product of this reaction is water, which has a significant heat capacity and heat of vaporization. This serves to keep the reaction temperature at or below 100 ºC, effectively slowing the reaction kinetics and rapid formation of CO₂ is avoided. The urea hydrogen peroxide adduct induced oxidation in graphite, but no oxidation was observed using CaO₂, ZnO₂, or Na₂CO₃•1.5H₂O₂.
Graphite oxide produced by the Hummers’ method has an ill-defined structure with functionalities that include hydroxyl groups, epoxide linkages, ether linkages, and carboxyl groups.\textsuperscript{117} The zeta potential titration and the observation of CO\textsubscript{2} in the reaction container suggest that carboxyl groups are being introduced into the graphite structure. X-ray photoelectron spectroscopy (XPS) analysis indicates the presence of sp\textsuperscript{2} and sp\textsuperscript{3} carbon\textsuperscript{118} as well as oxidation - C=O\textsuperscript{119} (Figure 24).

![X-ray photoelectron spectrum of graphite oxidized with urea hydrogen peroxide. The π system is intact, as indicated by the π – π* shakeup peak. Partial oxidation is indicated by the presence of a peak at 285.83 eV.](image)

Coupled with the fact that this material retains the conductivity of graphite, it can be inferred that no epoxide bonding is present and that oxygenation is only occurring at the edges.
This is further corroborated by the increase in oxygenation efficiency with an increase in starting material surface area (Table 3).

Table 3: A representative sample of reactions producing oxidized graphite with mass% oxygen, initial, and final surface areas (SA)

<table>
<thead>
<tr>
<th>Grade</th>
<th>Mass % Oxygen</th>
<th>CnO</th>
<th>Initial SA (m² g⁻¹)</th>
<th>Final SA (m² g⁻¹)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC306</td>
<td>8.94</td>
<td>13.5</td>
<td>352</td>
<td>154.47</td>
<td></td>
</tr>
<tr>
<td>TC306</td>
<td>12.03</td>
<td>9.8</td>
<td>352</td>
<td>150.17</td>
<td>Graphite was premilled for 12 h</td>
</tr>
<tr>
<td>5991R</td>
<td>1.84</td>
<td>71.1</td>
<td>5</td>
<td>19.31</td>
<td></td>
</tr>
<tr>
<td>3806</td>
<td>2.85</td>
<td>45.4</td>
<td>24</td>
<td>58.24</td>
<td></td>
</tr>
<tr>
<td>T301</td>
<td>2.70</td>
<td>48.0</td>
<td>12</td>
<td>60.22</td>
<td></td>
</tr>
<tr>
<td>3243</td>
<td>2.23</td>
<td>58.4</td>
<td>3</td>
<td>59.85</td>
<td></td>
</tr>
<tr>
<td>146</td>
<td>6.02</td>
<td>20.8</td>
<td>6</td>
<td>NA</td>
<td>UHPA added in 3 portions; washed with acetone in between.</td>
</tr>
<tr>
<td>146</td>
<td>0.00</td>
<td>NA</td>
<td>6</td>
<td>296.91</td>
<td>Milled 12 h in a SPEX mill with no UHPA</td>
</tr>
<tr>
<td>146</td>
<td>17.26</td>
<td>6.4</td>
<td>296.91</td>
<td>292.16</td>
<td></td>
</tr>
</tbody>
</table>

For example, as received Asbury carbons grade 146 has a particle size centered at approximately 20 µm, with about 50% of the particles finer than 20 µm. An oxygen content of 6.02% was realized using this graphite source. Milling in a SPEX mill for 12 hours increased the surface area nearly 50 fold and allowed the synthesis of a material with 17.26% oxygen. As received, TC306 and TC307 give products with high oxygen content. Both of these graphites are
manufactured using a proprietary milling process. Our milling process uses a SPEX mill. Although it is not scalable, we are able to achieve greater size reduction and a corresponding increase in oxygen content. Grinding graphite can lead to amorphization. The presence of the sp$^3$ carbon peak in the XPS spectrum suggests that some amorphization is occurring. In order, to gauge the effect of amorphous carbon on the oxygen content of the product we used carbon black as a precursor. Little oxygen uptake was observed (Grade 5991R, 1.84%) In order to achieve oxidation levels above 6 mass%, starting graphites must be crystalline and possess high surface areas.

It has been suggested that graphite oxide produced by the Hummers’ method consists of oxidative debris covering functionalized graphite sheets. Approximately 30% of the material is removed by washing in strong base$^{120}$ with a corresponding reduction in oxygen content.$^{121}$ We did observe loss of hydrophilicity on treatment with 1 M NaOH solution, but no mass loss was measured. This suggests that oxidized graphite produced via our mechanochemical route does not have the oxidative debris that Hummers’ graphite oxide possesses. This assertion is confirmed by ATR-IR (Figure 25) since our samples do not have the characteristic absorptions observed in graphite oxide. The oxidized graphite produced does have a higher concentration of –OH stretches, but any C=O stretch is masked by the strong peak at 1630 cm$^{-1}$ that is also observed in ground graphite.$^{122}$ In contrast, the Hummers’ graphite oxide shows a clear C=O stretch because the graphite was not subjected to milling before conversion to the oxidized form. The oxidized graphite also shows features at 1270 cm$^{-1}$ (C-O stretch), 2855 cm$^{-1}$ (C-H stretch), and 2935 cm$^{-1}$ (C-H stretch). These features are highlighted in Figure 26.
Figure 25: ATR-IR spectra of the starting materials (TC306), graphite oxide produced by the Hummers’ method, and oxidized graphite produced by this method. All the samples were dried in vacuo at 170 °C for 24 h prior to analysis. A higher concentration of –OH stretches are observed in the oxidized graphite sample.

Figure 26: Annotated ATR spectra comparing Hummers’ graphite oxide, grade TC306 graphite, and our material. All of the samples show absorption in the –OH stretch region. The C=O stretch (dotted line) in our material is masked by the broad graphene peak. Additional C-H and C-O stretches attributable to carboxylic acids are observable in the spectrum for our material.
In summary, the IR, XRD, XPS, zeta potential, and GC/MS data suggest that the material consists of sheets of graphene with derivatized edges. Infrared measurements do not indicate the presence of epoxide groups that are found in Hummers’ graphite oxide. This is consistent with the XRD data that shows 001 distances on par with graphite. Little or no in-sheet derivatization would account for this observation. XPS data shows the presence of sp\(^3\) carbon and C=O functionality coupled with the zeta potential measurements the functional groups can be described as –COOH. These would give rise to –COO\(^-\) species in solution and explains the loss of hydrophilicity on exposure to Na\(^+\), which results in a salt being formed. The GC/MS data shows that carbon is being oxidized to CO\(_2\).

Equations 2-6 present a reaction sequence that will lead to the observed product. All of the steps occur under the high transient pressures achievable in a ball mill. The reaction in Equation 4 will lead to production of the sp\(^3\) carbon observed via XPS and the CO\(_2\) observed via GC/MS. The product from reaction 5 will be rapidly oxidized to the carboxylic acid (Equation 6) in the presence of hydrogen peroxide and the free oxygen it generates (Equation 3). In this reaction sequence, the edge atoms would be much more reactive than the sheet atoms. Additionally, the reaction in Equation 4 will introduce additional reactive edge atoms.

\[
\text{Urea} \cdot \text{H}_2\text{O}_2 \rightarrow \text{Urea} + \text{H}_2\text{O}_2 \quad (2)
\]

\[
\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (3)
\]

\[
n\text{C}_{\text{graphite}} + \text{O}_2 \rightarrow (n-1)\text{C}_{\text{graphite}} + \text{CO}_2 \quad (4)
\]

\[
\text{C}_{\text{graphite}} + \text{H}_2\text{O}_2 \rightarrow \text{C}_{\text{graphite}}(\text{OH})_2 \quad (5)
\]
\[
\text{C}_{\text{graphite}}(\text{OH})_2 + \text{O}_2 \rightarrow \text{C}_{\text{graphite}}(\text{COOH})_2
\] (6)

Attack of the edge carbons would preserve the graphene structure. This is confirmed by
the fact that this partially oxidized material retains much of the electrical conductivity of
graphite, which is consistent with the low degree of in-sheet oxidation and the introduction of –
COOH groups on the sheet edges. Mechanochemical oxidation of graphite rapidly breaks down
the sheets of graphite. After oxidation there is a drastic reduction in any diffraction peaks due to
in plane ordering. Scherrer analysis was performed by measuring the FWHM of the 001 graphite
peak and applying the Scherrer equation \((\tau = K\lambda/\beta\cos\theta)\). A spherical shape factor \((K=0.9)\), copper
\(K_{\alpha}\) \((\lambda=1.5418 \text{ Å})\), and no instrument broadening \((\beta=001 \text{ FWHM})\) was used for the analysis. This
approach gives a lower limit to the 001 ordering. The volume average crystalline region in the
00l direction was 6.6 nm or 10 graphene layers. Any graphite oxide produced by our method
will not be observable by XRD since amorphization of C\text{2}O occurs after as little as one hour of
milling (Figure 19).

![Raman spectrum of oxidized graphite deposited from methanol.](image)

**Figure 27:** Raman spectrum of oxidized graphite deposited from methanol.
Raman spectroscopy (Figure 27) also indicates that the material exhibits partial amorphization. This is indicated by the shift in the G peak from 1600 cm\(^{-1}\) to the observed 1567.1 cm\(^{-1}\) and the I\(_D\)/I\(_G\) ratio of 0.41.\(^{123}\) The 2D band can be fit to four bands, but in practice only two are required (Figure 28). The energy difference between these two bands gives a measure of the number of graphene layers present in the sample.\(^{124}\) This approach gives a thickness of more than 6 layers, which is consistent with the X-ray data.

![Graph showing Raman spectroscopy results](image)

**Figure 28:** The 2D band fit to two Lorenzians. The distance between the two fit peaks indicate that the bulk consists of a material greater than 6 layers thick.

Oxidized graphite produced by this method is very hydrophilic. Coating a transparent substrate such as glass is difficult since the material has a greater affinity for the solvent than the surface. Improved coatings were achieved by using hydrophilized glass manufactured by Saint-Gobain glass. Drop casting onto this glass produced better coatings, but the coffee ring effect was still observed. Spray coating with an internal mix airbrush produced the beast coatings.
Relatively thick layers were needed to get good electrical conductivity leading to low optical transparency (20%). Analysis using optical microscopy indicated that the coating consisted of small “coffee ring” domains. Increasing the hydrophilicity of the glass and switching to a less polar dispersal solvent may realize improved coatings.

3.5 Conclusions

We have demonstrated a novel mechanochemical oxidation process for the bulk synthesis of oxidized graphite. This approach allows the relatively benign oxidizing agent urea hydrogen peroxide to be used for the production of partially oxidized graphite. Our approach is green and does not generate the large amounts of acidic waste associated with Hummers’ method. The partially oxidized graphite prepared is fully dispersible in water and can be deposited as thin films. This offers the potential for improved electronic displays, solar cells, lithium ion batteries, water-based lubricants, polymer composites, and catalyst supports.
CHAPTER 4: MECHANO CHEMICALLY ASSISTED SYNTHESIS OF VANADIUM OXIDE NANOTUBES AND NANORODS USING CYCLIC AMINE TEMPLATES

4.1 Introduction

The past few decades have brought significant interest in nanostructures because of their novel chemical and physical properties in comparison to bulk materials. A variety of nanostructured materials exist, including nanotubes,\textsuperscript{125,126} nanobelts,\textsuperscript{127,128} and nanowires.\textsuperscript{129} Out of these nanostructures, nanotubes have become attractive due to the advantage of three different contact regions, which are the inner and outer walls of the tubes, as well as the ends of the tubes.\textsuperscript{130} Vanadium oxide nanotubes and nanorods are of particular interest because of their catalytic and electrochemical properties.\textsuperscript{131-134} These materials are considered useful for applications including catalytic oxidation,\textsuperscript{134,135} cathode materials in lithium batteries,\textsuperscript{130,133,136,137} gas sensors,\textsuperscript{138} thermal sensors, optical switching devices,\textsuperscript{139} optoelectronics and laser protection.\textsuperscript{140} In addition, VO\textsubscript{2} has the ability to undergo a reversible semiconductor-to-metal transition at \textasciitilde68\textdegreeC, which leads to a significant reduction in resistance.\textsuperscript{141}

The traditional method for the synthesis of vanadium oxide nanotubes involves sol-gel formation from a vanadium precursor and H\textsubscript{2}O\textsubscript{2}, adding an amine template, followed by hydrothermal treatment.\textsuperscript{131,132,142,143} Initial studies allowed hydrothermal treatment to proceed for 7 days,\textsuperscript{131,132} but have been recently reduced from 2 to 4 days.\textsuperscript{142,143} In addition, there are several different ways to obtain nanotubes using this method based on the precursors used to obtain the gel. Vanadium precursors used include ammonium metavanadate\textsuperscript{128,134}, vanadium (V)
oxide triisopropoxide, NH₄VO₃, and V₂O₅. The benefit to using V₂O₅ over vanadium alkoxides results from its air and moisture stability, low cost, can be easily handled, and is not significantly affected to changes in the reaction set-up. In addition, the templating agent can also be varied. The templating agents are generally primary amines, such as hexadecylamine, undecylamine, dodecylamine, and 3-phenylpropylamine. Alternatively, a more recent method has produced vanadium oxide nanotubes by mechanically grinding the precursors instead of gel formation, followed by hydrothermal treatment.

Hydrothermal treatment has also been employed in the synthesis of VO₂ nanorods, which involves the treatment of a vanadium precursor, such as V₂O₅ or NH₄VO₃, and a reducing or templating agent for at least 24-48 hours at 180 °C. Reducing or templating agents include formaldehyde, cetyltrimethylammonium bromide (CTAB), and primary aromatic amines. Other methods of synthesizing nano-VO₂ include thermal oxidation of vanadium sheets, reduction of aqueous vanadate ions followed by heating at 230 °C under vacuum, thermotreatment of a vanadium precursor hydrate, and the hydrolysis of [NH₄]₅[(VO)₆(CO₃)₄(OH)₉]•10H₂O.

The current study introduces an alternative way to synthesize vanadium oxide nanotubes and nanorods via mechanochemistry followed by hydrothermal treatment. Primary aromatic amines have been used as a template to synthesize nanostructured vanadium oxides. Cyclic and secondary amines have also been successfully employed as templates using this method. Vanadium oxide nanotubes were successfully synthesized using rhodamine 6G as the templating agent. However, nanorods were observed using diphenylamine and theophylline as a template.
This approach offers a quick, easy, and reproducible method to synthesize nanotubes or nanorods depending on what precursors are used.

4.2 Experimental

4.2.1 Materials

Vanadium pentoxide nanotubes were synthesized from vanadium pentoxide (Alfa Aesar, 99.8%) and different amines: N,N-diphenylamine (Alfa Aesar, 98+%), theophylline (Sigma Aldrich), rhodamine 6G (Matheson Coleman and Bell) and rhodamine B (Matheson Coleman and Bell), dodecylamine (Acros Organics, 98% purity), and di-n-decylamine (Lancaster Synthesis).

4.2.2 Preparation

Vanadium pentoxide was milled along with an amine listed above (Section 4.2.1) in a molar ratio of 2:1 for a total mass of 2 grams. The amines used were N,N-diphenylamine, theophylline rhodamine 6G, rhodamine B, dodecylamine, and di-n-decylamine. All milling experiments were performed in 8000M and 8000D SPEX Certiprep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 mL. Viton and Buna-N quad O-rings were used to maintain a seal during milling. High kinetic energy milling
was performed with three 0.5” stainless steel balls weighting approximately 8 g each. Milling was carried out for 1 hour in 30-minute increments, followed by 30 minutes of cooling to reduce wear on the mill’s motor. The ground precursors were placed in a mixture of 10 mL absolute ethanol and 15 mL H₂O. The solution was allowed to stir for a total of 30 minutes prior to hydrothermal treatment. The resulting suspension was placed in a polytetrafluoroethylene liner, sealed in an autoclave, and placed in an oven at a temperature of 180 °C for 1 to 5 days, which resulted in a black powder. The final product was washed with ethanol and hexane to remove any unreacted amine or undesired products and was dried under vacuum overnight.

4.2.3 Characterization

Powder X-ray diffraction (XRD) was taken using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu Kα λ = 1.5418 Å). Spectra were collected from 5 to 80 degrees 2θ using 0.010-degree steps and 0.3 seconds of dwell time. Scanning electron microscopy (SEM) was performed on a Tescan Vega SBH operating at 30 kV.

4.3 Results and Discussion

Diphenylamine, theophylline, rhodamine 6G, and rhodamine B (Figure 29) were utilized as new amine templates for the formation of vanadium oxide nanostructures enhanced by mechanical treatment. All of these compounds are solids at room temperature. This enhances the
transfer of mechanical energy into the reaction mixture. After the initial mechanical treatment, the amine/oxide mixtures were different colors. Diphenylamine produced a dark green powder, theophylline produced a green-brown powder, rhodamine 6G produced a blue powder and rhodamine B produced a dark violet powder. Vanadium (V) oxide is a yellow orange powder; the change to green suggests that V(V) was reduced to V(III). The colors obtained using the rhodamine dyes are less instructive since they are both highly colored themselves. Upon the addition to water, the solution became murky and changed colors depending on which amine was used. After a few minutes of stirring, the solution became lighter in color. All powders became blue-black after hydrothermal treatment, indicating a reduction of V(V) caused by the organic template.\textsuperscript{154} Dodecylamine and di-n-decylamine produced no color change upon grinding, but dodecylamine did result in a black powder after hydrothermal treatment.

![Figure 29: Several amine templates used in the synthesis of VO\textsubscript{x} nanostructures.](image)

\textsuperscript{154} Dodecylamine and di-n-decylamine produced no color change upon grinding, but dodecylamine did result in a black powder after hydrothermal treatment.
Figure 30: XRD patterns for VO$_2$ nanorods synthesized using diphenylamine as the template. All patterns match JC-PDS 65-7960.

The XRD patterns for VO$_2$ nanorods treated for a varied amount of time are shown in Figure 30. Diphenylamine was used as the template for the time study, which shows that nanocrystalline VO$_2$ is obtained after 1 day. All patterns correspond with monoclinic VO$_2$ phase (JC-PDS 65-7960). There is no significant increase in the crystallinity with increased length of hydrothermal treatment. The XRD patterns for several different amine templates are shown in Figure 31. Diphenylamine, theophylline and rhodamine B patterns indicate the formation of VO$_2$ nanorods (JC-PDS 65-7960). The diphenylamine and rhodamine B templates produced more crystalline material. Although poorly crystalline, the material prepared using rhodamine 6G shows long range ordering (the peak at ~5º 2θ) indicative of a layered or tube structure. Similarly, dodecylamine and di-n-decylamine show this same feature.
Figure 31: XRD patterns for different precursors: a) diphenylamine, b) theophylline and f) rhodamine B yielded nanorods of VO$_2$ matching JC-PDS 65-7960; c) rhodamine 6G has a peak forming 5 (2θ), which indicates layering of the nanostructures; d) dodecylamine and e) di-n-decylamine also show a peak around 5 (2θ), indicating layering as well.

Figure 32 shows the morphology of the vanadium oxide nanostructures using different templates. Nanorods were obtained using diphenylamine, theophylline and rhodamine B, while nanotubes were formed using rhodamine 6G. Diphenylamine produced good rod structures with lengths up to 1.80 µm and an aspect ratio of 22.3. The layering in the XRD pattern for rhodamine 6G and tube-like nanostructures seen by SEM indicates that formation of nanotubes occurred. Table 4 summarizes the approximate size distribution for the nanostructures and approximate aspect ratios. Layered plates were observed when dodecylamine or di-n-decylamine was used. However, the fact that formation of nanotubes or nanorods did not occur with these suggests that hydrothermal synthesis alone is insufficient and that mechanical grinding plays a role in the synthesis using the formerly mentioned amines.
Figure 32: SEM images of VO₃ nanostructures using different amine templates.

Table 4: Tube diameters and lengths of synthesized vanadium oxide nanostructures using different amine templates.

<table>
<thead>
<tr>
<th>Amine Template</th>
<th>Diameters (nm)</th>
<th>Lengths (μm)</th>
<th>Average Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenylamine</td>
<td>56 to 89</td>
<td>0.760 to 1.80</td>
<td>22.3</td>
</tr>
<tr>
<td>Theophylline</td>
<td>77 to 98</td>
<td>0.800 to 1.60</td>
<td>12.0</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td>59 to 100</td>
<td>0.430 to 0.800</td>
<td>8.74</td>
</tr>
<tr>
<td>Rhodamine Bᵃ</td>
<td>53 to 95</td>
<td>0.340 to 1.40</td>
<td>8.63 &amp; 12.5</td>
</tr>
</tbody>
</table>

ᵃNanorods were asymmetrical, therefore produced two separate diameters.
4.4 Conclusion

We have developed a rapid and facile method for the synthesis of nanostructured vanadium oxides with new templating agents. This approach allows for the formation of nanorods or nanotubes of vanadium oxide depending on the template used in the synthesis. The XRD patterns show evidence of VO$_2$ nanorods as well as layering. Symmetric nanorods with high aspect ratios were successfully prepared using these new templating agents. Asymmetric nanorods were produced using rhodamine B as the templating agent. We have shown that the templating agent does not need to be restricted to a primary amine. Vanadia nanostructures prepared from the amines utilized in the study or other amines.
CHAPTER 5: MECHANOCHEMICAL SYNTHESIS OF CALCIUM AND SODIUM TANTALATES

5.1 Introduction

Photocatalysis using oxide semiconductors has been studied extensively due to their ability to photocatalytically split water into H₂ and O₂ under UV irradiation²,¹⁵⁵ to provide a source of renewable energy. Several mixed oxide catalysts have been studied for their photocatalytic activity, including tantalates and titanates with a perovskite-type crystal structure, such as NaTaO₃, KTaO₃, Ca₂Ta₂O₇, SrTiO₃, and La₂Ti₂O₇.²,¹⁵⁶-¹⁵⁸ Of these materials, modified-NaTaO₃ has the highest activity reported.² Group 1 and 2 tantalates also have applications in the treatment and remediation of dyes, such as rhodamine¹⁵⁹ and methylene blue,¹⁶⁰ water disinfection, air purification, hazardous waste remediation, water purification,¹⁶¹ photocatalytic reduction of CO₂,¹⁵⁷ and photoluminescence applications.¹⁶²

In addition, mixed metal oxides, such as Ca₂Ta₂O₇ and CaTa₂O₆, have potential applications as thick film resistors, catalysts for hydrocarbon oxidation,¹⁵⁸ capacitors,¹⁶³ ionic conductors in methanol combustion,¹⁶⁴ and in communication devices as a microwave resonator in mobile phones.¹,¹⁶⁵ In particular, CaTa₂O₆ has been proposed as a potential material for generating and transmitting optical signals over a wide range of wavelengths.¹⁶⁶ Calcium tantalates also have the potential to be used as a host material for phosphors, allowing for tunable color.¹⁶²
The traditional methods for the synthesis of alkali metal tantalates, alkaline earth tantalates and lanthanide tantalates involve sol-gel formation, solid-state reaction or hydrothermal treatment. The former involves gel formation from a tantalum source, such as TaCl$_5$, Ta(OEt)$_5$. Gel formation is followed by calcination at 350-500 °C, 600 °C or 800 °C. Solid-state reactions involve calcination of the starting materials, typically alkali carbonates, rare-earth oxides and Ta$_2$O$_5$ or Ta$_2$O$_3$, with intermediate grinding in certain cases. Typical calcinations times varied between 10 to 20 h in air at temperatures between 1170 K and 1420 K. However, these techniques are energy intensive due to the prolonged times at high temperatures. In addition, the tantalum precursors used are relatively toxic and moisture sensitive.

Hydrothermal treatment has also been employed in order to synthesize nanomaterials of NaTaO$_3$. Nanocubes of NaTaO$_3$ were obtained by hydrothermally treating a solution containing NaOH and Ta$_2$O$_5$ at 140 °C for 12 h. Thin films can be obtained by hydrothermal-electrochemical synthesis. Bismuth-doped NaTaO$_3$ has also been synthesized by hydrothermal treatment at 200 °C for 24 h. Calcium tantalate was synthesized from treatment of Ca(NO$_3$)$_2$•4H$_2$O and Ta(OEt)$_5$ under air-free conditions at 100 °C for 120 h.

The current study introduces an alternative method to synthesize metal tantalates through a solid-state method known as mechanochemistry. The tantalates synthesized in this study include NaTaO$_3$, Ca$_2$Ta$_2$O$_7$, Ca$_4$Ta$_2$O$_9$, and CaTa$_2$O$_6$. This process is facile, reproducible, is performed at room temperature and does not require calcination, thus avoiding high temperature and energy intensive steps. Ball milling has been employed in the past for certain metal
tantalates, but have been performed under a solvent and required calcination steps to react completely.\textsuperscript{174,175} The kinetics of the synthesis of $\text{Ca}_2\text{Ta}_2\text{O}_7$ is also reported.

### 5.2 Experimental Section

#### 5.2.1 Reagents

All tantalates were prepared from stoichiometric amounts of the corresponding hydroxide and $\text{Ta}_2\text{O}_5$ (Alfa Aesar, 99% metals basis). $\text{NaTaO}_3$ was prepared from $\text{NaOH}$ pellets (Acros Organics, 98.5%); $\text{Ca}_2\text{Ta}_2\text{O}_7$ was prepared from $\text{Ca(OH)}_2$ (Matheson Colman & Bell, 93%). $\text{Mg(OH)}_2$ (Alfa Aesar, 95-100.5%) was used as the reference material for yield analysis. Rare-earth tantalates were prepared from the corresponding rare-earth hydroxides, whose syntheses were described in Section 2.2.1.

#### 5.2.2 Milling

All milling experiments were performed in 8000M and 8000D SPEX Certiprep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 mL. Viton and Buna-N quad O-rings were used to maintain a seal during milling. High kinetic energy milling was performed with three 0.5” stainless steel balls weighting approximately 8 g each. A total sample mass of 2 g was used in each synthesis, giving a ball-to-
sample ratio of 12:1. Milling was carried out for 1 to 10 h for Ca$_2$Ta$_2$O$_7$ and CaTa$_2$O$_6$, up to 30 h for Ca$_4$Ta$_2$O$_9$, and 1 to 3 h for NaTa$_3$. Milling was performed in 30-minute increments, followed by 30 minutes of cooling to reduce wear on the mill’s motor.

5.2.3 X-ray Diffraction

Powder X-ray diffraction (XRD) was taken using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu K$_\alpha$ $\lambda = 1.5418$ Å). Diffractograms were collected from 5 to 80 degrees 2θ using 0.010-degree steps and 0.3 seconds of dwell time. For yield determinations, the Reference Intensity Ratio (RIR) method was used. Standards of Ca$_2$Ta$_2$O$_7$, Ca(OH)$_2$ and Ta$_2$O$_5$ were made with a 10-vol% Mg(OH)$_2$ reference material. Samples were prepared in a similar manner. Diffractograms were collected from 12 to 26 degrees 2θ using 0.002-degree steps and 1 second of dwell time.

5.3 Results and Discussion

5.3.1 Formation of NaTaO$_3$

The XRD patterns for NaTaO$_3$ mechanically ground for a varied amounts of times are shown in Figure 33. All patterns correspond to the orthorhombic NaTaO$_3$ phase (JC-PDS 25-0863). An impurity of Ta$_2$O$_5$ (JC-PDS 25-0922) is also detected for samples milled for 1 and 2
h, and a very small amount after 3 h. However, NaTaO₃ is the only phase present at 4 h of mechanical grinding. The crystallinity of the product also increases from 1 to 2 h, and decreases for 2 to 3 h, indicating that reduction of particle size is occurring in between.

Figure 33: XRD patterns for NaTaO₃ samples mechanically ground at different times. The black lines correspond to NaTaO₃ (JC-PDS 25-0863). The ● corresponds to unreacted Ta₂O₅ (JC-PDS 25-0922).

5.3.2 Kinetics of the Ca₂Ta₂O₇ System

The XRD patterns for the synthesis of Ca₂Ta₂O₇ mechanically ground for different times are shown in Figure 34. The expected reaction is given by Equation 7:
2 \text{Ca(OH)}_2 + \text{Ta}_2\text{O}_5 \rightarrow \text{Ca}_2\text{Ta}_2\text{O}_7 + 2 \text{H}_2\text{O} \hspace{1cm} (7)

Figure 34: XRD patterns for \text{Ca}_2\text{Ta}_2\text{O}_7 mechanically ground between 1 and 10 h. The black lines correspond to \text{Ca}_2\text{Ta}_2\text{O}_7 (JC-PDS 44-1008), while ◻ corresponds to unreacted \text{Ta}_2\text{O}_5 (JC-PDS 25-0922) and □ correspond to \text{Ca}_4\text{Ta}_2\text{O}_9 (JC-PDS 31-0308).
However, during the course of the reaction, an intermediate, Ca₄Ta₂O₉, forms within 1 h and the majority is consumed after 5 h. Figure 34 also shows the progression of the reaction, with a single phase present after 10 h corresponding to Ca₂Ta₂O₇ (JC-PDS 44-1008). The progression of the reaction follows Equation 8 to form the intermediate, which then reacts with the remaining tantalum pentoxide to form the desired product, as shown in Equation 9:

\[
4 \text{Ca(OH)}_2 + \text{Ta}_2\text{O}_5 \rightarrow \text{Ca}_4\text{Ta}_2\text{O}_9 + 2 \text{H}_2\text{O} \tag{8}
\]

\[
\text{Ca}_4\text{Ta}_2\text{O}_9 + \text{Ta}_2\text{O}_5 \rightarrow 2 \text{Ca}_4\text{Ta}_2\text{O}_9 \tag{9}
\]

The amount of each phase present over the course of the reaction is shown in Figure 35. The percentages were determined using reference intensity ratio (RIR) analysis. The amount of Ta₂O₅ slowly decreased over the first 4 h as the intermediate perovskite phase, Ca₄Ta₂O₉, slowly formed. After 5 h, the intermediate was consumed along with the majority of Ta₂O₅ to yield the pyrochlore phase, Ca₂Ta₂O₇, as the dominant phase. Over the next 5 h, the remainder of the Ta₂O₅ was consumed. The crystallite sizes for each phase were also monitored (Figure 36). In general, the crystallite size for Ta₂O₅ and Ca₄Ta₂O₉ decreased from 318 nm to 240 nm and 147 nm to 93 nm, respectively, within the first 5 h. From 5 to 10 h, the crystallite size of the pyrochlore phase increased from 44 nm to 82 nm.
Figure 35: Percent crystalline phase vs. time for Ta$_2$O$_5$ (solid black line), Ca$_2$Ta$_2$O$_7$ (solid gray line), and the intermediate, Ca$_4$Ta$_2$O$_9$ (dashed black line) as the reaction progressed to completion.

Figure 36: Crystallite sizes of Ta$_2$O$_5$ (solid black line), Ca$_2$Ta$_2$O$_7$ (solid gray line) and the intermediate, Ca$_4$Ta$_2$O$_9$ (dashed black line) at varying mill times.
It should be noted when Ca$_2$Ta$_2$O$_7$ was milled further, the formation of a distorted perovskite phase, CaTa$_2$O$_6$, occurred. The water that was released from the formation of Ca$_2$Ta$_2$O$_7$ from Equation 8 and 9 reacts with the pyrochlore product, as shown in Equation 10:

\[
\text{Ca}_2\text{Ta}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow \text{CaTa}_2\text{O}_6 + \text{Ca(OH)}_2
\]  

(10)

This reaction was more prevalent during periods of high humidity. However, drying the reaction in between periods of milling inhibited formation of CaTa$_2$O$_6$ by removal of water.

5.3.3 Formation of Ca$_4$Ta$_2$O$_9$ and CaTa$_2$O$_6$

The discovery of an intermediate during the synthesis of Ca$_2$Ta$_2$O$_7$ drove the desire to isolate Ca$_4$Ta$_2$O$_9$, given by Equation 8. The XRD patterns for the synthesis of Ca$_4$Ta$_2$O$_9$ are shown in Figure 37. Compared to the pyrochlore phase, the complete formation of Ca$_4$Ta$_2$O$_9$ required a longer milling time. The formation of the perovskite was not observed until 8 h. After 18.5 h (Figure 37c), a small amount of Ta$_2$O$_5$ remained and did not react completely until after 27 h (Figure 37e), where only a single phase corresponding to Ca$_4$Ta$_2$O$_9$ (JC-PDS 31-0308) was present.
Figure 37: XRD patterns for the formation of Ca₄Ta₂O₉ milled for a) 8 h; b) 14 h; c) 18.5 h; d) 24.5 h; and e) 27 h. The black lines correspond to Ca₄Ta₂O₉ (JC-PDS 31-0308) while ○ corresponds to unreacted Ta₂O₅ (JC-PDS 25-0922).

Similarly, the distorted perovskite was also synthesized mechanochemically following Equation 11:

$$\text{Ca(OH)}_2 + \text{Ta}_2\text{O}_5 \rightarrow \text{CaTa}_2\text{O}_6 + \text{H}_2\text{O} \quad (11)$$

Figure 38 shows the XRD patterns for the synthesis of CaTa₂O₆. The desired product was formed within 2 h and was the only phase present after 10 h.
Figure 38: XRD Patterns for CaTa$_2$O$_6$ milled for a) 0.5 h; b) 2 h; c) 4.5 h; d) 7 h; and e) 10 h. The black lines correspond to CaTa$_2$O$_6$ (JC-PDS 39-1430) while ◦ corresponds to unreacted Ta$_2$O$_5$ (JC-PDS 25-0922).

5.4 Conclusion

Sodium and calcium tantalates were synthesized via high-energy ball milling without the need of elevated temperatures. In addition, this process does not require expensive or hazardous starting materials. NaTaO$_3$, Ca$_2$Ta$_2$O$_7$, Ca$_4$Ta$_2$O$_9$ and CaTa$_2$O$_6$ were obtained as the only phase
detected by XRD after 4 h, 10 h, 27 h and 10 h of milling, respectively. During the synthesis of Ca$_2$Ta$_2$O$_7$, an intermediate phase, Ca$_4$Ta$_2$O$_9$, formed within 1 h and reacted after 5 h to form the desired product. From the RIR analysis, it was determined that nanocrystalline Ca$_2$Ta$_2$O$_7$ was synthesized mechanochemically.
CHAPTER 6: SIZE CONTROLLED MECHANOCHEMICAL SYNTHESIS OF ZrSi$_2$

This work was previously published as “Size Controlled Mechanochemical Synthesis of ZrSi$_2$” by David Restrepo, Sandra M. Hick, Carolin Griebel, Juan Alarcón, Kyle Giesler, Yan Chen, Nina Orlovskaya and Richard G. Blair in Chemical Communications, Volume 49, Issue 7, 2013, pp. 707-709 Copyright © 2013 Royal Society of Chemistry. Reproduced by permission of The Royal Society of Chemistry.  http://xlink.rsc.org/?doi=C2CC36323B

6.1 Introduction

Transition metal silicides, which are refractory, conductive, strong, and relatively inert, offer an attractive choice for reinforcement materials. In particular, nanocrystalline refractory silicides are more desirable due to their novel properties, such as high strength, hardness, and electrical conductivity. Because of these properties and its low electrical resistivity ($13 - 34 \ \mu \Omega \ \text{cm}$), zirconium silicide is used in composites as a reinforcement material, in microelectronic devices, and potentially in neutron deflectors.

Traditional routes to producing zirconium disilicide include silicothermic reduction, electrochemical, mechanochemical, sintering, arc-melting, and self-propagating metathesis reactions. However, these reactions are difficult to scale, do not yield pure ZrSi$_2$, and do not allow for control of crystallite size. In addition, some routes require temperatures above 1000 °C.
The current study focuses an alternative synthetic route to ZrSi$_2$ using mechanochemical synthesis via a metathesis reaction. This approach involves mechanically grinding the starting materials in a high-energy ball mill. By using a diluent, we are able to control the size of the crystallites. This method allows for the production of ZrSi$_2$ of varying crystallite sizes dependent on the conditions used. Size control in self-propagating metathesis reaction has been investigated in the past,$^{194}$ but the extent of control was limited by the need for self-propagation. A mechanochemical approach eliminates this restriction. Although mechanochemical methods have been used to prepare a variety of nanomaterials,$^{195-200}$ the synthesis of refractory materials by solid-state metathesis has not been investigated thoroughly.

6.2 Experimental

6.2.1 Synthesis of ZrSi$_2$ Nanocrystallites

Zirconium disilicide was prepared using high-energy ball milling of a stoichiometric amount of zirconium (IV) chloride (Strem Chemicals, 99.6%) with calcium silicide (CaSi) (GFS Chemicals, Inc., 99.5%), or mechanochemically synthesized CaSi in an argon environment. Calcium chloride (Bryant Lab, Inc.) was used as a diluent to control the size of the ZrSi$_2$ crystallites. Milling experiments were carried out using 8000M and 8000D SPEX CertiPrep mixer/mills. The milling vials were constructed from 440C stainless steel with an approximate volume of 65 mL. Viton O-rings were used to maintain a seal during the milling process. Three stainless steel balls (1.27-cm dia.) were used as the milling media, weighing approximately 8 g.
each. Commercial calcium silicide contains a significant amount of iron impurities. In order to reduce these impurities,\textsuperscript{201} calcium silicide was mechanochemically prepared from the elements using a method similar to that reported by Bux \textit{et al} for Mg\textsubscript{2}Si.\textsuperscript{202} One gram of calcium (granules, redistilled -6 mesh, 99.5\% Alfa Aesar) was added in three increments to a stoichiometric quantity of silicon (Virgin poly fines 99.999\%, Alfa Aesar, ground for 12 h in a tungsten carbide SPEX vial and sieved to -270 mesh under argon). Grinding for 30 minutes in a steel SPEX vial followed each calcium addition. Size controlled ZrSi\textsubscript{2} was prepared by milling 2 g reaction masses for 8 h in 30-minute increments, followed by 30 min of cooling to reduce wear on the mill’s motor. The product was isolated in an argon environment to prevent oxygen contamination.

Formamide (Aldrich, 99\%) and N,N-dimethylformamide (DMF, Acros, 99.8\% extra dry) were used to wash away the calcium chloride by-product. The formamide was dried over molecular sieves (4-8 mesh, Acros) prior to use. The reaction mass was transferred to a 100-mL serum vial along with 15 mL of formamide, crimped with a cap and septum, and centrifuged at 3000 RPM using an RC-5 Superspeed Refrigerated Centrifuge operating at room temperature. The supernatant was decanted in an argon atmosphere and this process was repeated two more times. N,N-dimethyl formamide (in three 15 mL portions) was used to rinse off the remaining formamide. The DMF was removed by heating under vacuum inside a glove box.
6.2.2 Characterization

Powder X-ray diffraction (PXRD) was performed using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu Kα λ = 1.5418 Å). Diffractograms were collected from 5 to 80 degrees 2θ using 0.010-degree steps and 0.3 seconds of dwell time. Transmission electron spectroscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were performed using an FEI Technai F30 transmission electron microscope operating at an accelerating voltage of 300 kV.

6.3 Results and Discussion

Mechanochemical routes to zirconium silicide from the elements have been reported, however these routes required long reaction times\(^\text{189}\) or yield impure materials\(^\text{188}\). Therefore, an alternative route via a mechanically driven metathesis reaction (Equation 12) was investigated. Zirconium silicide has been previously synthesized via a self-propagating solid-state metathesis (SSM) reaction at elevated temperatures. However, this is the first time such a reaction has been performed at nominally ambient conditions.

\[
\text{ZrCl}_4 + 2 \text{CaSi} \rightarrow \text{ZrSi}_2 + 2 \text{CaCl}_2
\]  

(12)

An added benefit is that it is possible to scale mechanochemical reactions through modification of mill design\(^\text{29}\). The crystallite size of ZrSi\(_2\) was controlled by the addition of an inert diluent, such as CaCl\(_2\). Figure 39 shows the XRD patterns of ZrSi\(_2\) at different diluent
loadings. Size analysis was performed using the Scherrer method. As the diluent load was increased, the crystallite size decreased. This allowed for the preparation of nanocrystalline materials ranging from 9-30 nm. Figure 40 shows that the crystallite size of ZrSi$_2$ obtained is dependent upon the concentration of ZrCl$_4$ used.

**Figure 39:** XRD patterns of the mechanochemically synthesized ZrSi$_2$ at different diluent loadings. By adding an inert diluent (CaCl$_2$) the crystallite size can be reduced. All patterns match ZrSi$_2$ (JC-PDS 32-1499).
Figure 40: Control of the average crystallite size in the mechanochemical synthesis of ZrSi$_2$. The concentration of ZrCl$_4$ is expressed in terms of moles/liter of free volume.

Since the reactor volume is fixed it is useful to define concentration as moles of reagent per liter of free volume of the vessel (total volume excluding the volumes of the milling media and reactants). This has been successfully applied to the kinetic analysis of the mechanochemical formation of alkaline earth carbides.$^{201}$ As ZrCl$_4$ concentration was increased, the crystallite size of the synthesized ZrSi$_2$ increased linearly. This analysis approach is a departure from the typical mechanochemical reaction analysis, which characterizes reactions in terms of ball to reactant ratios.$^{203}$ Although this method takes into account the increase in the kinetic energies available by using more or larger balls, it does not take into account the restriction in motion by increased ball volumes. The analysis presented here takes both into account for a single ball material. The addition of CaCl$_2$ reduced the effect of Ostwald ripening and resulted in smaller crystallite sizes. It is important to note that none of these reactions self-
propagate. The continuous input of energy from milling is required for the reaction to go to completion.

In order to remove the diluent and by-product (CaCl$_2$), the product required a washing step under argon to prevent surface oxidation. The solvent choice is critical. It must be polar enough to dissolve CaCl$_2$, but not possess –OH groups. Past reports have used dilute acid to remove by-products and obtain a pure silicide product.$^{187,204}$ However, we found that washing with water or aqueous acids causes a reaction, which converts the surface to oxides and hydroxides as well as produces silane gas. It is known that ZrSi$_2$ forms a stable colloid in water due to surface oxidation.$^{205}$

We minimized surface oxidation by using an alternative washing method, which produces a material suitable for conductive composites. Both dimethylformamide and formamide can be used to dissolve CaCl$_2$ and preserve the product. With a high dielectric constant, formamide is the preferred solvent for CaCl$_2$ removal. Dimethylformamide can also be used, but the removal of CaCl$_2$ is much less efficient due to its lower polarity. The CaCl$_2$ by-product was completely removed when formamide was used as an extraction solvent. The EDS spectrum, Figure 41, has no detectable chlorine peaks implying an upper limit of 1 at% for the chlorine content.
Figure 41: TEM images of ZrSi$_2$ prepared mechanochemically from a reaction diluted 50 mass% with CaCl$_2$. The material was isolated air-free using formamide: a) particles range from 100 nm to 20 nm; b) each particle is composed of crystalline regions as small as 5 nm in diameter; c) elemental analysis shows that calcium chloride was effectively removed. The remaining calcium is due to calcium oxide in the starting material.

A small amount of CaO impurity was also present; this may be due to the presence of CaO in the commercially obtained CaSi. Figure 41 also shows TEM image obtained from no diluent loading. Mechanically driven reaction can suffer from iron contamination when steel is used for the media and reaction vessel. Using iron-free milling materials such as alumina and tungsten carbide can eliminate this. However, there were no measureable iron peaks in the EDS spectrum. Given the sensitivity of the spectrometer this implies an upper limit for iron contamination of 1 at%. The particle size ranged from 20 nm to 100 nm with crystalline regions as small as 5 nm.

6.4 Conclusion

In conclusion, unfunctionalized zirconium disilicide nanomaterials of varying sizes were synthesized through a mechanochemical metathesis reaction. The crystallite sizes ranged from 9
to 30 nm depending on the amount of diluent used. Removal of the diluent and salt product using formamide resulted in isolation of polydisperse nanoparticles without capping groups or a passivating oxide layer. Oxygen-free ZrSi$_2$ could be produced by utilizing ultrapure CaSi. This would allow for nanoelectroceramic particles of the desired size to be incorporated into a composite as a reinforcement material for a variety of applications.
CHAPTER 7: MECHANOCHEMICAL SYNTHESIS OF ReB₂ POWDER


7.1 Introduction

Rhenium diboride (ReB₂) is a boron-rich ceramic that has been receiving a lot of attention in the scientific community because of its unusual properties. It has been reported as a superhard material²⁰⁶-²⁰⁸ with a hardness of 48 GPa measured at a small applied load (0.5N). It was also reported that it exhibits strong and highly covalent bonding, while a strong hybridization between the Re 5d and B 2p states indicates that Re-B bonds have also prevalent covalent character with some degree of ionic bonding present.²⁰⁹-²¹¹ Covalent boron-boron bonds are significantly stronger than the covalent Re-B bonds,²¹² and such difference between the B-B and Re-B bonds, as well as between nonequivalent Re-B bonds is responsible for anisotropic compressibility and rigidity of the structure.²¹³ The strong directional B-B bonding complimented by Re-B covalent bonds are responsible for the high resistance to elastic and plastic deformations resulting in high shear, bulk, and Young’s moduli, which are indicative of high hardness of the compound.²¹⁴ It was also reported that both Re 5d and B 2p states are at the
Fermi level and, hence, ReB$_2$ exhibits metallic behavior.$^{208,215}$ There have been numerous discussions in regard to the actual hardness of ReB$_2$ which was reported in Science.$^{206}$ Several reports$^{216-218}$ suggest that the hardness of ReB$_2$ was overestimated since it was measured in the region where the indentation size effect (ISE) is known to exist. According to different studies$^{216-218}$ the hardness value for ReB$_2$ lies well below the threshold of 40 GPa, and claims of ReB$_2$ being a super-hard material cannot be justified. However, evidence was produced$^{219}$ that the measured mechanical properties are strongly compositional dependent, where Re to B stoichiometry and morphology of the grains play important roles in the mechanical behavior of ReB$_2$. In particular, the presence of excess of amorphous boron along the grain boundaries of spark plasma sintered (SPS) ReB$_2$, where 1:2.5 Re to B stoichiometric ratio was used to synthesize polycrystalline material, was responsible for the measured lower hardness and Young’s modulus values.$^{219}$ Another problem, which makes ReB$_2$ very difficult material to work with, is that it slowly degrades in the presence of moist air. When ReB$_2$ interacts with water in air it becomes covered with a viscous solution within a few months. This property becomes especially serious when high surface area powders are exposed to water vapors in air, which may complicate ReB$_2$ implementation in industrial applications.

Although, the stoichiometric compound is ReB$_2$, a phase of highest boron content in the Re-B phase diagram,$^{220}$ it is difficult to synthesize a stoichiometric phase, and excess boron is usually required to ensure the formation of ReB$_2$ due to boron loss during the synthesis. Several approaches are reported on the synthesis of ReB$_2$.$^{206-208,213,214,217-225}$ In Ref. 213, ReB$_2$ was prepared using the solid state synthesis in an alumina crucible at 1300K for 4 hours in vacuum from elemental B and Re taken in a molar ratio of 2.5:1.$^{213}$ It was reported that the synthesized
material contained 5% impurity. Hexagonal platelets ReB$_2$ crystals were synthesized using (B$_3$H$_6$)Re(CO)$_4$ molecular precursor through the confined-plume chemical deposition (CPCD) technique.$^{221}$ The precursor has a 1:3 Re/B stoichiometry, which mitigated the loss of boron during synthesis. Arc melting of the 1:2.5 ratio of elemental Re and $^{11}$B in Ar atmosphere was used in Ref. 214 to synthesize a composition of ReB$_2$. $^{214}$ Three different techniques, all with some excess of B, were reported to be used for the synthesis of ReB$_2$. SPS, tri-arc crystal growing technique, and arc-melting are reported as techniques of choice to produce dense ReB$_2$. $^{219}$ Solid state synthesis from Re and B powders in Re/B molar ratio of 1:2.5 under pressure of 5 GPa and high temperature 1600°C for 60 minutes, followed by quenching to the room temperature at 100 °C/s was reported. $^{218}$ ReB$_2$ crystals have also been synthesized by arc melting, $^{206}$ zone melting, $^{222}$ and optical floating zone furnace synthesis $^{217}$ techniques. Thin ReB$_2$ films were produced by pulsed laser deposition (PLD) technique using ReB2 target, which was prepared by electron beam melting of the mixture of 1:2.5 Re to B powders. $^{207}$ Although most of the techniques used to synthesize ReB$_2$ used excess boron, a few works $^{208,223-225}$ utilize a 1:2 stoichiometric ratio for ReB$_2$ synthesis. In Ref. 223 two methods are reported, where one part of spectroscopically pure Re was heated with two parts of amorphous B. $^{223}$ One method was by heating the powder mixture in sealed evacuated silica tubes at 1200 °C for 12 hours and another method was by induction heating under the atmosphere of helium in vitrified alumina crucibles at 1500 °C. Both methods yielded ReB$_2$ structure. $^{223}$ In Ref. 224, the 1:2 mixture of Re to crystalline $^{11}$B powders were pressed into pellets, which were heated in an induction furnace under Ar atmosphere. $^{224}$ The pellets were melted at 2600 K for one hour. After synthesis, ReB$_2$ samples were ground down using a ball mill with tungsten carbide (WC) milling cups and balls.
The 1:2 Re to B ratio was also used for synthesis of ReB₂, but with the significant presence of aluminum as the growth medium. The mixture was heated to 1400 °C and held at temperature for 5 hours, it was slowly cooled to 700 °C and then quickly cooled to room temperature. After synthesis, the aluminum flux was dissolved in NaOH, and ReB₂ crystals were washed with deionized water and dried in air. SPS technique was also used to sinter dense ReB₂ pellets by using 1:2 Re to B powder mixture, but besides the ReB₂ phase, Re₇B₃ phase along with C impurity was also obtained during sintering. All the described techniques, used for the synthesis of ReB₂, involved using of high temperatures, sometimes as high as 2600 K. Since the vapor pressure of boron is much higher than that of rhenium, it created a problem with the stoichiometry of the ReB₂ compound. A technique for ReB₂ synthesis at nominally room temperature would represent a major advance in the material’s manufacture. The discussion in the literature inspired us to examine a new synthetic route to ReB₂ powders. These powders, as well as those of other boron-rich solids are typically not commercially available; therefore, techniques that allow synthesis of boron-rich solids are of high interest, especially if synthesis is performed at room or near room temperatures.

One technique that is highly suitable for producing different powdered materials is through mechanochemical methods. This approach allows synthesis of numerous novel materials and very complex compounds by applying mechanical force to mixtures of elemental powders. It involves repeated cold welding, fracturing, and rewelding of powder particles due to heavy deformation. As a result, the microstructure gets refined and the increased diffusivity (due to creation of a high density of crystalline defects) and reduced diffusion distances (due to refinement of microstructure) allow synthesis to take place at or near room temperature. In a
mechanochemical synthesis, attrition results in the reduction of particle size. This effectively creates micro reaction regimes where frictional heating can supply the activation energy for the production of line compounds from the elements. At this point, the heat of reaction can drive the reaction forward and even result in a self-propagating reaction. This method has been used to produce intermetallic phases, metallic glasses and composites, and different borides. Here we report the mechanochemical synthesis of ReB$_2$ powders.

7.2 Experimental Section

7.2.1 Materials and Preparation

Rhenium metal powder (99.99% pure, -325 mesh; Cerac, Inc) and boron powder (99% pure, -325 mesh, amorphous; Alfa Aesar) were used as received. A total of 20 grams of a stoichiometric amount of rhenium and boron powders were loaded into a SPEX WC vial with two 12.7-mm diameter WC balls. The grinding was done by a SPEX 8000 mixer mill for a total of 80 hours.

7.2.2 Phase Analysis

Every 5 hours, a small sample was removed for phase analysis by X-ray diffraction (XRD) method. No protective atmosphere was present during the vial opening and collection of
small amount of ground powders. A Rigaku D/MAX X-ray diffractometer was used to record XRD patterns of the powder.

7.2.3 Microscopy

The morphology and grain size of the powders were examined using a scanning electron microscope (Zeiss ULTRA-55 FEG SEM). A transmission electron microscope (FEI Technai F30 TEM) was used to get finer resolution images of the synthesized particles and to produce an area map distribution of Re, B, and W elements in the material.

7.2.4 Compositional Analysis

Adept 1010 Dynamic SIMS System (Physical Electronics USA) has been used to collect mass spectra for the samples. Cs primary beam of 3 kV and 25 nA or 50 nA was rastered over an area 1000 × 1000 μm². Both negative and positive secondary ions were collected. An auxiliary e-gun was used for charge neutralization.
7.2.5 Micro-Raman Spectroscopy

A Renishaw inVia Raman spectrometer was used to study the vibrational spectra of ReB$_2$ powders. The Raman spectrometer system is comprised of two lasers (532 and 785 nm) to excite the sample, a single spectrograph fitted with holographic notch filters and a Leica optical microscope rigidly mounted and optically coupled to the spectrometer. The generated laser power was 25 mW. Before collecting spectra of ReB$_2$, the spectrometer was calibrated with a Si standard using a Si band position at 520.3 cm$^{-1}$. The average collection time for a single spectrum was 300 s. Five measurements were performed from different locations of the powder in order to obtain the repeatable data. The 50x objective was used for illumination of the spot of 3-4 μm in diameter.

7.3 Results and Discussion

The synthesis of the desired ReB$_2$ phase out of elemental Re and B was monitored by powder XRD. The XRD patterns of metallic Re and B amorphous powders used for mechanochemical synthesis of ReB$_2$ are shown in Figure 42(a) and (b). Figure 42(c) shows the XRD patterns of ReB$_2$ powders after different milling times. The quantity of ReB$_2$ increased with increased milling time. After 5, 10, 15 or even 20 h of milling, significant amounts of Re metal were still present. After 30 hours of milling a small amount of Re was still evident with the ReB$_2$ formed. After 50h of ball milling, no Re was detected by XRD. The peaks of (002), (100) and (103) ReB$_2$ planes are sharper and have an increased intensity after 50 h in comparison with
30 h of milling, which indicates the presence of a more crystalline product. The WC phase was also present due to degradation of the milling media and vial upon contact with the abrasive product. Table 5 lists the lattice parameters of the synthesized ReB$_2$ after mechanical alloying for 30, 50 and 80 h and lattice parameters of ReB$_2$ reported in the literature (PDF card No. 01-073-1392) are also given for comparison.$^{223}$ As one can see from the Table 5, the measured lattice parameters match closely to the reported values. It is also noted that the lattice parameters slightly decrease with increase in mechanical alloying time, while the $c/a$ ratio increases with longer mechanical alloying time approaching the reported value.

Table 5: Lattice parameters of the synthesized ReB$_2$ after mechanical alloying for 30, 50 and 80 h.

<table>
<thead>
<tr>
<th>Mechanical alloying time (h)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2.9176</td>
<td>7.5023</td>
<td>2.5714</td>
</tr>
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<td>80</td>
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<td>PDF No. 01-073-1392$^{223}$</td>
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<td>7.4780</td>
<td>2.5786</td>
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</table>
Figure 42: X-ray diffraction patterns of a) Re powder, b) B powder, c) ReB₂ mechanically alloyed powders after 30, 50 and 80 h of milling, and d) ReB₂ powder after 1-year storage in the plastic bag without any protective atmosphere. The observed broad peak at $\sim 18^\circ$ 2θ in b) is a common peak seen for amorphous materials.
Figure 43 presents an SEM micrograph of the ReB$_2$ powders after 80 h of milling. It can be seen that a wide particle size distribution is observed. The size of the largest agglomerates is about 1 µm. Along with morphology study of agglomerates by SEM, high resolution characterization of selected particles was performed using TEM. A typical particle of mechanochemically synthesized ReB$_2$ and its electron diffraction are shown in Figure 44. The particle size is about 60-nm wide and 150-nm long. It consists of a number of crystallites 5-10 nm in diameter agglomerated together. The selected area electron diffraction pattern of the particle shows clearly defined diffraction spots, indicating that the particle is crystalline in nature. The maps of the distribution of Re, B, and W (Figure 45) show that the distribution of B is not homogeneous, and a high concentration of boron can be seen in a location at one side of the particle under study. Tungsten was also located on the opposite side of the particle, thus confirming the XRD data of contamination of the ReB$_2$ by the material used to make the vial and milling media.
Figure 43: SEM micrograph of ReB\(_2\) powders after ball milling for 80 h.

Figure 44: a) TEM micrograph of a particle of ReB\(_2\) powder after 80 h of milling; b) electron diffraction of ReB\(_2\) particle; and c) TEM micrograph of ReB\(_2\) lattice fringes.
The presence of a number of impurities was also confirmed by secondary ion mass spectrometry (SIMS). It can be seen from Figure 46, that oxygen was detected in the mixture after milling for 0.5 h since the $^{16}$O peak was present along with other oxygen-containing peaks such as O + B, O$_2$, and BO$_2$. The intensity of the $^{16}$O peak increased relative to the intensity of $^{10,11}$B peak as milling time was increased indicating the further O contamination of the powders. The relative intensity of O, BO and BO$_2$ peaks over the $^{10,11}$B peak is shown in Table 6, and one can see that the oxygen content increased as milling time increased from 0.5 h to 40 h reaching a saturation point since the oxygen content did not increase significantly from 40 h to 80 h of milling. The Re + O peak intensity was also compared to the Re + B peak intensity for all three milling times. The intensity ratios of these peaks are presented in Table 6, and it is consistent with the increase in oxygen content after milling. Prominent among the other impurities were C, F, and Cl. Although it was detected that the carbon content decreased with increased milling time, the F and Cl content increased upon milling for 40 h, but decreased after 80 h milling.
Figure 46: Negative secondary ion mass spectrometry (SIMS) of ReB₂ powders after (a,d) 0.5 h, (b,e) 40 h, and (c,f) 80 h of milling time.

Figure 47: Positive SIMS of ReB₂ powders after a) 0.5h, b) 40 h, and c) 80 h of milling time.
<table>
<thead>
<tr>
<th>Intensity Ratio</th>
<th>0.5</th>
<th>40</th>
<th>80</th>
</tr>
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<tbody>
<tr>
<td>Negative</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>secondary ions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BO$^{10,11}$B</td>
<td>9.6900</td>
<td>138.89</td>
<td>136.99</td>
</tr>
<tr>
<td>BO$_2$$^{10,11}$B</td>
<td>0.9414</td>
<td>91.743</td>
<td>125.00</td>
</tr>
<tr>
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<td>secondary ions</td>
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<tr>
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<tr>
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<td>0.0102</td>
<td>0.0441</td>
<td>0.0065</td>
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</tbody>
</table>

This indicates that the impurities were not distributed homogeneously in the powder, and the probes that were taken for analysis were not homogeneous; otherwise we should see the
increase of the impurities content as time of milling increased. Interestingly, hydrogen was detected in the powder after 30 min and as after prolonged milling. The relative intensity of the H peak was the lowest after 30 minutes of milling and increased after longer milling. This could indicate the presence of water in the batch during milling. Positive secondary ions are more sensitive to detect metallic contaminations and they were used to detect metallic impurities present as shown in Figure 47. Both Na and K were detected and their quantity increased upon increase in the milling time. However, their quantity was small after 80 h of milling in comparison with 40 h of milling time, which could be explained by the non-homogeneous distribution of the elements in the batch. Co was also detected as WC alloy contains Co as a soft binder in WC-Co cement composite.

Raman spectra of ReB$_2$ powders were acquired using two 532- and 785-nm lasers (Figure 48). Factor group analysis of ReB$_2$ hexagonal structure results in 2 $E_{1g}$ and 2 $E_{2g}$ Raman active phonon modes, where $E_{1g}$ and $E_{2g}$ modes are reported as B-B pair atom vibrations in $a$-$b$ plane of the unit cell as an “out-of-phase” vibrations with a calculated phonon energy of 85.2 MeV for $E_{1g}$ mode and 90.4 MeV for $E_{2g}$ mode$^{209}$. In the spectrum collected with infrared frequencies, two bands are detected: one at 190 cm$^{-1}$ and another at ~786 cm$^{-1}$. In the spectrum collected using visible laser, two peaks at ~228 and 780 cm$^{-1}$ wave numbers are also detected, but in addition two ~1400 and 1580 cm$^{-1}$ broad bands are present. These 1400 and 1580 cm$^{-1}$ bands indicate the presence of carbon, which is explained by contamination of the ReB$_2$ powders by milling. Due to the current experimental set up of the notch filter in the inVia spectrometer, only bands with wave numbers higher than 180 cm$^{-1}$ could be detected.
Upon storing ReB$_2$ powder in air, packed in the plastic bag, it was found that the powders formed hard agglomerates. This may be due to a sequential attack by oxygen and water. Initially oxygen may react with the surface of ReB$_2$ to form Re$_2$O$_7$ and B$_2$O$_3$ (Equation 13).

$$2\text{ReB}_2 + 5\text{O}_2 \rightarrow \text{Re}_2\text{O}_7 + \text{B}_2\text{O}_3$$  (13)
This reaction is thermodynamically favored with a heat of reaction of -1235.3 kJ/mol of ReB₂. Not only is there a severe lattice mismatch between these oxides and the ReB₂ compound but they quickly react with atmospheric water to form boric acid (Equation 14, -629.3 kJ/mol) and perrhenic acid (Equation 15, -55.812 kJ/mol).

\[ \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3 \]  \hspace{1cm} (14)

\[ \text{Re}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{HReO}_4 \]  \hspace{1cm} (15)

The net reaction (Equation 16) is enthalpically favored by -7.592 kJ/mol.²³⁵,²³⁶

\[ 2\text{ReB}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3 + 2\text{HReO}_4 \]  \hspace{1cm} (16)

These acids are hygroscopic and create a liquid layer that allows further degradation of the bulk material. In fact, storage of this material in air while in contact with nylon 6,6 results in holes in the nylon due to acidic degradation. Equations 14 through 16 suggest that applications of ReB₂ will require exclusion of oxygen or water vapors since the reaction sequence cannot proceed without both. High surface area powders are more susceptible than solid billets.

7.4 Conclusions

We have shown that ReB₂ powders can be synthesized mechanochemically from elemental crystalline Re and amorphous B powders in the stoichiometric 1:2 ratio. A complete reaction was realized after 70-80 h of milling in a SPEX-8000 high-energy ball mill. By using this approach, we have eliminated the need for excess boron reported by others. The synthesized
powders were agglomerates of small crystallites as evidenced by SEM. High-resolution TEM showed that the material had a clear crystalline structure. The batch became contaminated both with WC-Co milling media during milling and with oxygen and hydrogen coming from the environment during selection of the intermediate samples for analysis. It is our expectation that powders free of excess of boron will facilitate a thorough understanding of the role composition on the hardness and elastic moduli of ReB₂ ceramics. This is also a scalable solution that will ultimately allow larger quantities of this potentially useful material to be prepared.
CHAPTER 8: MECHANOCHEMICAL SYNTHESIS OF HEXAGONAL OsB$_2$

8.1 Introduction

For the past decade, extensive resources have been spent on the synthesis and study of OsB$_2$, ReB$_2$, RuB$_2$, IrB$_{1.1}$, and WB$_4$ transition metal borides.$^{237-241}$ OsB$_2$ and ReB$_2$ have received special attention, as they were reported to have high valence-electron density due to presence of Os and Re ions in the lattice while, at the same time, ultra incompressibility and high stiffness arising from the high degree of B-B and Os(Re)-B bond covalency.$^{238,242}$ It was also reported$^{238}$ that upon incorporation of B atoms, the Os hexagonal closed packed lattice expands by approximately 10%, forming orthorhombic OsB$_2$ $Pmmm$ (#59, oP$_6$ type) with lattice parameters $a$ = 4.684 Å, $b$ = 2.872 Å and $c$ = 4.076 Å.$^{243}$ ReB$_2$, unlike OsB$_2$, crystallizes in the hexagonal $P6_3/mmc$ (NO. 194) structure with lattice parameters $a$ = 2.9Å and $c$ = 7.478Å.$^{238}$ Incorporation of B into the interstitial tetrahedral site of Re lattice produces a 5% expansion of the lattice when ReB$_2$ is formed. This smaller expansion results in shorter Re-Re bonds, and increased bond strength, which in turn lead to increased stiffness and improvement of other mechanical properties. Hexagonal ReB$_2$ contains strong covalent B-B and Re-B bonds, which also contribute to the superior reported mechanical properties of the material.

Orthorhombic OsB$_2$, exhibits a very small anisotropic volume compressibility when subjected to pressures up to 32 GPa in a high-pressure diamond anvil cell.$^{237}$ The c-direction of the orthorhombic lattice is the least compressible and b-direction of the crystal is the most
compressible. It was found that the OsB$_2$ structure remained orthorhombic all the way up to 32 GPa and no phase transition was detected during in situ compression experiments. Other high-pressure hydrostatic experiments report the stability of this phase up to 34 GPa. The anisotropy in lattice compressibility implies the elastic moduli and hardness are highly dependent on the crystallographic orientation of OsB$_2$. The pressure stability and stress-strain relationship at large structural deformation of OsB$_2$ was also studied by applying density functional theory. The ideal critical stress at which a perfect OsB$_2$ lattice becomes unstable under tensile or shear deformation was calculated to be 20 GPa in tension and only 9.1 GPa in shear. It has been shown that while interstitial boron atoms enhance tensile strength by forming strong, directional covalent bonds with Os atoms, the Os-Os metallic bonds are prone to deform under applied shear stresses, thus, greatly reducing the resistance of OsB$_2$ to large shear deformation in certain easy-slip directions. It was also predicted that hexagonal ReB$_2$ might also be transformed to different metastable phase by applying the shear stress, as it has relatively low ideal shear strength of 34 GPa, albeit it is much higher than that of OsB$_2$ at 9.1 GPa. Thus, it is not hydrostatic, but deviatoric stress, which significantly affects both the crystal structure and mechanical properties of OsB$_2$ and ReB$_2$ components.

While most published work report the existence of a thermodynamically stable oP$_6$-type OsB$_2$ Pmmm orthorhombic structure, other OsB$_2$ structures have also been predicted. Using local density approximation, Hao et. al. predicted that OsB$_2$ can adopt an oP$_{12}$ OsB$_2$ Pnma structure. In addition to the orthorhombic OsB$_2$ structure, two pressure-stabilized hexagonal OsB$_2$ phases are also predicted to exist. The hexagonal ReB$_2$-type P6$_3$/mmc structure and hexagonal AlB$_2$-type P$_6$/mmm structure of OsB$_2$ have never been reported experimentally,
but their existence was predicted by first-principles calculations.\textsuperscript{212} Using local density approximation, it was calculated that only 2.5 GPa of pressure is required to transform orthorhombic into a hexagonal ReB\textsubscript{2}-type OsB\textsubscript{2} structure.\textsuperscript{212} The phase stability and pressure-induced structural phase transition of OsB\textsubscript{2} was also investigated,\textsuperscript{253} which predicted an orthorhombic to hexagonal phase transition pressure of 10.8 GPa. However, the authors did not specify what type of stress -- uniaxial, hydrostatic or shear -- was required to cause the transition. It is expected that hexagonal ReB\textsubscript{2}-type OsB\textsubscript{2} structure is a stable phase, as no soft mode at any wave vectors of the phonon band structure was found. It was also predicted that the hexagonal OsB\textsubscript{2} would have a higher bulk and shear moduli than those phases with an orthorhombic structure.\textsuperscript{253}

Mechanochemical syntheses, in a high-energy ball mill, have recently been implemented for the production of boron rich phases.\textsuperscript{203,254} This approach, i.e. strain-induced synthesis of compounds, utilizes both strong elastic and plastic shear deformations upon milling, leading to the appearance of new phases by solid state chemical reactions. This facilitates phase transitions at lower pressure, as well as substituting reversible phase transformations with fully irreversible phase transformations.\textsuperscript{255} The strain-controlled kinetics governs the rate of the chemical reactions for new phase formation. Acceleration of chemical reactions is caused by rapid corrugation of reaction interfaces triggered by shear stress driven rearrangement instabilities.\textsuperscript{256} It was also proposed that elastic shear strain accelerates chemical reactions by lowering the energy gap between the highest occupied bonding and lowest unoccupied anti-bonding molecular orbital.\textsuperscript{257,258} It was shown in elegant rotational diamond anvil cell experiments that structural changes do not happen unless plastic shear deformation occurs during compression.\textsuperscript{259} Here we
report the mechanochemical synthesis of hexagonal ReB$_2$-type OsB$_2$ phase, which has only been predicted to exist, but has never been experimentally reported.

8.2 Experimental

Osmium metal powder (99.95% pure, Heraeus, South Africa) and boron powder (99% pure, -325 mesh, a mixture of amorphous and crystalline phases, Alfa Aesar) were used for the mechanochemical synthesis of OsB$_2$. Enough Os and B powders (molar ratio 1:3) were loaded into a WC vial with two 12.7 mm WC balls to produce a ball to powder weight ratio was 4:1. All loading operations were carried out in an argon-filled glovebox. The vials were sealed with Viton gaskets to reduce oxygen contamination during milling. The milling was performed in a SPEX 8000D mixer mill for a total of 33 h. Every 30 min the milling was interrupted and vials were left for 30 min without grinding in order to decrease the vials’ temperature and reduce wear on the mill’s motor. After every two hours of milling, a small amount of sample powder was removed from the vial for X-ray diffraction (XRD) analysis. In a separate experiment, all the procedures were repeated except the ball to powder weight ratio was decreased to 2.7:1 and the balls used in the milling were covered with OsB$_2$ product formed from previous milling syntheses. A Rigaku D/Max X-Ray Diffractometer with a copper source (Cu K$_\alpha$ $\lambda$ = 1.5418 Å) was used to record the powder XRD patterns. A PANalytical X'Pert Pro MPD system was used to collect XRD patterns at low temperature under vacuum (using an Oxford PHENix stage) and at high temperatures under argon atmosphere (using an Anton Paar XRK900 reaction chamber). The OsB$_2$ sample was protected in argon atmosphere during high temperature (25 °C to 875 °C)
XRD and *in vacuo* during low temperature (-223 °C to 25 °C) XRD experiments. Refinement of the structure was performed using the HighScore Plus software. The morphology and grain size of the powders were examined in a Zeiss ULTRA-55 FEG scanning electron microscope (SEM) equipped with a silicon drift energy dispersive X-ray spectroscopy (EDS) detector capable of detecting low Z elements such as B. A JEOL JEM2200FS aberration-corrected scanning transmission electron microscope (STEM) was used to obtain high-resolution images of the hexagonal OsB$_2$ nanoparticles. After the OsB$_2$ powder was synthesized, a small quantity was loaded into a fused silica ampule, sealed under vacuum, and annealed up to 6 days at 1050 °C.

### 8.3 Results and Discussion

The powder X-ray diffractograms of the products produced by the mechanochemical synthesis of hexagonal OsB$_2$ from the elements are shown in Figure 49. After the first 2.5 h of grinding, a group of peaks, which does not correspond to the orthorhombic OsB$_2$ structure previously reported$^{244}$ is evident. The reaction is not complete since elemental Os peaks are prevalent in the diffractogram. After grinding for 6 h, the intensities of peaks from the new phase begin to dominate the diffractogram. A detailed analysis of these peaks showed a close match with the pattern of hexagonal ReB$_2$ (PDF # 00-011-0581), which can be obtained through similar mechanochemical synthesis.$^{254}$ It was hypothesized that a new hexagonal ReB$_2$-type OsB$_2$ phase was synthesized by mechanochemical synthesis. After 8 h of grinding, the amount of crystalline Os metal phase decreased drastically with the Os peaks became almost undetectable after 12 h of grinding. After 18 h of grinding, hexagonal OsB$_2$ became the major phase. As the high-energy
Ball milling was performed in a milling vial lined with tungsten carbide (WC) and WC balls were used as the grinding media. Contamination of the powder WC material is expected, and WC phase was detected even after only 2.5 h of milling. As grinding time increased, the WC contamination increased.

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**Figure 49**: XRD patterns of a 1:3 Os and B mixture after different milling times.
Figure 50: Rietveld refinement of the OsB₂ XRD pattern. After mechanochemical synthesis, the hexagonal OsB₂ produced was annealed *in vacuo* at 1050 °C for 48 h. The unindexed peak around 36° (▲) may be due to Os₂B₃.

While the contamination of OsB₂ with WC phase during milling is a major issue for the synthesis of a phase pure powder, a decrease of WC ball to raw powder weight ratio provided a clear pathway to synthesize hexagonal OsB₂ powder where no WC phase was present (Figure 50). Rietveld refinement was performed using the X-ray diffraction pattern (Figure 50) to calculate the lattice parameters of hexagonal OsB₂ phase. They are reported in Table 7, where
lattice parameters of hexagonal ReB$_2$ are also reported in addition to the calculated lattice parameters of the predicted hexagonal OsB$_2$ structure.$^{253}$ In addition to hexagonal OsB$_2$ structure, one extra peak, tentatively assigned to Os$_2$B$_3$ phase, was also present in Figure 50. The structure of the hexagonal OsB$_2$ unit cell based on measured lattice parameters is shown in Figure 51.

Figure 51: The crystal structure of hexagonal OsB$_2$. Osmium atoms are the larger gray spheres and boron atoms are the smaller black spheres.
Table 7: The lattice parameters of hexagonal OsB$_2$.

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanochemically Synthesized OsB$_2$</td>
<td>2.911</td>
<td>7.392</td>
<td>2.565</td>
</tr>
<tr>
<td>ReB$_2$ PDF#01-073-1392$^{223}$</td>
<td>2.900</td>
<td>7.478</td>
<td>2.579</td>
</tr>
<tr>
<td>Calculation data (GGA) of OsB$_2$$^{253}$</td>
<td>2.941</td>
<td>7.338</td>
<td>2.495</td>
</tr>
</tbody>
</table>

In order to verify the high-temperature stability of hexagonal OsB$_2$ structure, the OsB$_2$ powder was annealed at 1050 °C in vacuo for 6 days. It was determined that after annealing, the OsB$_2$ maintained its hexagonal structure and did not transform to the orthorhombic ($Pmmn$, No. 59, oP$_6$ type) phase, which shows the relatively high stability of hexagonal OsB$_2$ at high temperature in vacuum. After annealing, the crystallinity of the OsB$_2$ phase increased, as one would expect after such high-temperature exposure. The phase stability of hexagonal OsB$_2$ structure was also studied in the temperature range of -223 °C to 875 °C by in situ XRD under protective atmospheres (-223 °C to 25 °C in vacuo, 25 °C to 875 °C under argon). A change in $a$ and $c$ lattice parameters and unit cell volume as a function of temperature is presented in Figure 52. It was determined that the hexagonal OsB$_2$ structure is stable within the entire -223 °C to 875 °C temperature range both upon cooling and heating. The increase of $a$ and $c$ lattice parameters is confirmed as temperature increases. While there is a clear trend for an increase in the lattice parameters as the temperature rises, the $a$ lattice parameter shows a decrease in value indicating a
negative thermal expansion of the material in this crystallographic direction in the 300°C to 500°C temperature range.

Figure 52: The $a$ and $c$ lattice parameters of hexagonal OsB$_2$ along with the volume of the unit cell in the -223 °C to 875 °C temperature range.

The morphology of the agglomerates of mechanochemically synthesized hexagonal OsB$_2$ in the first experiment was investigated by SEM. The irregular shape of the agglomerates as well as the wide agglomerate size distribution is seen in the SEM image of the powder ground for 18
h (Figure 53). Most of the agglomerates are smaller than 10 μm, although some of the agglomerates exceed 30 μm in effective diameter. EDS analysis confirmed the presence of Os, B, W and C as well as some oxygen.

Figure 53: a) An SEM micrograph and b) EDS of OsB₂ after 18 h of milling.

Aberration-corrected scanning transmission electron microscopy (STEM) was also used to study the atomic arrangement of the hexagonal OsB₂ powder. Characteristic high-angle annular dark-field (HAADF) images of OsB₂ particles are presented in Figure 54. By sonicking the powder in methanol for 1 min, the larger agglomerated particles were broken down into smaller aggregates of 100-500 nm in size, as shown in Figure 54a. These aggregates were made up of nanocrystallites ranging in size from 1 to 10 nm (Figure 54b). High-resolution STEM
images of OsB$_2$ nanocrystallites aligned along the major zone axes are presented in Figure 54c-d, with the corresponding fast Fourier transform (FFT) in the inset. Figure 54c presents OsB$_2$ nanocrystallites aligned along the [001] direction, and Figure 54d presents other OsB$_2$ nanocrystallites aligned along the [100] direction. Diffractograms of both particles match those of hexagonal OsB$_2$ phase.

Figure 54: HAADF-STEM images of (a,b) OsB$_2$ powder, and (c,d) individual nanocrystallites. The corresponding fast Fourier transforms of the images are included in the insets.
8.4 Conclusion

We have shown that OsB$_2$ powders can be synthesized mechanochemically from elemental crystalline Os and amorphous B powders in the stoichiometric 1:3 ratio. After 2 h of milling in a SPEX-8000 high-energy ball mill, OsB$_2$ begins to form. Hexagonal OsB$_2$ is the major phase after 18 h of milling, with only a WC secondary phase present due to failure of the grinding media. The lattice parameters corresponding to the hexagonal OsB$_2$ were determined to be $a = b = 2.9047$ Å, $c = 7.4500$ Å; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. OsB$_2$ particles were analyzed by TEM and the corresponding electron diffraction patterns were obtained. STEM and HAADF show large agglomerates composed of smaller nanocrystallites ranging from 1 to 10 nm. No phase change was observed upon annealing the synthesized OsB$_2$ at 1050 °C for 6 days under vacuum. Therefore, it can be concluded that hexagonal OsB$_2$ is very stable.
CHAPTER 9: MECHANOCATALYSIS FOR BIOMASS-DERIVED CHEMICALS AND FUELS


9.1 Introduction

Lignocellulosic biomass represents a rich source of feedstock for fuels\(^{260}\) and chemicals; major work in developing this resource is underway. Biological sources such as switch grass, corn stover, bagasse, and other agricultural waste are largely underutilized. Most lignocellulosic biomass is processed in one of three ways: acid hydrolysis, enzymatic hydrolysis, and pyrolysis.\(^{261,262}\) New biological\(^{263,264}\) and chemical\(^{265}\) approaches seek to circumvent the drawbacks associated with these processes.

Catalytic processing of these materials is an important topic. Although efficient catalysts have been developed for a wide range of heterogeneous systems, they are not suitable for solid-solid catalysis. A major difficulty with these solids is mass transport. High surface area structures suited to liquid and gas systems do not work as efficiently in solid systems. Two typical structures, porous solids and supported particles have limitations when applied to solid...
systems. Porous solids have pore sizes too small to accommodate molecules much larger than 30 Å; and supported particle systems still require some method to overcome the solid-solid diffusion barrier.

Biochemical pathways are also important in processing these polymers. However, enzymes have limited pressure/temperature regimes in which they can function and are not as robust as inorganic solids.

There are two issues that need to be addressed in order to realize effective catalysis in solid-solid reactions. The solid-solid diffusion barrier (mass transport) must be overcome and the catalyst must be structured to allow access to catalytic sites. Currently, most catalytic depolymerization involves solvent systems to overcome this diffusion barrier.266-269

We have found that it is possible to overcome diffusion in a solid-solid reaction by using mechanical force without the addition of solvents. This phenomenon is often referred to as mechanocatalysis or tribocatalysis. Little work has been done on this phenomenon.270-273 In fact, recent work has focused on using traditional heterogeneous catalysts (such as zeolites) in mechanochemical processes.274-280 This approach ignores the aggressive nature of mechanical processing. Effective mechanocatalysts must be mechanically robust, and possess sites that are physically accessible and chemically active.

Mechanocatalytic processes require no external heat. All of the energy for the reaction comes from the pressures and frictional heating provided by the kinetic energy of milling media moving in a container. Although there is large body of work examining mechanochemical
to date no one has examined the properties required for an effective mechanocatalyst.

In a mechanocatalytic system, it is important that intimate contact between the catalyst and reactant be maintained. Although most biomass processing facilities utilize some form of attrition technology, it is usually in the form of hammer mills, disk mills, or roller mills. These technologies are being actively researched, but they do not allow good interaction between a solid catalyst and the material being treated. Pebble (or rolling) mills, shaker mills, attrition mills, and planetary mills are a few examples of mills that effectively “push” the catalyst into contact with the material being treated (biomass).

9.2 Experimental

9.2.1 Reagents

Pure microcrystalline cellulose (Avicel, Brinkmann) was utilized to investigate the performance of different solid catalysts. The natural cellulose sources Z. mays indurata (flint corn), Prunus stone, paper, aspen wood, and mixed biomass were collected from local sources. The grasses: A. gerardii (Big Bluestem), S. scoparium (Little Bluestem) and P. virgatum (Switchgrass) were supplied by Agricol Corporation (Madison, WI). All natural cellulose sources were dried at room temperature to a moisture content of <10% and cut to 2 cm or smaller pieces.
The materials kaolinite (Edgar Plastic Kaolin, Axner Pottery), delaminated kaolinite (Kaopaque 10, IMERYS), aluminum phosphate (Fisher Scientific), aluminum oxide (J.T. Baker), talc (Nytol 100HR, Axner Pottery), Y-type zeolite (HS-320, hydrogen Y, Wako Chemicals), bentonite (Asbury Carbons), vermiculite, quartz, muscovite mica, silicon carbide(-325 mesh, Electronic Space Products International), graphite (grade TC306, Asbury Carbons), and aluminum sulfate (Fisher Scientific) were used as received. Layered silicates were H⁺ exchanged by soaking in 1 M hydrochloric acid for 12 h, filtering and dried at 80 °C overnight. Chemically delaminated kaolinite was prepared by intercalating with urea and deintercalating by washing with water. The super acid was prepared by stirring aluminum oxide (J.T. Baker) in 2.5 M H₂SO₄ followed by calcination at 600 °C.

9.2.2 Mechanical Processing

Various amounts of cellulose and catalyst were ground using a rolling mill (custom), mixer mill (SPEX Certiprep, Metuchen, NJ), or attrition mill (Union Process Inc., Akron OH). Initial catalyst assessment was performed using a mixer mill. Typically, 2 grams of a 1:1 mixture of catalyst and cellulose were ground in a 65 mL vial (1.5” ID x 2.25” deep) made of 440C steel, utilizing three 0.5” balls made of the same material as the milling vial. Attrition milling experiments were performed by Union Process, Inc. in a 1-SD attrition mill run at 350 rpm with a 1.5 gallon tank, 40 lbs of 0.25” chrome steel (SAE 52100) balls as the milling media, and 1200 g of a 1:1 mixture of cellulose and catalyst. Rolling mill experiments were performed
in a custom rolling mill constructed of 316 stainless steel with a diameter of 1.37” and a length of 4.93”. The mill was charged with 25 0.5” balls made of 440C steel and 2 grams of a 1:1 mixture of cellulose and catalyst.

9.2.3 Gravimetric Analysis

The extent of hydrolysis was monitored gravimetrically. Conversion of cellulose to water-soluble oligosaccharides was determined by stirring 0.1 g of the reaction mixture in 30 mL of water. Any oligosaccharide with a degree of polymerization <5 will be solvated.\textsuperscript{302} The production of water-soluble products was measured by filtration through a 47 mm diameter Whatman Nucleopore\textsuperscript{©} track etched polycarbonate membrane filter with a pore size of 0.220 \(\mu\text{m}\). The residue was dried in a 60 \(^\circ\text{C}\) oven for 12 h and then weighed.

9.2.4 Gas Chromatography with Mass Sensitive Detection

Gas chromatography – mass spectrometry (GC-MS) analysis was performed on an Agilent 6850 GC with an Agilent 19091-433E HP-5MS column (5% phenyl methyl siloxane, 30 m x 250 \(\mu\text{m}\) x 0.25 \(\mu\text{m}\) nom.) coupled with a 5975C VL mass selective detector. Saccharide composition was analyzed by silanizing\textsuperscript{303} the product. Dehydration products were extracted with 60 \(^\circ\text{C}\) chloroform and analyzed by GC-MS.
9.2.5 *Thin Layer Chromatography*

Thin layer chromatography was used to assess the composition of the hydrolysis product. Solutions were spotted onto cellulose plates and developed with a 20:7:10 mixture of n-butanol, acetic acid, and water. The plates were stained with a 3% urea and 1 M phosphoric acid in n-butanol saturated water solution.

9.2.6 *Discrete Element Modeling*

Discrete element models of the milling process were generated using EDEM (DEM Solutions Ltd.).

9.2.7 *Degree of Polymerization*

The degree of polymerization of the insoluble cellulose residue was determined using viscometry according to the method outlined in ASTM D 4243.
9.3 Results

Three milling modes were investigated for the mechanocatalytic depolymerization of cellulose — shaking, rolling, and stirring. Figure 55 illustrates solubilization achievable in a SPEX shaker mill. No appreciable solubilization was realized on samples of microcrystalline cellulose milled without a catalyst. The catalysts' chemical and physical properties effect on conversion efficiency was studied by choosing materials with specific structural and chemical properties. Figure 56 summarizes the solubilization results for cellulose mechanocatalytically treated for two hours in a shaker mill.

![Graph showing solubilization of cellulose as a function of milling time in a SPEX 8000D mixer mill. Catalysts were milled with microcrystalline cellulose in a 1:1 ratio. The most rapid solubilization was measured using 1:1 aluminosilicates such as kaolinite.](image)

Figure 55: Solubilization of cellulose as a function of milling time in a SPEX 8000D mixer mill. Catalysts were milled with microcrystalline cellulose in a 1:1 ratio. The most rapid solubilization was measured using 1:1 aluminosilicates such as kaolinite.
Figure 56: Mechanocatalytic activity for a sample of compounds investigated. Catalysts were milled with microcrystalline cellulose in a 1:1 ratio for 2 h. Layered compounds with a surface acidity, $\text{H}_0 < -3.0$, as determined by dicinnamalacetone gave the best yields. The catalytic efficiency of kaolinite was improved through physical delamination and proton exchange (*).

A shaker mill was chosen to assess catalyst efficacy since cellulose hydrolysis is observed after as little as 6 minutes of milling. This mode is a high-energy process with the possible realization of localized high pressures. After 3 hours of milling, up to 84% of the cellulose can be converted to water-soluble fractions allowing rapid assessment of catalysts parameters.

The layered silicate mineral kaolinite was determined to be a good mechanocatalyst and the composition of the solubilized fraction produced was analyzed utilizing thin layer chromatography and gas chromatography with mass sensitive detection. Both methods confirmed that depolymerization occurs rapidly with no oligosaccharides larger than $n = 2$.
detected even after 30 min of treatment. The three major water-soluble components detected were levoglucosan, fructose, and glucose. The degree of polymerization of the insoluble residue was measured and found to decrease linearly with time.

The variation in product composition was studied as a function of milling mode and time. A study of the energy input through milling, and its effect on products, was investigated using a variable speed rolling mill. Models were developed using discrete element methods (EDEM™, DEM Solutions Inc.) to estimate the compressive forces achieved during milling. These models indicate that, in a 10 second period, a shaker mill can produce 9 impacts with forces between 400 and 3000 N; an attrition mill can produce 9 impacts between 400 and 2000 N; a rolling mill at 30 rpm generates 4 impacts between 60 and 110 N; and at 100 rpm, 10 impacts between 60 and 130 N.

High-energy processing in a shaker mill resulted in the production of levoglucosan, fructose and glucose with a ratio of 9:1:4.3 after 30 min of treatment and a ratio of 4.6:1:4.1 after two hours of treatment. The product distribution was similar for samples prepared in an attrition mill. Low-speed processing in a rolling mill (30 rpm) resulted in no measurable catalytic activity; increasing the rotation velocity to 100 rpm resulted in 13.2±0.8% solubilization after 96 h of treatment. The product consisted of levoglucosan, fructose, and glucose in a 1:1:5.8 ratio. With continued high energy milling the levoglucosan fraction decreased and other dehydration products were observed - levoglucosenone and 5-hydroxymethylfurfural (HMF), as well as the retro-adol condensation product furfural (Figure 57). This result is encouraging since HMF is of interest for use as a fuel or chemical feedstock.260,304,305
Figure 57: Cellulose can be mechanocatalytically converted to glucose and, with prolonged treatment, into a variety of products. The formaldehyde produced was not observed with the analytical techniques utilized.

9.4 Discussion

Milling alone (without a catalyst present) is not sufficient to hydrolyze the glycosidic bond in cellulose. Acidic solids such kaolinite (Al₂Si₂O₇•2H₂O), alumina super acid, aluminum phosphate (AlPO₄), alumina (Al₂O₃), Y-type zeolite, and bentonite (Al₂Si₃O₁₁•H₂O) showed good catalytic ability. Low-acidity solids such as talc (H₂Mg₃(SiO₃)₄), vermiculite ((MgFe,Al)₃(Al,Si)₄O₁₀(OH)₂•4H₂O), quartz (SiO₂), mica (KF)₂(Al₂O₃)₃(SiO₂)₆(H₂O), silicon
carbide (SiC), graphite (C), and aluminum sulfate (Al₂(SO₄)₃) were less effective. The hardness of the catalyst did not play a role in the efficiency of the depolymerization. Both kaolinite and talc are soft, but kaolinite is a much more efficient catalyst. Silicon carbide and aluminum oxide are both very hard, but silicon carbide showed little or no catalytic ability. The use of harder catalysts resulted in undesirable wear on the container and milling media. The most effective catalyst is the layered mineral kaolinite. Kaolinite is an aluminosilicate consisting of aluminum-containing (as AlO₆ units) layers covalently bound to silicon-containing (as SiO₄ units) layers as in a 1:1 ratio. These layers are held together by hydrogen bonds from protons on open Al-O-Al sites to open Si-O-Si sites. The structurally similar bentonite has each aluminum-containing layer covalently bound above and below by a silicon-containing layer in a 2:1 configuration; this prevents the active sites from interacting with the cellulose (Figure 58).

Figure 58: The structures for the 2:1 smectite bentonite (left) and 1:1 smectite kaolinite (right). The octahedral are AlO₆ unites and the tetrahedral are SiO₄ units. The sheets in bentonite are charged due to an Al:Si imbalance. The sheets are held together by ionic forces between the sheets and a cation (dark sphere). The sheets in kaolinite are held together by hydrogen bonds from protons on the Al layer to the oxygens on the Si layer.
The role of aluminum in the active sites was confirmed by comparing the catalytic ability of quartz and aluminum phosphate. These compounds are isostructural; substituting the SiO$_4$ units in quartz with AlO$_4$ and PO$_4$ units, as in aluminum phosphate, results in an increase in active sites and the observed increase in catalytic ability. Layered compounds are effective mechanocatalysts because the layers are typically held together by weak forces such as hydrogen bonding and van der Waals forces. These bonds can be easily broken via mechanical processing (grinding or rubbing). The result is a material with a high specific surface area (SSA) that is only dependent upon the number of layers in each particle.

\[
SSA_{\text{hard sphere}} = \frac{3}{rd_{\text{solid}}} 
\]  

\[
SSA_{\text{layered}} = \frac{2}{(n+nf-1)td_{\text{solid}}} 
\]

Equation 17 and 18 give the specific surface areas (SSA) in area/unit mass for hard spheres and layered materials where \( n \) = the number of layers, \( d_{\text{solid}} \) = the density of the solid, \( r \) = the radius of the particle, \( t \) = the interlayer spacing, and \( f \) = the ratio of the layer thickness to the interlayer spacing. Equation 17 is derived from the surface area of a solid sphere \( (4\pi r^2) \) and the mass of the sphere as determined by its density \( \text{mass} = \frac{4}{3} \pi r^3 d_{\text{solid}} \). Equation 18 is derived from the surface area of a fragment using its length and width \( (2lw) \) and the mass of \( n \) layers using the material's density and interlayer spacing \( \text{mass} = lw(n+nf-1)td_{\text{solid}} \). This derivation assumes both sides of the sheet are catalytically active. For kaolinite, only one side of the sheet (the AlO$_6$ side) is catalytically active. This results in a SSA half of that predicted by Equation 18. Using the \( d_{\text{solid}}=2.599 \text{ gcm}^{-3} \), \( t = 2.892 \text{ Å} \), and \( f = 1.561 \) for kaolinite, we find that reducing it
to a collection of single aluminosilicate sheets (through delamination) would result in an active specific surface area of 852 m$^2$g$^{-1}$. This would be equivalent to 1.35 nm spherical particles. Structures consisting of 5 layers would have a specific surface area equivalent to 10.2 nm particles (113 m$^2$g$^{-1}$). It has been suggested that mechanochemical processes are dependent on the area of surface sites available. This is in line with our observation that layered materials are the ideal structure for mechanocatalysts. Delamination of kaolinite to single sheets has been observed during grinding. In fact, it is not unreasonable to expect delamination to single layers; this has been observed in talc.

It is important to note that anhydrous kaolinite showed a decrease in catalytic ability. This is due to the fact that water is required to break the cellulose glycosidic bond.

**9.4.1 Kinetics and Depolymerization Mechanism**

Concentrations in chemical reaction are typically expressed in terms of moles/l. In a solventless, solid-solid reaction this expression is meaningless. If percent composition is used, the resulting expression does not accurately reflect the consequences of increasing the milling load without increasing the vessel size (which results in a decrease in reaction rate). We have found that reaction rates can be examined by expressing the concentration of reactants and products in terms of mass/free volume. Here the free volume is the volume of the milling container not occupied by balls, reactants, or products. This value is calculated by converting the masses of the reactants, products, and milling media to volumes based on the materials' densities.
This volume is subtracted from the container volume to give a free volume. This approach indirectly incorporates the motions available to the milling media. The milling media, for the same mode of milling, in systems with large free volumes will have a greater mean free path than in systems with small free volumes.

We determined the reaction order by generating kinetic plots. Although attrition is quite rapid in a SPEX mill, finely ground cellulose (Avicel) and catalysts were used to minimize the effect of initial particle size. The reaction cannot be zeroth order since reaction rate would be independent of concentration. The concentration of the reactants directly affects the free volume and, subsequently, the motion of the milling media. Higher concentrations result in less motion. In the most severe case the concentration would be so high that no media motion is allowable. A zeroth order model would predict yield in this case - an unphysical prediction. Figure 59 compares a first and second order plot in this system.

The differentiation between first and second order behavior is a little more subtle. Both kinetic plots can be fit to lines representing initial and final kinetics. Although the first order plot gives slightly better linear correlation coefficients, a second order model more accurately describes the data. For example, using H⁺ exchanged, physically delaminated kaolin the linear correlation coefficient for the initial kinetics is -0.9986 for first order kinetics and 0.9974 for second order kinetics. In the final kinetic region this coefficient is -0.9969 for first order kinetics and 0.9952 for second order kinetics. The important feature is the data point near the intersection of the two regression lines (inset Figure 59). It does not fall on the first order curve that would be generated by the sum of the two linear fits. It does fall on the curve generated by
the two linear second order fits. This behavior was observed for all catalysts listed in Table 8, which summarizes the rates observed in several systems. The uncertainties reported are the standard deviations in the slope of the second-order plot calculated using linear regression. The uncertainty in the time change was determined by propagating these uncertainties through the equation describing the intersection of these lines. Second order behavior has also been observed in the hydrolysis of the glucose dimer cellobiose in super critical water.\textsuperscript{308}

![Figure 59: A first (left) and second (right) order plot of the hydrolysis of cellulose in a SPEX shaker mill. Both plots show strong linear relations, but the data point near the intersection of the two fit lines (inset) indicates that a second-order process is the more accurate description. The catalyst used was H\textsuperscript{+} exchanged, physically delaminated kaolinite.](image-url)
Table 8: Second-order rates observed in the catalytic depolymerization of cellulose in a SPEX shaker mill. The column labeled “time change” indicates when the rate changes.

<table>
<thead>
<tr>
<th></th>
<th>Initial Rate (second order) L g⁻¹ h⁻¹</th>
<th>Second Rate (second order) L g⁻¹ h⁻¹</th>
<th>Time Change (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite, physically delaminated, H⁺ exchanged</td>
<td>0.0522 ± 0.0022</td>
<td>0.1460 ± 0.0058</td>
<td>1.21 ± 0.14</td>
</tr>
<tr>
<td>Kaolinite, H⁺ exchanged</td>
<td>0.0464 ± 0.0017</td>
<td>0.0836 ± 0.0054</td>
<td>1.08 ± 0.29</td>
</tr>
<tr>
<td>Kaolinite, chemically delaminated</td>
<td>0.0433 ± 0.0013</td>
<td>0.0902 ± 0.0035</td>
<td>1.13 ± 0.15</td>
</tr>
<tr>
<td>Kaolinite, physically delaminated</td>
<td>0.0330 ± 0.0013</td>
<td>0.0832 ± 0.0027</td>
<td>1.16 ± 0.11</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.03240 ± 0.00085</td>
<td>0.0825 ± 0.0056</td>
<td>0.75 ± 0.17</td>
</tr>
<tr>
<td>Bentonite</td>
<td>0.0268 ± 0.0015</td>
<td>0.00639 ± 0.00018</td>
<td>1.86 ± 0.18</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>0.01147 ± 0.00050</td>
<td>0.00230 ± 0.00016</td>
<td>1.383 ± 0.049</td>
</tr>
<tr>
<td>Talc</td>
<td>0.00943 ± 0.00014</td>
<td>0.00415 ± 0.00026</td>
<td>3.567 ± 0.029</td>
</tr>
</tbody>
</table>

It was confirmed that the process was catalytic by performing turnover studies using kaolinite and cellulose in a shaker mill. Two hours of milling time resulted in loss of catalytic efficiency over 5 turnovers. One hour of milling resulted in no loss in catalytic efficacy over 8 turnovers. Although extended milling can induce significant defects in the crystal structure of the catalysts, the active sites on these catalysts are surface protons and should be unaffected by the defect structure of the solid. Prolonged milling may, instead, result in the formation of insoluble polymerization products. In particular, furfural polymerizes when heated in the presence of an acid. These insoluble by-products would interfere with the interaction between
the catalyst and the reactant. Limiting the milling time limits the production of these by-products.

In order to understand the mechanism of cellulose depolymerization, the degree of polymerization (DP) of the insoluble residue was measured. This can be compared to the change in DP observed in acid and enzyme hydrolysis. The three approaches to depolymerization - acid, enzymatic, and mechanocatalytic proceed by quite different kinetics and mechanisms. By examining the change in degree of polymerization of the residue with respect to the fraction of oligomers with a DP<5 (or degree of solubilization) the role of these factors can be reduced and the approaches can be compared.

Figure 60: Change in the degree of polymerization for the insoluble residue of cellulose hydrolysis as a function of degree of solubilization. The dotted line represents a model where hydrolysis only occurs at the ends of the polymer chain.
Figure 60 shows the change in DP as a function of degree of solubilization. Values for acid hydrolysis were simulated using a model that all bonds have an equal probability of cleavage.\(^{309}\) Change in DP from enzyme hydrolysis was taken from the literature.\(^{310}\) It can be seen that mechanocatalytic depolymerization does not follow a mechanism like acid or enzyme hydrolysis. Mechanocatalytic hydrolysis does not randomly cleave cellulose chains like acid hydrolysis. Initially, depolymerization more closely matches the enzymatic process. The accessibility of surface sites gives rise to the evolution of the degree of polymerization in enzyme hydrolysis.\(^{311}\) Similarly, mechanocatalysis is dominated by two processes - attrition and hydrolysis. During the initial milling time, cellulose particles are being broken down physically and chemically. There are three main chemical reactions occurring. The reactions are: hydrolysis catalyzed by the catalyst's surface protons, dehydration by the catalyst, and retro-aldol condensation due to the localized high pressures. The surfaces of these particles are accessible to the catalyst. At a certain point, attrition slows and only the end units of the cellulose chain are accessible. This results in a change in DP that coincides with a model where only the ends of a polymer chain are allowed to react (dashed line in Figure 60). For the layered catalysts, bentonite, talc, and kaolinites the rate changes (Table 8) when solubilization is between 30 and 40\%. This corresponds to the region in Figure 60 where the DP of the residue matches an end-only hydrolysis model and further corroborates the second-order model.
9.4.2 Industrial Applicability and Economics

In order for mechanocatalysis to be an effective industrial tool, it must be effective for real world materials. We tested the conversion efficiency for a wide range of relevant cellulose sources. Figure 61 illustrates the efficiency observed in the depolymerization of cellulose after two hours of milling in a mixer mill. Initial particle size was kept to less than 2 cm. In all cases, the cellulose source and catalyst were reduced to fine powders in 5 to 10 minutes due to the vigorous nature of the attrition process. Agricultural wastes from corn (corn stover), wood (aspen), and fruit (Prunus stone) production were examined; all showed improved water solubility after mechanocatalytic treatment. Commercial and residential waste such as paper and mixed waste from clearing land can also be efficiently treated. The grasses A. gerardii (Big Bluestem), S. scoparium (Little Bluestem) and P. virgatum (Switchgrass) are crops that are of interest for use as a biomass source. It should be noted that 90% of a corn kernel’s mass can be converted to soluble matter in a single pass.
Our survey experiments have utilized a SPEX mixer mill, which allows us to rapidly assess the viability of catalytic materials and develop kinetic models for cellulose conversion. We have found that the reaction goes as a second-order process in cellulose. However, this technology is not scalable without significant redesign. Rolling-mode and stirring-mode are among the scalable approaches. Utilizing our DEM model, it was determined that rolling mills do not develop the high pressures encountered in a shaking mill. Processing in a rolling mill produced a product composed primarily of glucose. This suggests that the forces that occur during the milling process are directly related to the composition of the soluble fraction produced. Low forces result in no observable solubilization; increasing the rotational velocity of the roller mill results in compressive forces and a measurable yield of sugars. The most energetic process, shaking-mode, results in an increase in the levoglucosan fraction.
implies that there is a critical energetic region favorable for the production of fructose and glucose.

Attritors are scalable, can be run in a batch or continuous mode, and can produce compressive forces similar to those achieved in a shaker mill (0.4 to 3 GPa, as predicted by out DEM models). We performed a limited number of kilogram-scale tests using a small Union Process attritor. Figure 62 illustrates the energy costs associated with the two milling technologies. The dashed line is the energy obtainable from the ethanol produced from one gram of glucose. It can be seen that the SPEX mill is an energy intensive process. Switching to an attritor allowed the process to be scaled-up by 1000 fold; the result was nearly a 46-fold decrease in the energy consumption as expressed in kJ/gram glucose produced. It was found that conversion in a small attritor required a 4-hour initiation time before the rate became appreciable. The kinetic data from this batch was used, in conjunction with the behavior observed in the shaker mill, to develop a predictive model for a 100 kg batch. The gray trace in Figure 62 shows the projected energy consumption for an attritor with a 150 hp motor and fast reaction kinetics. It is important to note that the four-hour induction period must be eliminated for this approach to produce glucose at an energy cost lower then the energy released by burning the ethanol prepared from the glucose. This process is energy positive for 0.9 hours of milling with a predicted conversion efficiency of 20.2%.
Figure 62: The energy consumed to produce 1 gram of glucose from 1 gram of cellulose treated in a shaker mill, 1 kg of cellulose treated in an attritor, and modeled consumptions for 100 kg in a large attritor. The dashed line is the energy released by burning the ethanol produced from 1 gram of glucose.

9.5 Conclusion

The natural layered structure of clays is ideally suited for use as a catalyst in milling processes. We have shown that layered structures are particularly suited to mechanocatalytic processes. This opens up a new area for catalyst synthesis. A new set of catalysts based on this paradigm could be synthesized to take advantage of the unique conditions in a ball mill. Using this idea, it may be possible to depolymerize other biopolymers such as chitin or protein as well
as synthetic polymers such as nylon, polyethylene terephthalate, polycarbonate, and polylactic acid.

The observation of the glucose dehydration products levoglucosan, levoglucosenone, and 5-hydroxymethylfurfural as well as the retro-aldol condensation product furfural suggest that it will be possible to design mechanocatalysts for the direct conversion of cellulose into these compounds. In fact, many of the synthetic pathways utilized to produce derivatives from these compounds should be directly accessible through solventless milling.

Mechanocatalytic processing of materials has significant advantages over current methods. The best catalyst so far, kaolinite, costs around $80/ton and can be reused. Any catalyst waste produced is innocuous and there are no toxic solvents needed. Additionally, no heating or high-pressure equipment is required, simplifying plant design. Mechanocatalytic conversion of cellulose is insensitive to lignin and hemicellulose content allowing any cellulosic biomass source to be utilized. This is an improvement over methods that utilize edible biomass (such as corn) for ethanol production.
CHAPTER 10: HETEROGENEOUS METAL-FREE HYDROGENATION OVER DEFECT LADEN HEXAGONAL BORON NITRIDE

10.1 Introduction

Originally discovered in 1897 by Sabatier, who received a Nobel prize for this work in 1912, catalytic hydrogenation is widely used in industry and is heavily utilized in the synthesis of many pharmaceutical and agricultural chemicals.\(^\text{313}\) Although the conversion of olefins to alkanes is thermodynamically favored under appropriate conditions, such reactions are so sluggish that a catalyst is required to facilitate hydrogenation. It was first observed that traces of nickel could mediate the addition of H\(_2\) to olefins\(^\text{314}\) and later that palladium, platinum, rhodium, and other precious metals exhibited similar catalytic activity, owing to the overlap between the metal d-orbitals and the hydrogen molecular orbitals.

Two disadvantages in the use of these metals are cost and leaching of metals into the product. Utilizing nickel-based catalysts, particularly in the hydrogenation of oils, has largely circumvented the problem of cost. However, nickel is readily poisoned by sulfur-containing compounds when natural oils or decomposition products introduce sulfides into the catalytic system.\(^\text{315}\) Additionally, unacceptable levels of nickel can leach into the final product.\(^\text{316,317}\) These and other factors have stimulated research efforts to develop benign, nonmetallic hydrogenation catalysts.

Although the concept of nonmetallic catalysis is not new, the field has experienced major strides forward in recent years. In 2007, Stephan and co-workers developed the first non-
transition-metal system capable of releasing and absorbing molecular hydrogen using frustrated Lewis pairs (FLPs).\textsuperscript{318} When a sterically encumbered Lewis acid approaches a bulky Lewis base, adduct formation is hindered, giving rise to electronic “frustration,” which effectively mimics the donor-acceptor properties of the transition metals previously described. Stephan and his team demonstrated that upon exposure to 1 atm H\textsubscript{2} at 25 °C, a solution of red phosphino-borane [(C\textsubscript{6}H\textsubscript{2}Me\textsubscript{3}-2,4,6)\textsubscript{2}P(C\textsubscript{6}H\textsubscript{4})BF(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}] readily transforms to the colorless zwitterionic salt [(C\textsubscript{6}H\textsubscript{2}Me\textsubscript{3}-2,4,6)\textsubscript{2}PH(C\textsubscript{6}H\textsubscript{4})BH(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}].\textsuperscript{318} Upon thermolysis at 150 °C, the salt loses H\textsubscript{2} and converts back to the original substrate. These and related phosphonium borates have been shown to successfully catalyze the hydrogenation of select imines, enamines, aldehydes\textsuperscript{314,318,319} and olefins.\textsuperscript{320} The documented success of these investigations inspired the study of solid FLP systems, particularly single or few-layer hexagonal boron nitride (h-BN) sheets. Hexagonal boron nitride is structurally analogous to graphite and may be described as a honeycomb network of fused borazine rings. The sheets are loosely held together by van der Waals interactions between adjacent boron and nitrogen atoms, which stack in an ABAB fashion.\textsuperscript{321,322}

10.2 Materials and Methods

10.2.1 Synthesis of Defect-Laden h-BN

Defect-laden h-BN was prepared using two methods. In the first, pristine h-BN (Grade PCTF5, Saint-Gobain Ceramic Materials) was dried at 180 °C under dynamic vacuum and transferred to an argon-filled glovebox. Approximately 2 grams of h-BN were mixed with 0.200
g of lithium (99.9%, Alfa Aesar) and reacted via high-energy ball-milling in an 8000M and/or 8000D SPEX Certiprep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 ml. Buna-N quad O-rings were used to maintain a seal during milling. Kinetic energy was supplied for 30 minutes with one 0.5” stainless steel ball weighing approximately 8.0 g. After 30 minutes, two additional 0.5” stainless steel balls were added and the reaction was milled for an additional 7.5 hours. The resulting lithiated solid was subsequently hydrolyzed using excess H$_2$O to remove Li$_3$N, producing vacancies in the $h$-BN sheets. The morphology of this defect-laden $h$-BN was examined via scanning electron microscopy (SEM) performed on a Tescan Vega SBH operating at 30 kV.

Alternatively, 20 grams of dry $h$-BN were loaded into a custom pebble mill, with the milling container constructed of 304 stainless steel. Spherical milling media (440C) were added in the following quantities and sizes: (12) 0.75” balls, (27) 0.5” balls, and (50) 0.25” balls. The mill was run at 60 rpm for 96 hours under 120 psi of UHP hydrogen. The milling vial was transferred to an argon-filled glovebox and the prepared catalyst powder was removed and stored until needed.

10.2.2 Hydrogenation

Hydrogenation was performed in a custom pebble mill with a gas-tight milling container constructed of 304 stainless steel (Figures 63 and 64).
Figure 63: Configuration of the mechanochemical reactor.

Figure 64: A close-up of the reaction vessel. Hydrogen is introduced through the solenoid at the left. Heat is applied by the NiChrome element (top center). Temperature is monitored by two thermocouples; the larger one on the left also serves as the control thermocouple for the heating element. The reaction vessel is rotated by a drive wheel that is driven by a pulley.
The reaction vessel is shaped as a double truncated cone to ensure adequate tumbling of the milling media. Conflat flanges with silicone O-rings and Deublin rotary feedthroughs with Kalrez O-rings and Krytox lubricant were used to maintain gas tight conditions during operation. Stainless steel frits (Applied Porous Materials) were fitted to the entry and exit feedthroughs to eliminate the accumulation of dust in the sealing surfaces of the feedthroughs. Spherical milling media (440C) was added in the following quantities and sizes: (12) 0.75” balls, (27) 0.5” balls, and (50) 0.25” balls. Temperature was controlled with an Omega CN3000 process controller and a K-type thermocouple spring mounted to the inlet flange. Heat was applied by a wound NiChrome heating element embedded in shaped firebrick. Pressure was monitored with a NOSHOK pressure transducer and controlled with a MicroMod 53MC5000 loop controller. The mill’s rotational speed was controlled with a 1/3 hp variable speed DC motor. Hydrogenation reactions were carried out at temperatures up to 170 ºC, pressures between 150 and 50 psi, and rotary speeds of 60 rpm. Hydrogenations were performed with 20 grams of substrate and 2 grams of defect-laden h-BN. Two substrates were investigated: trans-cinnamic acid (Eastman, Practical Grade) and oleic acid (Fisher Scientific, Lab Grade).

10.2.3 Gas Chromatography with Mass Sensitive Detection

GC-MS analysis was performed on an Agilent 6850 GC with an Agilent 19091-433E HP-5MS column (5% phenyl methyl siloxane, 30 m x 250 µm x 0.25 µm nom.) coupled with a 5975C VL mass selective detector. Samples were pulled from the reactor, dissolved in dichloromethane and filtered through a Whatman 0.2 µm PTFE syringe filter before injection.
Quantitation of the cinnamic acid hydrogenation products was performed by using external standard solutions of cinnamic acid (Eastman, Practical Grade) and hydrocinnamic acid (Acros Organics, 99%) in dichloromethane.

10.2.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra were recorded on a Physical Electronics 5400 photoelectron spectrometer with a magnesium source.

10.2.5 Computational Details

Density functional theory (DFT) calculations were performed to evaluate the binding energies and electronic structure of the C$_2$H$_4$ molecule on defected boron nitride single layers employing the formalism of the van der Waals density functional (vdW-DF)$^{323,324}$ as implemented in the VASP code$^{325-328}$. In this formalism, the exchange-correlation energy is calculated as from Equation (19):

$$E_{xc} = E_{GGA}^x + E_{lc}^c + E_{nlc}^c$$

(19)

Where $E_{GGA}^x$ is a semi-local exchange functional from the revised generalized-gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof functional (revPBE)$^{329}$, $E_{lc}^c$ is
a local correlation energy described within the local density approximation, \( E_{nlc}^C \) is the nonlocal correlation energy as described by Dion\textsuperscript{323}. The efficient algorithm proposed by Román-Pérez and Sole\textsuperscript{330} is used to reduce the computation effort. The projector augmented wave (PAW) scheme\textsuperscript{331,332} is utilized with the potentials taken from the potential-library provided with Vienna Ab-initio simulation package (VASP). The electronic wave functions were expanded in a plane wave basis set with a cutoff of 500 eV. A single k-point (Gamma) was found to be sufficient to sample the Brillouin zone of a (6x6) BN slab with 15 Å vacuum on top of it. The systems were optimized so that all force components acting on each atoms are smaller than 0.01 eV/Å. The lattice parameters of \( h \)-BN were optimized to be 2.523 Å (in agreement with experimental value of 2.505 Å\textsuperscript{333}).

### 10.3 Results and Discussion

Density functional theory (DFT) calculations reveal a 0.56 electron transfer from B to N for free-standing BN sheets.\textsuperscript{322} This suggests that \( h \)-BN has the potential to behave as an FLP. However, experimental evidence reveals pristine sheets of \( h \)-BN are exceptionally robust and chemically inert.\textsuperscript{321,322,334,335} This does not preclude the possibility of hydrogen adsorption and boron nitride sheets have been extensively studied as potential hydrogen storage materials. Computational studies have shown that hydrogen absorption on the surface of pristine \( h \)-BN is endothermic with respect to dissociation but may be enhanced by introducing defects such as nitrogen vacancies into the structure.\textsuperscript{336} Experimental studies show that \( h \)-BN nanotubes can adsorb up to 2.6 mass% hydrogen.\textsuperscript{337} In the present work, defective \( h \)-BN single sheets were

153
synthesized and examined as possible FLP catalysts for the selective hydrogenation of alkenes. Our DFT computations confirm the experimental observation of hydrogenation over defect laden $h$-BN. In the presence of $H_2$ and defect-laden BN sheets, trans-cinnamic acid undergoes the transformation shown in Figure 65. No hydrogenation was observed at temperatures below 170 °C.

![Figure 65: Hydrogenation of trans-cinnamic acid over defect laden $h$-BN selectively reduces olefin moiety.](image)

In addition to hydrogenation products, decarboxylation, dehydration, and amination products were also found in trace quantities (Table 9). These by-products were reduced when the catalyst was recycled. Hydrogen uptake, decarboxylation, and dehydration were observed in the pressure changes (Figure 66) of the reactor during hydrogenation. Initial increases in pressure were observed followed by a slower uptake of hydrogen. Most of the hydrogenation occurred during the first three hours of treatment. The reaction product was a dark-brown liquid. Hydrocinnamic acid yields of 45% were observed with fresh $h$-BN and 51% with recycled $h$-
BN. Hydrogenation of oleic acid produced octadecenyl nitrile and octadecanyl nitrile in equal proportions. No oleic acid was observed in the product. Hydrogenation over stainless steel has recently been observed. In order to eliminate this possibility, runs were performed with no defect-laden h-BN. A thin layer of h-BN adhered to all parts of the hydrogenation apparatus and some hydrogenation was observed with recycled milling media. Limited hydrogenation was observed when pristine milling media were utilized.

Table 9: Product distribution by GC peak area of the 5 most abundant products in the hydrogenation of trans-cinnamic acid over defect-laden h-BN and recycled defect-laden h-BN.

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>First Run</th>
<th>Recycled</th>
<th>Route</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocinnamic acid</td>
<td><img src="image" alt="Structure" /></td>
<td>40.50</td>
<td>55.31</td>
<td>hydrogenation</td>
</tr>
<tr>
<td>trans-Cinnamic acid</td>
<td><img src="image" alt="Structure" /></td>
<td>9.60</td>
<td>32.45</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td><img src="image" alt="Structure" /></td>
<td>7.40</td>
<td>0.33</td>
<td>decarboxylation then hydrogenation</td>
</tr>
<tr>
<td>Phenylpropanamide</td>
<td><img src="image" alt="Structure" /></td>
<td>6.00</td>
<td>2.36</td>
<td>hydrogenation, reaction with edge nitrogen atoms, then dehydration</td>
</tr>
<tr>
<td>1-Penten-3-one, 1,5-diphenyl-</td>
<td><img src="image" alt="Structure" /></td>
<td>2.20</td>
<td>0.23</td>
<td>formation of acid anhydride with hydrocinnamic acid then decarboxylation</td>
</tr>
</tbody>
</table>
Figure 66: Absolute pressure (black trace) and gas concentration (red trace) during the hydrogenation of trans-cinnamic acid over h-BN. The initial pressure increase is due to heating from room temperature to 170 °C. The rapid pressure drops are from the pressure control in the hydrogenation apparatus.

Single sheets and nanotubes of boron nitride have attracted interest as a potential hydrogen storage material. It has been shown that such materials can take up to 2.6 mass% hydrogen and that chemisorption is favored on defect sites.\textsuperscript{336,339} If h-BN has a high affinity for hydrogen then it may also have one for alkenes. Binding-energy calculations confirm this assertion, with ethene and hydrogen binding energies on par with those of metals with known hydrogenation activity (Pt, Pd, and Ni). In the pristine state, h-BN consists of rings of alternating electron-deficient boron and electron-rich nitrogen. It can be thought of as a geometrically frustrated Lewis pair, since the lone pairs on the nitrogen atoms are restricted from fully
interacting with the boron atoms. This frustration is reduced by interaction of these lone-pairs with boron atoms in the neighboring layers. Through delamination and the introduction of defects the degree of frustration can be increased. Defects and delamination can be introduced through the application of mechanical force. By designing a hydrogenation reactor around a pebble mill we have been able to produce defect-laden h-BN by mechanically inducing defects and delamination. The continuous grinding motion within the mill prevents cluster formation and maximizes the number of few-layer sheets. In order to verify the presence of these sheets, scanning electron microscopy was used to characterize the morphology of the defective BN catalyst. Few-layer sheets are observed by SEM and appear to form tubular structures or nanoscrolls as seen in Figure 67. In order to gauge the hydrogenation ability of defect-laden h-BN, trans-cinnamic acid was chosen as a substrate. The compound possesses aromatic, olefinic, and carboxylic moieties. Non-selective hydrogenation would result in complete hydrogenation of the molecule such as occurs with Raney nickel, which produces 3-cyclohexanepropionic acid from trans-cinnamic acid. Additionally, nanocrystals of BN have been shown to activate the C-H bond in benzene, producing oligomers. Similar reactions may occur with defect-laden h-BN. The presence of carboxylic groups allows the study of any hydrogenolytic activity as well. Oleic acid is a good model for biodiesels, which require hydrogenation to improve storage life. The h-BN possesses several potentially active sites – defect sites in each sheet and edge sites. Initial utilization of defect-laden h-BN produced the desired hydrogenation product along with decarboxylation and amination products. Although trans-cinnamic acid is known to undergo decarboxylation at elevated temperatures, a recycled catalyst produced less of these by-products, indicating that the observed decarboxylation products were not from the thermal
decarboxylation of trans-cinnamic acid alone. This suggests that the by-products were produced by reaction with edge nitrogen atoms in $h$-BN, which would have lower concentrations in a recycled catalyst. XPS analysis of the catalyst after hydrogenation confirmed the presence of carbon (Figure 68).

![SEM image of defect-laden $h$-BN](image)

**Figure 67**: An SEM image of defect-laden $h$-BN produced by mechanochemical intercalation and reaction with lithium metal. Clusters and single-sheets of BN can be seen, with the few-layer sheets adopting a scroll-like secondary structure.
The application of mechanical force is essential for the delamination and formation of defects in h-BN. This force can be applied during hydrogenation or may be utilized as a pretreatment step, since the defect sites are stable up to 900 °C.\textsuperscript{344} The application of force during milling requires the efficient transfer of mechanical force to the h-BN. Oleic acid has a
much lower viscosity than molten trans-cinnamic acid and also acts as a lubricant. This results in the formation of nitriles by edge attack of the h-BN, followed by dehydration.

10.3.1 Binding Energies

The initial steps of hydrogenation on a catalytic substrate of an olefin are chemisorption, followed by reduction of the C-C bond order in the chemisorbed molecule. In order to understand this process it is useful to evaluate the binding energies and electronic structure of the cinnamic acid molecule on the boron nitride substrate. Ethene (C$_2$H$_4$), the simplest possible molecule with such a bond, was investigated as a model for the olefinic carbons in trans-cinnamic acid. First-principles electronic structure calculations of a C$_2$H$_4$ molecule on a single BN layer were employed by utilizing the van der Waals density functional (vdW-DF)$^{323,324}$ It quickly became clear that C$_2$H$_4$ does not chemisorb on BN sheets. This was also noted for hydrogen adsorption on BN sheets, which is at best weakly favored.$^{336}$ Given that point defects favor hydrogen chemisorption, it was expected that point defects in BN sheets would also promote ethene chemisorption. The adsorption and electronic structure of the C$_2$H$_4$ molecules on the 8 types of defects were modeled and the results are illustrated in Figure 69.
Figure 69: Top view of different defect structures in BN. These are (from top left to bottom right): 180° rotation of a BN bond (B/N), 90° rotation of a BN bond {Stone-Wales defect} (SW), nitrogen substitution for boron (N_B), boron substitution for nitrogen (B_N), carbon substitution for boron (C_B), boron vacancy (V_B), and a nitrogen vacancy (V_N). Gray, green, and pink balls represent boron, nitrogen, and carbon atoms, respectively. The light-gray backgrounds indicate the defected areas.

Table 10: Binding energy (in eV) of C_2H_4 on the defects of a (6x6) BN system

<table>
<thead>
<tr>
<th>System</th>
<th>B/N</th>
<th>SW</th>
<th>N_B</th>
<th>B_N</th>
<th>C_N</th>
<th>C_B</th>
<th>V_B</th>
<th>V_N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding</td>
<td>NA*</td>
<td>-0.23</td>
<td>NA</td>
<td>-1.95</td>
<td>NA</td>
<td>NA</td>
<td>-3.71</td>
<td>-1.90</td>
</tr>
</tbody>
</table>

*Not Available

Binding energies of all the defects are presented in Table 10. The binding energy is calculated using Equation 20:
\[ E_{BE} = E_{System} - (E_{Mol} + E_{BN}) \]  

(20)

Where \( E_{System} \), \( E_{Mol} \), and \( E_{BN} \) are the total energy of the molecule on the substrate, the molecule alone, and of the defective \( h \)-BN substrate, respectively. The more negative the binding energy, the stronger the chemisorption of \( \text{C}_2\text{H}_4 \) on the defective BN sheets. The binding energies of ethene on BN with these defects are presented in Table 10.

Figure 70: A) Charge-density redistribution after the adsorption of \( \text{C}_2\text{H}_4 \) on \( B_N \), \( SW \), \( V_B \), and \( V_N \) defects in a BN substrate. Isosurfaces are drawn at 0.01 e/Bohr\(^3\). The blue and red surfaces represent, respectively, the charge-deficient and –accumulation regions (i.e. charge flows from blue to red regions). B) Side view; C) top view of the respective configurations without showing the charge density.
Table 11: Binding Energy for ethene on BN, hydrogen on BN, ethene on platinum group metals, hydrogen on Pt(100), hydrogen on Pd(100), and hydrogen on Ni(100).

<table>
<thead>
<tr>
<th></th>
<th>BN</th>
<th>Ethene</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_B$</td>
<td>-3.71</td>
<td></td>
<td>-5.58</td>
</tr>
<tr>
<td>$V_N$</td>
<td>-1.90</td>
<td></td>
<td>-1.64</td>
</tr>
<tr>
<td>SW</td>
<td>-0.23</td>
<td></td>
<td>0.64</td>
</tr>
<tr>
<td><strong>Pt 100</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>di sigma</td>
<td>-2.32</td>
<td></td>
<td>-2.88</td>
</tr>
<tr>
<td>pi-top</td>
<td>-1.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pd 100</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>di sigma</td>
<td>-0.84</td>
<td></td>
<td>-2.92</td>
</tr>
<tr>
<td>pi-top</td>
<td>-0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ni 100</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>di sigma</td>
<td>-1.76</td>
<td></td>
<td>-2.81</td>
</tr>
<tr>
<td>pi-top</td>
<td>-0.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Chemisorption occurs on BN with four types of these defects: boron substitution for nitrogen ($B_N$), Stone-Wales defects (SW), boron vacancies ($V_B$), and nitrogen vacancies ($V_N$). The binding energies (in eV) of $C_2H_4$ on BN with these defects are -1.95, -0.23, -3.71 and -1.90, respectively. The top and side views of these systems are shown in columns B and C of Figure 70. Table 11 compares the binding energies of both ethene and hydrogen on BN to those of traditional hydrogenation catalysts.
The charge density redistribution of the system was calculated using the following Equation 21:

\[ \Delta n(\vec{r}) = n_{\text{System}}(\vec{r}) - [n_{\text{Mol}}(\vec{r}) + n_{\text{BN}}(\vec{r})] \]  

Where \( n_{\text{System}}(\vec{r}) \), \( n_{\text{Mol}}(\vec{r}) \), and \( n_{\text{BN}}(\vec{r}) \) are, respectively, the charge density of the system, of \( \text{C}_2\text{H}_2 \) molecule, and of BN sheet with defect. The first step in hydrogenation, after chemisorption, is the reduction of the C-C bond order in ethene. A plot of total charge density of (A) \( \text{C}_2\text{H}_4 \), (B) \( \text{C}_2\text{H}_6 \), and (C) \( \text{C}_2\text{H}_4 \) molecule after adsorption on \( \text{B}_N \), \( \text{SW} \), \( \text{V}_N \) and \( \text{V}_B \) defects, along the vertical plane passing through two carbon atoms of \( \text{C}_2\text{H}_4 \) molecule shows the reduction of this bond order (Figure 71). In the gas phase, \( \text{C}_2\text{H}_4 \) is \( \text{sp}^2 \) hybridized (i.e., has a C=C bond), while \( \text{C}_2\text{H}_6 \) is \( \text{sp}^3 \) hybridized (i.e., has a C–C bond). The total charge density of a \( \text{C}_2\text{H}_4 \) molecule on \( \text{SW} \), \( \text{V}_N \) and \( \text{V}_B \) defects shows similarities with that of gas phase of \( \text{C}_2\text{H}_6 \). The total charge density of \( \text{C}_2\text{H}_4 \) molecule on \( \text{B}_N \) looks much more like that of single \( \text{C}_2\text{H}_4 \). This difference in bond order reduction is due to the fact that there are two distinct ways in which \( \text{C}_2\text{H}_4 \) can adsorb on defective BN surface: \( \pi \) and di-\( \sigma \), as similarly discussed by Zaera. In the \( \pi \)-bonded mode, both carbons adsorb on top of a single atom of the substrate, as in chemisorption of \( \text{C}_2\text{H}_4 \) on a \( \text{B}_N \) defect. In \( \pi \)-bonding the molecular \( \text{sp}^2 \) hybridization is partly retained upon adsorption. In contrast, di-\( \sigma \) bonding results from the interaction of each carbon atom with a separate atom of the substrate (the substrate atoms can be the same or different species), as in the chemisorption
of C$_2$H$_4$ on SW, V$_N$ and V$_B$ defects (See column B, Table 11) Di-$\sigma$ bonding is characterized by a sp$^3$ rehybridization of C atomic orbitals.

Figure 71: Vertical plane cross-sections, passing through the center of the two ethene carbon atoms, of the total charge density of gas-phase a) C$_2$H$_4$ and b) C$_2$H$_6$, and of c) C$_2$H$_4$/defective BN for defect types B$_N$, SW, V$_N$ and V$_B$. Contours are drawn in a linear scale (9 contours from 0 to 0.27 e/Bohr$^3$).

Column A in Figure 70 demonstrates the increased charge density between the molecule and the substrate. The charge-enhanced regions located between the carbon atoms and substrate atoms indicate chemical bonding. The charge-deficient regions between two carbons coincide with the $\pi$-bond in an isolated C$_2$H$_2$ molecule, indicating the loss of charge from the $\pi$-bond and a decrease in the C-C bond order. In the case of SW, V$_N$ and V$_B$ defects, charge from the original $\pi$-bond is mostly removed from the area between two carbons. In these cases, it can be
concluded that the π-bond is broken. Since in B\textsubscript{N} there is still some charge between the two carbons, it can be concluded that the double bond is partially weakened. More light can be shed on the effect these defects have on the carbon double bond by focusing on precisely how they affect hybridization. When C\textsubscript{2}H\textsubscript{4} adsorbs on a B\textsubscript{N} defect, its C atoms partially retain their original sp\textsuperscript{2} hybridization (C=C), but when it adsorbs on a SW, V\textsubscript{B}, or V\textsubscript{N} defect, its C atoms rehybridize to sp\textsuperscript{3} (C-C), facilitating hydrogenation and desorption of C\textsubscript{2}H\textsubscript{6}.

10.4 Conclusion

The first metal-free heterogeneous hydrogenation catalyst has been produced from defect-laden h-BN. Hydrogenation of olefinic carbons was observed in \textit{trans}-cinnamic acid and oleic acid with yields up to 51\%. DFT calculations show that the carbon double bond in ethene is weakened over four types of defect sites: boron/nitrogen substitution (B\textsubscript{N}), nitrogen (V\textsubscript{N}) vacancies, boron (V\textsubscript{B}) vacancies, and Stone-Wales defects. The binding energies at these sites is on par with those of metals currently used for catalytic hydrogenation. The use of metal-free hydrogenation catalysts will reduce the risks associated with incorporation of metals into hydrogenation products.
CHAPTER 11: LOW-TEMPERATURE (210 ºC) DEPOSITION OF CRYSTALLINE GERMANIUM VIA IN-SITU DISPROPORTIONATION OF GeI₂

This work was previously published as “Low-temperature (210 ºC) deposition of crystalline germanium via In-Situ Disproportionation of GeI₂” by David T. Restrepo, Kristen E. Lynch, Kyle Giesler, Stephen M. Kuebler, and Richard G. Blair in Materials Research Bulletin, Volume 47, Issue 11, 2012, pp. 3484-3488 Copyright © 2012 Elsevier B.V. Reproduced by permission of Elsevier. http://dx.doi.org/10.1016/j.materresbull.2012.06.072

11.1 Introduction

Interest in using germanium thin films for photonic applications and telecommunications has steadily increased due to its high refractive index\(^{350}\) and strong absorption at optical wavelengths near 1.55 μm.\(^{351,352}\) Germanium has long been used for various types of photodetectors,\(^{353}\) and has also been shown to be useful as a filter for short-wave infrared.\(^{350}\) It has the additional feature of being compatible with silicon and silicon-based optoelectronics,\(^{351,353,354}\) so it can be integrated into existing materials processes.\(^{354}\) Two-dimensional photonic crystals with functional stop bands at telecommunication wavelengths have been created in germanium supported on SiO₂-on-Si substrates.\(^{355}\) The optical properties of germanium support efficient light emission and optical gain\(^{356}\), which has enabled the development of an integrated Ge-on-Si laser.\(^{357}\) Traditional methods for depositing germanium onto a substrate include chemical vapor deposition (CVD)\(^{358}\), ultrahigh vacuum CVD\(^{351}\), rapid-
thermal CVD, plasma-enhanced CVD, and sputtering. These methods utilize digermane (Ge$_2$H$_6$), germane (GeH$_4$) diluted in H$_2$ gas, or in situ disproportionation of germanium diiodide (GeI$_2$) synthesized from the elements. The disadvantage of these techniques is that germanes are toxic and unstable, and I$_2$ is corrosive. In addition, these methods require temperatures between 280 – 550 ºC to obtain crystalline germanium, as processing at lower temperatures yields amorphous material.

GeI$_2$ has been previously synthesized by reacting Ge with GeI$_4$ or I$_2$. If excess I$_2$ is used, the formation of the tetraiodide is favored. Alternatively, germanium sulfide has been reacted with silver halides to obtain the tetrahalide as the major product. Analogous to this is the formation of SiCl$_4$ synthesized from Si and CuCl. The tetraiodide is favored in this case. A similar reaction was carried out using lead halides. Other methods have been reported that yield a mixture of iodides.

The current study introduces a new in situ synthesis and disproportionation of GeI$_2$ that enables low temperature deposition of germanium, even onto a polymeric surface. Previously, disproportionation of GeI$_2$ to Ge and GeI$_4$ was shown to occur at ~330 ºC, but we show here that this can be made to occur between 210 – 260 ºC to form polycrystalline germanium films.
11.2 Experimental

11.2.1 Reagent Preparation

Copper iodide was used as received (Acros Organics, 98%). Germanium (Alfa Aesar, 99.999%) was mechanically ground in a tungsten carbide vial with four tungsten carbide ball bearings (1.27-cm dia.) for 30 min using a SPEX 8000M Mixer/Mill. The resulting powder was sieved to 270 mesh. CuI and Ge were mixed in stoichiometric quantities by grinding for five minutes in a SPEX vial.

11.2.2 Substrates for Germanium Deposition

Germanium was deposited onto either borosilicate glass microscope slides or slides supporting a film of cross-linked SU-8 polymer, hereafter referred to as the “sample”. Sample sizes of 25 mm × 25 mm and 38 mm × 25 mm were used. Borosilicate microscope slides were cleaned in a 50/50 by-volume solution of concentrated nitric and sulfuric acid for two hours, rinsed with copious deionized water, then dried in an oven at 100 °C for 20 min.
11.2.3 Polymer Film Preparation

An adhesion layer was applied to a cleaned substrate by immersing it into 5 vol-% 3-glycidoxypropyl-trimethoxysilane (98%, CAS# 2530-83-8) in methanol for 24 h at room temperature, rinsing with methanol, and drying for one hour in an oven at 100 °C. The pre-polymer resin SU-8 2035 (MicroChem) consisted of 70 - 80 wt-% of the cross-linkable epoxide SU-8 (CAS# 28906-96-9) and 3.4 wt-% of two triarylsulfonium photo-acid generators (CAS# 89452-37-9 and 71449-78-0), dissolved in a mixture (circa 19 wt-% volatiles) of cyclopentanone (CAS# 120-92-3) and propylene carbonate (CAS# 108-32-7). A 1 mL portion of filtered resin (0.4 µm pore) was dispensed onto the substrate and spin-coated according to the following program: ramp at 100 rpm s\(^{-1}\) to 500 rpm, hold for 10 s, ramp at 300 rpm s\(^{-1}\) to 1400 rpm, hold for 30 s, then stop. Surface profilometry measurements indicate that this procedure yields films having a thickness of 30 ± 5 µm. Following spin-coating, the slides were heated on a hot plate at 65 °C for 15 min, 95 °C for 2 h, 65 °C for 15 min, then removed from the hot plate and allowed to cool to room temperature. The films were then irradiated for 2 min in a Zeta Loctite UV system (RPR 3500 Å lamps, emission maximum at 350 nm) equipped with a long-pass filter (Omega Optical PL-360LP, 350 nm cut-off). Following exposure, the films were baked on a hot plate at 65 °C for one min, 95 °C for 15 min, hard-baked at 250 °C for 12 h, then removed and allowed to cool to room temperature.
A borosilicate glass sublimation tube was used as the reactor vessel for germanium deposition (Figure 72). The samples were affixed in a holder consisting of an adjustable-height clip mounted on a base constructed from steel, graphite, or quartz. In addition to the steel sample holder, graphite and quartz holders were also used. The graphite sample holder was 13.9 mm × 3.3 cm × 0.29 cm with a 1/4-28 graphite screw centered at 1.4 cm from the edge. The samples were held in place with two graphite nuts (1.7 cm × 1.6 cm × 0.70 cm) and two graphite plates (2.8 cm × 1.7 cm × 0.30 cm). A 52.7-mm quartz sample holder was cut from a quartz tube of 26.4-mm I.D. with 1.8-mm thick walls. All holders were positioned in order to have the glass substrates or polymer samples within the deposition zone. The reagents were loaded into a borosilicate vial in a glove box. The reagent vial and the sample were inserted into the reaction vessel, removed from the glove box, and inserted into a three-zone tube furnace (Lindberg Hevi-Duty 54357-A, 76.5 cm length). Zone one was used to control the temperature of the sample. Zone two served as a hot zone that initiates formation of GeI₂ upon reaction of the solid reagents.
Figure 72: Side view of reactor vessel design and set up.  a) End cap (6.6 cm O.D. × 13.1 cm) with valve and vacuum line inlet.  b) No. 65 clamp.  c) O-ring; d) Bottom (6.6 cm O.D. × 18-1/4 in.).  e) Piece of steel (22.8 cm × 2.5 cm × 0.32 cm).  f) Clamp used to hold substrates.  g) Socket cap screw (1-¼ in., 1/4-28) with two nuts (1/4-28) holding the clamp (2 cm to 3 cm from edge of steel).  h) Borosilicate reagent cup (1.9 cm O.D. × 6.5 cm).

Zone three was not used. The temperatures of zones one and two (length 15 cm and 29 cm, respectively) were monitored with K-type thermocouples positioned 22.3 cm and 35 cm from the end of the furnace and connected to an ADAM-4019+AE eight-channel universal analog input module (Advantech Co., Ltd). Temperature data were logged with a computer running LabView. Heat transfer was reduced by placing mineral wool insulation between zones one and two, at 22.8 cm - 25.0 cm from the end of the furnace. The sample was positioned in zone one at a distance from the end of the furnace adjustable between 18.5 cm and 22.3 cm. The reagent vial was centered within zone two. Dynamic vacuum was applied for one hour with a
two-stage rotary vane pump, reducing the pressure to 330 mTorr. The system was closed to vacuum after one hour to prevent contamination of the line by germanium iodides. Deposition was initiated by heating zone two to 75 °C over 15 minutes, then increasing to a final set point of 175 °C, while zone one was heated to 400 °C. The reaction was allowed to proceed overnight in most cases.

11.2.5 Deposition Rate Measurements

A quartz crystal microbalance (QCM) was used to determine the rate of germanium deposition. For these measurements, the sample slide was replaced by a quartz crystal. The temperature near the crystal and its resonant frequency were measured as Ge deposited onto it. One thermocouple was placed between the crystal and the sample holder. The reaction vessel was fitted with an aluminum cap equipped with a vacuum tap and three electrical feedthroughs for the thermocouples and leads to the crystal. The thermocouple and crystal leads were insulated with single-hole fish spline and sealed with epoxy and Celva-2 sealant (Duniway Stockroom Corp.). Data were measured using a Princeton Applied Research QCM922 and WinEChem software at 10 s intervals over 18 h, with a scan frequency \( \nu = 9.00 \text{ MHz} \), \( \Delta \nu = \pm 20 \text{ kHz} \), and a gate time of 1 s. The QCM response versus temperature was calibrated by performing a blank run for 18 h with only Ge powder loaded into the reagent vial.
11.2.6 Characterization

Powder X-ray diffraction (XRD) data were collected using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu Kα λ = 1.5418 Å). Diffractograms were collected over a 2θ angle of 5 – 80 degrees using 0.010 degree steps and a dwell time of 0.3 s per step. The morphology of deposited Ge was characterized by scanning electron microscopy (SEM, Zeiss ULTRA-55 FEG SEM, 2.5 – 5.0 kV accelerating voltage).

11.3 Results and discussion

While heating stoichiometric quantities of CuI and Ge at 400 °C under vacuum, we observed that yellow GeI₂, red GeI₄, and reflective germanium deposit in bands on the walls of the reactor tube (Figure 73). Germanium deposited in regions of zone one where the temperature was near 210 °C. No germanium deposited in zone two, where the temperature was 260 °C - 400 °C, or in regions further along the reaction vessel that were cooler than 210 °C. GeI₂ can form initially in the hot-zone from the reaction between Ge and CuI, as described by Equation 22.

\[ 5\text{Ge} + 6\text{CuI} \rightarrow 3\text{GeI}_2 + 2\text{Cu}_3\text{Ge} \]  \hspace{1cm} (22)

This suggests there is a narrow temperature region where GeI₂ disproportionation to Ge and GeI₄ is favored. These observations led us to investigate the possibility of depositing Ge onto glass and polymer substrates. The X-ray diffractogram for Ge deposited onto a polymer
substrate is shown in Figure 74. The deposited material is composed mainly of polycrystalline Ge with a small impurity of CuI. Unreacted CuI can sublime from the hot-zone and deposit in the cooler zones, mostly above the band where Ge forms, although some can co-deposit onto the sample. The diffractograms show that this surface impurity is easily removed by washing the sample with acetonitrile.

Figure 73: Reaction vessel after 18 h of deposition. Germanium (shiny, black mirror) has deposited onto the sides of the reactor vessel, along with crystals of GeI₂ (yellow-orange) and CuI (white). GeI₄ is deposited in the region at room temperature (left of yellow band, not visible).
Figure 74: Powder X-ray diffraction patterns for germanium deposited onto various surfaces after 18 h, before and after washing with acetonitrile. The black lines correspond to Ge (JCPDS 04-0545), which is visible for all samples. The CuI is removed by washing with acetonitrile. The broad hump around $2\theta = 25^\circ$ is due to the amorphous glass (or polymer) substrate.

Figure 75: SEM images of Ge deposited onto glass showing a) twinning of Ge Crystals and b) as viewed edge on.
The morphology of germanium deposited onto glass slides was examined by SEM and is shown in Figures 75 and 76. Deposition is initially uniform, but as the reaction proceeds, polycrystalline Ge begins to form. Growth on existing crystals appears to dominate over nucleation. This is consistent is observed for growth of germanium on silicon surfaces.

Figure 76: SEM images of germanium deposited onto glass, viewed a) normal to and b) nearly parallel to the substrate.
The by-products of this reaction, GeI$_2$ and GeI$_4$, were also identified by powder XRD, as shown in Figure 77. The synthetic approach reported here is similar to methods used to produce GeCl$_2$ from AgCl and Ge$^{371}$ and analogous to the preparation of the Cu$_3$Si reaction mass used for the direct synthesis of organosilicon compounds.$^{367}$ In our synthesis, formation of Cu$_3$Ge within the reagent vial was confirmed by powder X-ray diffractometry (Figure 78).

Figure 77: Powder XRD pattern for the by-products of germanium deposition. a) Yellow film corresponding to GeI$_2$ (JCPDS 15-0833). b) Red crystals corresponding to GeI$_4$ (JCPDS 07-0196).
Figure 78: Powder XRD pattern of the black residue remaining in the reagent vial following deposition of germanium. The peaks matching with the black lines correspond to CuI (JC-PDS 06-0246), and "***" represents peaks associated with Cu$_3$Ge (JC-PDS 06-0693).

Analysis shows that the reaction does not go to completion, and the solid residue consists of a mixture of Cu$_3$Ge and CuI. The reaction of germanium with iodine has been investigated in a flow system, which consists of a series of reactions in equilibrium. Equation 23 was found to proceed rapidly. Under high-flow conditions, comproportionation is favored over disproportionation due to Le Chatelier’s principle (Equation 24).

\[
\text{Ge} + 2\text{I}_2 \rightarrow \text{GeI}_4 \quad (23)
\]

\[
\text{GeI}_4 + \text{Ge} \rightleftharpoons 2\text{GeI}_2 \quad (24)
\]

Under the static conditions of our system, disproportionation is favored due to the stability of GeI$_4$ ($\Delta G_f = -155.4$ kJ mol$^{-1}$ for GeI$_4$ and -88.1 kJ mol$^{-1}$ for GeI$_2$). It is important to note that in the work reported here, elemental iodine is not used to prepare GeI$_2$; rather, it forms
in situ by the direct reaction of CuI vapor with Ge. The overall reaction is outlined in Equations 25 - 27.

\[
\text{CuI(s) → CuI(g)} \quad 400 \, ^\circ\text{C} \quad (25)
\]

\[
5\text{Ge(s)} + 6\text{CuI(g)} \rightarrow 3\text{GeI}_2(g) + 2\text{Cu}_3\text{Ge(s)} \quad 400 \, ^\circ\text{C} \quad (26)
\]

\[
2\text{GeI}_2(g) \rightarrow \text{Ge(s)} + \text{GeI}_4(g) \quad 210 \, ^\circ\text{C} \quad (27)
\]

The reaction in Equation 27 takes place in the presence of CuI vapor. We have found that CuI deposits before Ge. This CuI vapor may be responsible for the lowered deposition temperature. However, no germanium deposition was observed in separate experiments in which CuI and GeI$_2$ were co-sublimed. From this we conclude that Ge forms on the sample due to disproportionation of GeI$_2$, and not due to reaction of CuI with GeI$_2$.

Both the germanium deposition rate and uniformity were observed to depend strongly on the position of the sample holder and the material from which it was constructed. Deposition was poor, non-uniform, and highly dependent on sample position when the holder was made of steel. We reasoned that the deposition was either being hindered by the chemical composition of the holder or its large thermal mass. Unfavorable reactions could occur between iodides and bare metal surfaces or the holder could be lowering the local temperature at the sample, thereby hindering disproportionation of GeI$_2$. To explore these hypotheses, a lighter sample holder was constructed from a less reactive material - graphite. However, deposition was not improved. This was attributed to the porosity of graphite, and the possibility that oxygen adsorbed inside graphite pores might interfere with the disproportionation reaction. Another sample holder was
constructed from fused silica. This material has the advantage of a low thermal mass, negligible porosity, and low reactivity. When the fused silica sample holder was used, the deposition was consistently uniform and spanned the broadest region within zone one. The fused silica sample holder was used in preference to the others as it ensured better control over the deposition of germanium and improved reproducibility.

Figure 79 is a plot of relative mass change versus time observed from QCM measurements obtained during a deposition of germanium onto the quartz crystal. Over the interval 560 - 1080 s, the temperature increases from 164 °C - 210 °C (see Figure 80), but remains below that at which GeI₂ disproportionates. The QCM response in this period is distorted by condensation of CuI onto the crystal.

Figure 79: Plot of mass-difference versus time observed for a quartz crystal onto which Ge was deposited (gray line). The rate of deposition was obtained from the slope of line fit to the data in the period 1360 - 14500 s (dotted black line).
Figure 80: Plot of QCM temperature versus deposition time (red line). The frequency of the QCM crystal (dotted black line) shows an immediate change during deposition that corresponds to the condensation of CuI.

As discussed above, CuI sublimes from the hot-zone and co-deposits onto the sample surface. CuI is a conductive solid, so as it condenses onto the quartz crystal, a short circuit forms across the QCM leads that causes the large apparent mass increase observed at early times. As the temperature increases, CuI re-sublimes off the quartz crystal. Above 215 °C, proper response of the QCM is restored, and a uniform mass increase due to deposition of Ge is observed. The slope of a line fit to the data in the interval 1360 - 14500 s gives a Ge deposition rate of 25 ng min⁻¹, or 0.7 layers min⁻¹.
11.4 Conclusion

We have demonstrated a method for depositing crystalline films of germanium at low temperature (210 - 260 °C) through the in situ disproportionation of GeI₂. Ge films can be deposited onto both glass and polymer substrates. We have also demonstrated a new synthetic route to GeI₂, GeI₄, and Cu₃Ge. GeI₂ is a valuable precursor for the synthesis of germanium nanostructures. Cu₃Ge can be used for the direct synthesis of organogermanium compounds, in a process similar to that used to prepare organosilicon compounds from Cu₃Si. Additionally, Cu₃Ge has electrical and chemical properties that offer improved ohmic contact for GaAs devices. The process discussed here could have broad application for the preparation of functional micro- and nano-scale electronic and optoelectronic devices.\(^{373}\)
CHAPTER 12: MISCELLANEOUS MECHANOCHEMICAL REACTIONS

12.1 Mechanochemical Synthesis of Isomorphously Substituted Spinels

12.1.1 Introduction

Spinel (MgAl$_2$O$_4$) is a commonly investigated material that is used as a model for many solid oxide materials. The generic formula of the minerals that adopt the spinel structure is AB$_2$O$_4$, where A is a divalent cation and B is a trivalent cation. The oxygen atoms belong to a close-packed pseudo-face-centered cubic lattice. The divalent cations are at the center of a tetrahedral site coordinated with four oxygen atoms, while the trivalent cations are at the center of an octahedral site coordinated with six oxygen atoms.$^{374}$ The tetrahedral and octahedral positions can be isomorphously substituted with similarly charged cations at high pressure and/or temperature.

Traditional methods for the synthesis of spinels include the conventional solid-state-reaction (SSR), sol-gel processes, spray drying (atomization), and organic gel-assisted citrate complexation. The conventional SSR method is the most utilized technique in spinel preparation. However, it suffers from several disadvantages, including long processing time, requires high temperatures and intermediate grinding with need for repetition of calcinations stages, and may lead to non-uniform, abnormal grain growth and remnant porosity.$^3$
Our study focuses on the potential of high-energy ball milling to provide an alternative route for the synthesis of substituted spinels and the exploration of the thermodynamics of a mechanically driven synthesis. For example, reactions forming the spinels MgAl$_2$O$_4$ and ZnAl$_2$O$_4$ can both have negative $\Delta H_{\text{rxn}}$, but the zinc spinel forms a more crystalline product.

By incorporating emissive elements through substitution, one can describe how ions are incorporated into a solid produced mechanically via cathodoluminescence (CL) microscopy. This method utilizes a beam of electrons that interacts with the specimen surface. As a result of electron beam-specimen interaction, refractory materials produce characteristic CL colors. Trace elements, lattice defects, or intrinsic properties within the crystal cause this emission of photons by minerals, known as cathodoluminescence. Activators, such as transition metal ions (Mn$^{2+}$, Cr$^{3+}$, Fe$^{3+}$) and rare earth activators (Eu$^{2+}$, Sm$^{3+}$, Tb$^{3+}$) can create luminescence if present in trace amounts. Cation vacancies, anion vacancies and lattice defects can also cause CL to occur. This helps in understanding how cations are incorporated by means of ball milling.

Aside from a focus on their synthesis, cathodoluminescence, and ball milling thermodynamics, spinels also serve a special function in ceramics. One of most important characteristics of ceramic pigments is their thermal stability at high temperatures and their chemical stability with respect to phases, even liquid, forming during firing of glazes or bodies as a result of the sintering process and melting. The prepared spinels with incorporated dopants possess interesting tint properties for base glazes.
12.1.2 Experimental

12.1.2.1 Materials

The spinels were prepared from the metal hydroxides or metal oxides in stoichiometric amounts according to the theoretical metal cation content in the product spinel. The metal hydroxides and oxides used were magnesium oxide (Fisher Scientific), magnesium hydroxide (Alfa Aesar, 95-100%), aluminum hydroxide (J.T. Baker, 98.1%), aluminum oxide (J.T. Baker), zinc oxide (Zinc Corporation of America), copper hydroxide (Alfa Aesar, 94%), chromium oxide (Mallinckrodt, 99¾%), and barium hydroxide (Fisher Scientific).

Zinc hydroxide was prepared from zinc nitrate hexahydrate (Fisher Scientific, certified grade) as described in the literature.\textsuperscript{377} Rare earth hydroxides and chromium hydroxide were prepared as described in Chapter 2 Section 2.2.1. Cobalt (II) hydroxide, cobalt (III) oxide hydroxide, and nickel (II) hydroxide were prepared in a similar fashion, as described by Brauer,\textsuperscript{378-380} by dissolving cobalt (II) chloride hexahydrate (Fisher Scientific) and nickel nitrate hexahydrate (Acros, 99%), respectively, in deionized water, followed by addition of ammonium hydroxide to precipitate out the corresponding hydroxide. Cobalt (II) hydroxide was synthesized under inert atmosphere, whereas cobalt (III) oxide hydroxide was synthesized under air.\textsuperscript{87}
12.1.2.2 Milling

All milling experiments were performed in 8000M and 8000D SPEX Certiprep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 mL. Viton and quad Buna-N O-rings were used to maintain a seal during milling. High kinetic energy milling was performed with three 0.5” stainless steel balls weighing approximately 8 g each. A total of 2.5 g of starting material was milled for 1 h. Milling was carried out in 30-min increments, followed by 30 min of cooling to reduce wear on the mill’s motor.

12.1.2.3 Calcination

Approximately 100 mg of spinel powders was placed in a small mullite crucible, which was positioned in a tube furnace and calcined for 1-10 h. The calcination temperatures ranged from 500 °C to 1000 °C to determine the optimal temperature.
12.1.2.4 X-ray Diffraction

Powder X-ray diffraction (XRD) was taken using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu Kα λ = 1.5418 Å). Diffractograms were collected from 5 to 80 degrees 2θ using 0.010-degree steps and 0.3 seconds of dwell time.

12.1.2.5 Cathodoluminescence

Cathodoluminescence measurements were made in collaboration with Hope College using a CITL Mk5 cathodoluminescence stage with a Leica M80 stereomicroscope with a dual optical head. One head was connected to a USB2000 UV-Vis spectrometer and the other to a Leica DFC 290 HD digital camera. Samples were evacuated to millitorr pressure with a mechanical pump and the electron beam was accelerated to approximately 12-15 kV. Beam currents of approximately 200 mA were maintained on target for UV-Vis spectral acquisition times of 5-10 seconds.
12.1.2.6 Glazes

For spinels being tested in the glaze experiment a base glaze was first created. A powder mixture of 78% Ferrofrit, 11% silica, and 11% EPK kaolin was made and placed in an algae cup. In exploring each spinel, a set of four base glazes were created and labeled 1-4. Base glaze one had no additional tint added. Base glaze two had the 5% unheated spinel (total 105%). Base glaze three had 5% heat-treated spinel (total 105%), and base glaze four had a 5% mixture of the metal oxide reactants that composed the spinel (105% total). After all powders were added to the respective algae cup, 10-mL of deionized water was added and mixed in until the mixture was clumpy and just barely wet. This mixture was pressed through an 80-mesh sieve into a new algae cup and 10-mL of deionized water was added to the refined mixture.

12.1.3 Results and Discussion

The formation of the spinel structure through mechanochemical synthesis was explored for feasibility. The initial tests used the metal hydroxide reagents, Mg(OH)_2 and Al(OH)_3, to form MgAl_2O_4. Figure 81 shows a comparison between the milled sample at different calcination temperatures and the hand ground sample after calcination at 900 °C. Figure 81 provides evidence that input of mechanical energy plays a role in spinel formation. Grinding by hand does not yield the spinel structure, but instead leads to the formation of MgO due to dehydration of the hydroxide at 900 °C. It should be noted that for MgAl_2O_4, mechanical grinding does not
lead directly to the product. However, the temperature required for calcination decreases significantly, as compared to above 1000 °C. Spinel formation is observed as low as 500°C, resulting in a nanocrystalline material. As the calcination temperature increased, the crystallinity of the material increased.

Figure 81: XRD patterns of MgAl₂O₄ reactions milled for 3 h and calcined at different temperatures. The powders were calcined at a) 500 °C; b) 600 °C; c) 700 °C; d) 800 °C; e) 900 °C; f) 1000 °C; g) Hand ground powder calcined at 900 °C. The black lines correspond to MgAl₂O₄ (JC-PDS 21-1152) and the blue lines correspond to MgO (JC-PDS 45-0946).
The mechanochemical synthesis of ZnAl$_2$O$_4$ (gahnite) was also performed. Figure 82 shows the XRD patterns of ZnAl$_2$O$_4$ milled for different times. The calcination step was found to be unnecessary to form gahnite. The increase in peak size was accompanied by a tandem decrease in full width at half max (FWHM) as the mill time increased. This correlates the milling process with a more crystalline product. However, at 10 h of milling (Figure 82e) the pattern shows a slight decrease in intensity. This trend was noted in other experiments of different spinels and was attributed to mechanical attrition.
12.1.3.1 Thermodynamics

The ability to reproduce MgAl$_2$O$_4$ requiring calcination and ZnAl$_2$O$_4$ without calcination facilitated the investigation of the thermodynamics of mechanochemical spinel formation. Each reaction was studied through various routes using the four combinations of the metal hydroxide or metal oxide starting reactants. The enthalpy of reaction was used to compare which set of reactants would most likely be favored when processed under identical mechanochemical conditions. A comparison of product formation and crystallinity can be compared to the expected reaction enthalpies. Table 12 lists the $\Delta H_{\text{rxn}}$ values that correspond to the 8 different reactions studied. The thermodynamic predictions did not completely match the experimental product formation in the high pressure, low temperature environment of the ball mill. Figure 83 shows the XRD patterns for the MgAl$_2$O$_4$ system. Of the two enthalpically favored reactions, only the magnesium oxide/aluminum hydroxide reaction formed the spinel, along with the enthalpically unfavored magnesium hydroxide/aluminum hydroxide reaction.
Table 12: Calculated enthalpy of reactions for Spinel and Gahnite structures.\(^{381}\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta H_{\text{rxn}}) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mg(OH)}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4 + \text{H}_2\text{O})</td>
<td>0.73</td>
</tr>
<tr>
<td>(\text{Mg(OH)}_2 + 2\text{Al(OH)}_3 \rightarrow \text{MgAl}_2\text{O}_4 + 4\text{H}_2\text{O})</td>
<td>19.63</td>
</tr>
<tr>
<td>(\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4)</td>
<td>-36.37</td>
</tr>
<tr>
<td>(\text{MgO} + 2\text{Al(OH)}_3 \rightarrow \text{MgAl}_2\text{O}_4 + 3\text{H}_2\text{O})</td>
<td>-17.47</td>
</tr>
<tr>
<td>(\text{Zn(OH)}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{ZnAl}_2\text{O}_4 + \text{H}_2\text{O})</td>
<td>-38.54</td>
</tr>
<tr>
<td>(\text{Zn(OH)}_2 + 2\text{Al(OH)}_3 \rightarrow \text{ZnAl}_2\text{O}_4 + 4\text{H}_2\text{O})</td>
<td>-19.64</td>
</tr>
<tr>
<td>(\text{ZnO} + \text{Al}_2\text{O}_3 \rightarrow \text{ZnAl}_2\text{O}_4)</td>
<td>-44.14</td>
</tr>
<tr>
<td>(\text{ZnO} + 2\text{Al(OH)}_3 \rightarrow \text{ZnAl}_2\text{O}_4 + 3\text{H}_2\text{O})</td>
<td>-25.24</td>
</tr>
</tbody>
</table>

Figure 84 shows the XRD patterns for the \(\text{ZnAl}_2\text{O}_4\) system. All four reactions listed in Table 12 are enthalpically favored for the synthesis of gahnite. However, only the reactant pair containing zinc hydroxide and aluminum hydroxide formed the desired product. The selectivity for spinel formation when the aluminum source was \(\text{Al(OH)}_3\) was also observed for the formation of \(\text{MgAl}_2\text{O}_4\). The structure of the reagents of plays an important role their reactivity under mechanical forces. Aluminum hydroxide is a layered material, whereas aluminum oxide is a network solid. Figure 85 shows the crystal structures of \(\text{Al}_2\text{O}_3\) and \(\text{Al(OH)}_3\). Layered materials are known to exfoliate under milling conditions due to shear forces, thus exposing more surface area. In comparison, to networks solids are difficult to break apart. In this case, however, \(\text{Al}_2\text{O}_3\) is harder than steel, thus making this process more difficult. Another benefit of using \(\text{Al(OH)}_3\) comes from the formation of water, which is favorable.
Figure 83: XRD patterns for the MgAl\textsubscript{2}O\textsubscript{4} system using different reagents. a) MgO + Al(OH)\textsubscript{3}; b) Mg(OH)\textsubscript{2} + Al(OH)\textsubscript{3}; c) MgO + Al\textsubscript{2}O\textsubscript{3}; and d) Mg(OH)\textsubscript{2} + Al\textsubscript{2}O\textsubscript{3}. The blue lines correspond to MgAl\textsubscript{2}O\textsubscript{4} (JC-PDS 21-1152), the black lines correspond to Mg(OH)\textsubscript{2} (JC-PDS 44-1482) and the green lines correspond to MgO (JC-PDS 45-0946).
Figure 84: XRD patterns for the ZnAl₂O₄ system using different reagents. a) Zn(OH)₂ + Al(OH)₃; b) Zn(OH)₂ + Al₂O₃; c) ZnO + Al₂O₃; and d) ZnO + Al(OH)₃. The blue lines correspond to ZnAl₂O₄ (JC-PDS 05-0669) and the black lines correspond to ZnO (JC-PDS 65-3411).

Figure 85: The crystal structures of a) Al₂O₃ and b) Al(OH)₃.
12.1.3.2 Cathodoluminescence

By incorporating emissive elements through substitution, we are able to describe how ions are incorporated into a solid produced mechanically, specifically in a low temperature high pressure environment. This was performed using cathodoluminescence microscopy and corresponding emission measurements in collaboration with Hope College. Figures 86, 87 and 88 show comparisons of unsubstituted and isomorphously substituted spinels under reflected light and excited by an electron beam.

Figure 86: An unsubstituted spinel (MgAl$_2$O$_4$) under a) reflected light and b) electron beam.
Figure 87: A 5 at.% Mn-substituted spinel under a) reflected light, showing a beige powder; b) under an electron beam showing a green (majority) and red (minority) cathodoluminescence.

Figure 88: A 5 at.% Cr-substituted spinel under a) reflected light, showing a white powder; b) under an electron beam, yielding red cathodoluminescence.

The corresponding cathodoluminescence spectra for the isomorphously substituted spinels are shown in Figures 89 and 90. The 5 at.% Mn-substituted MgAl$_2$O$_4$ (Figure 89) shows
both green and red emissions. These correspond to the occupation of tetrahedral and octahedral
cites, respectively, by Mn\textsuperscript{2+} ions. The 5 at.% Cr-substituted MgAl\textsubscript{2}O\textsubscript{4} (Figure 90) shows a red
emissions. This correspond to the occupation of octahedral cites by Cr\textsuperscript{3+} ions, similar to when it
is incorporated in rubies. Both of these spinels, as well as a few others (Figure 91), show
evidence of an isomorphous cation substitution when a transition metal is used. Figure 91 shows
the XRD patterns for both substituted spinels mentioned above, as well as for substituted
ZnAl\textsubscript{2}O\textsubscript{4} powders. Patterns a) through c) match the spinel structure, MgAl\textsubscript{2}O\textsubscript{4} (JC-PDS 21-
1152) and patterns d) through f) match ZnAl\textsubscript{2}O\textsubscript{4} (JC-PDS 05-0669), and both sets do not show a
secondary phase present due to the substituted metal hydroxide or metal oxide.

![Cathodoluminescence spectrum](image)

**Figure 89:** The cathodoluminescence spectrum for 5 at.%-Mn substituted MgAl\textsubscript{2}O\textsubscript{4}. The
red emission is due to Mn\textsuperscript{2+} ions occupying the tetrahedral sites, while the green emission is
a result of Mn\textsuperscript{2+} ions occupying the octahedral sites.
Figure 90: The cathodoluminescence spectrum for 5 at.% Cr-substituted MgAl₂O₄. The red emission is a result of Cr³⁺ ions occupying the octahedral sites.

The ability to easily identify the occupation of the metal cations’ within the ceramic structure when ball milled in a low temperature high pressure environment allows us to better understand the mechanisms in ball milling and can be applicable to the field of petrology. Spinels are commonly used as geological markers to better understand the surrounding environment in which adjacent rocks formed. Through cathodoluminescence, one has the ability to pair cation placement with environment, making it easier to work backwards when working with a rock group (in this case spinel) to identify the formation environment. This will allow more insight on the processes that occur during mechanochemical synthesis of mixed oxide systems.
Figure 91: XRD patterns for substituted MgAl$_2$O$_4$ samples corresponding to a) 5 at% Mn$^{2+}$, b) 5 at% Cr$^{3+}$ c) 5 at% Ni$^{2+}$ and substituted ZnAl$_2$O$_4$ samples corresponding to d) 5 at% Mn$^{2+}$, e) 5 at% Mn$^{2+}$ and c) 5 at% Ni$^{2+}$. All traces were milled and calcined at 800°C, except for trace d), which was not calcined.
12.1.3.3 Ceramic Glazes

Figure 92: a) Base glaze used as a comparison; b) 5 at.% Co-substituted spinel that was not calcined prior to firing; c) 5 at.% Co-substituted spinel that was calcined prior to firing; b) 5 at.% Ni-substituted spinel that was not calcined prior to firing; c) 5 at.% Ni-substituted spinel that was calcined prior to firing.

Spinels have been lightly explored as a tint in ceramic glazes for artistic properties. The isomorphously substituted spinels produced for our cathodoluminescence studies were also tested in base ceramic glazes in order to explore color and texture properties that formed within a cone 04 firing (1945 °F). Figure 92 shows several ceramic pieces coated with a glaze using no
additive (base glaze), 5 at.% Co- or 5 at% Ni-substituted MgAl$_2$O$_4$. A significant advantage to using substituted spinels in a glaze was to tone down the associated colors that could be overpowering when applied in their hydroxide or oxide forms. The Ni-doped spinel prior to being fired had a teal color and changed oxidation state within the kiln. This particular glaze may fare well better in a lower fining cone range to retain the teal color. Using a spinel that had not been calcined prior to firing resulted in a smoother, more uniform glaze. These test samples successfully showed that even in simple base glazes, spinels could be used to impart vibrant colors.

12.1.4 Conclusion

A mechanochemical pathway has been applied to the synthesis of pure and isomorphously substituted spinels, specifically MgAl$_2$O$_4$ and ZnAl$_2$O$_4$. Mechanochemical reactions that synthesized these ceramic materials deviated in product formation from the corresponding thermodynamic predictions. These deviations were attributed to the structures of starting materials as well as the formation of water from the reaction. Emissive elements were successfully incorporated into the spinels, producing cathodoluminescent materials. This cathodoluminescence allowed the reaction environment to be related to the cation site occupation. In certain cases, the substitutional element occupied both tetrahedral and octahedral sites, as in the case of Mn$^{2+}$ ions, which yielded a green and red cathodoluminescence emission, respectively. Additionally, substituted spinels are promising candidates for the production of new and alternative glazes for ceramics.
12.2 Mechanochemical Synthesis of Organopnictide Compounds

12.2.1 Introduction

Trisubstituted stibines and bismuthines have many different uses in chemistry today. Triphenylstibine is widely used in pesticides, in gasoline as an anti-knock agent, as corrosion inhibitors \(^{382}\) as a precursor to high conducting solutions, \(^{383}\) and as a catalyst for vinyl ester monomer formation. \(^{384}\) Triphenylbismuthine can be used as a radiopaque agent in bone cements and other biomedical resins, \(^{385,386}\) as an efficient buffer ion for dimerization reactions, \(^{387}\) as a catalyst for oxidative cleave of \(\alpha\)-glycols and as a phenyl transfer reagent. \(^{388,389}\) Both of these compounds are also used as ligands for Rh, Ir, Pd and Pt catalysts as a replacement for triphenylphosphine, \(^{390,391}\) and in transition metal carbonyl chemistry. \(^{392}\) These trisubstituted pnictides can be prepared by sealing the reagents in an ampoule and heating in a furnace, \(^{393,394}\) reacting an organopnicogen precursor with LiBH\(_4\) \(^{395}\) or Li and the corresponding aryl halide, \(^{396}\) and through a Grignard reaction. \(^{389,392}\) These compounds have also been prepared by reduction of the bismuth or antimony salt. \(^{397}\) The issue with these methods is the cost of production and energy used due to heating a furnace for 10 h or more for each reaction, \(^{398}\) use of solvents and generation of waste. \(^{389,392,397}\)

This study present an alternative method for the preparation of organobismuthine and organostibine compounds via mechanochemistry. High-energy ball milling provides an effective way to synthesis these trisubstituted products in a way that is both cost effective and scalable.
compared to other methods. This method uses alkali pnictides as precursors, which are reacted with aryl or alkyl halides.

12.2.2 Experimental

12.2.2.1 Synthesis of Alkali Pnictides

The alkali pnictides precursors were synthesized from the corresponding elements in stoichiometric amounts: Sodium (99.95%, Alfa Aesar), lithium (99.9%, Alfa Aesar), antimony (99.5%, Matheson Coleman and Bell) and bismuth (99.999%, Alfa Aesar) were used as received. The metal and pnicogen were loaded under argon and reacted via high-energy milling in an 8000M and/or 8000D SPEX CertiPrep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 ml. Buna-N quad O-rings were used to maintain a seal during milling. Kinetic energy was supplied using three 0.5” stainless steel ball bearings weighing approximately 8.0 g each. The alkali metal was added in 0.2 g increments to the pnicogen in order to prevent aggregation of the alkali metal, which would prevent the reaction from occurring.\textsuperscript{201} Grinding for 30 minutes followed each sodium or lithium addition. Upon complete reactions (typically 1.5 to 2 h of milling), the materials were stored in a glovebox for later use. The powders were analyzed by XRD to confirm presence of desired phase.
12.2.2.2 Synthesis of Trisubstituted Pnictides

The trisubstituted pnictides were prepared from stoichiometric amounts of the corresponding sodium pnictides prepared above (Na$_3$Bi or Na$_3$Sb) and an aryl or alkyl halide. The aryl and alkyl halides used were bromobenzene (Fisher Scientific), 1-bromopentane (Eastman Kodak) and 1-bromobutane (J. T. Baker); they were freeze-pump-thawed for 3-4 cycles to remove all gases prior to use and stored over molecular sieves. All materials were handled in a glovebox under argon. Milling was performed using similar conditions as described above, without the need for step additions of either reagent. The product was extracted with dichloromethane and analyzed by GC-MS.

12.2.2.3 X-ray Diffraction

Powder X-ray diffraction (XRD) was taken using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu K$_\alpha$ $\lambda$ = 1.5418 Å). Diffractograms were collected from 5 to 80 degrees 2θ using 0.010-degree steps and 0.3 seconds of dwell time.
12.2.2.4 Gas Chromatography-Mass Spectrometry

Gas chromatography – mass spectrometry (GC-MS) analysis was performed on an Agilent 6850 GC with an Agilent 19091-433E HP-5MS column (5% phenyl methyl siloxane, 30 m x 250 μm x 0.25 μm nom.) coupled with a 5975C VL mass selective detector. Approximately 1 mg of the reaction paste was extracted using 1.5 mL of dichloromethane or chloroform and sonicated to help solubilize the product. The solution was centrifuged and syringe filtered to remove the solids.

12.2.3 Results and Discussion

The first step of the process was to synthesize the alkali pnictides precursors. Equation 27 illustrates the general reaction to produced these precursors:

\[ M + Pn \rightarrow MPn \]  \hspace{1cm} (27)

Where M represents the alkali metals, Na and Li, and Pn represents the pnictogens, Sb and Bi. The XRD pattern for the synthesis of Na₃Sb is shown in Figure 93. The material produced is poorly crystalline, but matches Na₃Sb (JC-PDS 63-3523) as the only phase present. The broad peak around 23° 2θ is due to the polyester shrink tubing used to house the material. The results for the lithium analogue are similar. Analysis of the Na₃Bi and Li₃Bi through XRD was inconclusive, as the materials produced were amorphous. Percent yield of the products could not
be reported because of the unstable nature of the stibine and bismuthine gas. Sodium antimonide
reacts with water to form the unstable stibine gas, which then decomposes back to elemental
form, and makes it difficult to analyze gravimetrically.

Figure 93: X-ray diffractogram of sodium antimonide.

The reaction schemes for the synthesis of triphenylstibine and triphenylbismuthine are
represented by Equation 29 and 30, respectively:

$$\text{Na}_3\text{Sb} + \text{C}_6\text{H}_5\text{Br} \rightarrow \text{Sb(C}_6\text{H}_5\text{)}_3 + 3\text{NaBr} \quad (29)$$

$$\text{Na}_3\text{Bi} + \text{C}_6\text{H}_5\text{Br} \rightarrow \text{Bi(C}_6\text{H}_5\text{)}_3 + 3\text{NaBr} \quad (30)$$
GCMS was used to identify the successful formation of the triphenylpnnictides. Figure 94 shows the chromatogram for the triphenylstibine reaction. The sharp peak at 20.25 min was identified to be triphenylstibine. There were other peaks present in the chromatogram between 18.7-19 min, which were identified to be the terphenyl isomers. These terphenyls are due to impurities present in the bromobenzene that underwent a Wurtz type coupling reaction. Biphenyl is also present due to homocoupling of the starting material and the dibromobenzene impurity.

![Figure 94: The chromatogram of the triphenylstibine reaction.](image-url)
The results for the formation of triphenylbismuthine are shown in Figure 95. The reaction produced the desired product (20.9 min), but produced more coupling products, such as the terphenyl isomers (18.7-20 min) and biphenyl (15.8 min). The increase in coupling side products was attributed to triphenylbismuthine acting as a catalyst for these Wurtz type coupling reactions.

![Figure 95: The chromatogram of the triphenylbismuthine reaction.](image)

Trialkyl-substituted stibine and bismuthine were also synthesized. The GCMS results for these products are shown in Figures 96 and 97. Both bromobutane and bromopentane were used
as the alkyl halide source. The results for the reactions using bromobutane were more successful than bromopentane. However, these reactions produced more side products than those seen for the reactions using bromobenzene. Similarly, the synthesis of tributylbismuthine and triptylbumthine produced even more Wurtz-type coupling products. The extra peak at 16.9 min in Figure 97 was misidentified, but is likely due to an oxidized analogue of tributylbismuthine.

![Chromatogram for the formation of tributylstibine](image)

**Figure 96:** The chromatogram for the formation of tributylstibine.
12.2.4 Conclusion

Through the process of ball milling, both triphenylstibine and triphenylbismuthine were produced. Using GCMS, the compounds were successfully identified to be triphenylstibine and triphenylbismuthine. The tributyl and tripentyl analogues were also attempted, which produced some of the desired products, but led to the formation of Wurtz-type coupling products as the major product. Ball milling has proven to be a successful method in synthesizing these
triphenylpnictide compounds, and may also be a more cost effective and scalable alternative to the techniques currently in use today. Work on increasing the yields of the desired product will be carried out, as well as the synthesis of other products using a variety of organic halides.
CHAPTER 13: CONCLUSION

The synthesis of oxidized graphite, NaTaO$_3$, calcium tantalates, vanadia nanostructures, ZrSi$_2$, ReB$_2$, and OsB$_2$, were carried out using mechanochemistry. In addition, several isomorphously substituted kaolinites and spinels were carried through mechanochemical activation of the precursors. Catalysis was also carried out, with the mechanocatalytic depolymerization of cellulose and hydrogenation of olefins. In all cases, mechanical energy was input to the system through use of stainless steel or WC grinding media, which allowed for chemical transformations to occur.

Mechanochemistry can be used in the place of traditional methods, like sol-gel and coprecipitation, to provide a variety of substituted mixed metal oxides systems. In particular, we have shown that isomorphously substituted kaolinite and spinels, particularly MgAl$_2$O$_4$ and ZnAl$_2$O$_4$, can be carried out with the use of mechanochemistry. This required the aid of other techniques, such as hydrothermal treatment and calcination, respectively, but reduced the synthetic conditions significantly. Several rare-earth metal hydroxides and transition metal hydroxides were successfully substituted into the desired structure. The incorporation of transition metals into the spinel structure led to interesting properties. Cathodoluminescence emission of Mn$^{2+}$ and Cr$^{3+}$ substituted spinels gave us insight into the site occupation upon successful substitution. A variety of colorful powders were also produced, which are promising as alternative glazes in ceramics.

Oxidized graphite was shown to be an alternative to Hummers’ graphite oxide and graphene. This material has carboxylic acid groups on the edges, which allow it to be
hydrophilic, but retain the electrical conductivity within the sheet. This makes it suspend readily in water, can be deposited as thin films, and eliminates the need to reduce the material unlike traditional graphite oxide. Another benefit is the use of mild oxidizing agents and minor waste produced, unlike what results from the Hummers’ method. This material shows promise for a variety of potential applications in polymer composites, batteries, transparent thin films and more.

Mechanochemical synthesis can be utilized to produce nanomaterials. The synthesis of vanadia nanorods and nanotubes were carried out. By changing the amine template used, nanorods or nanotubes of varying sizes were produced. It should be mentioned that this technique was used to activate the material, and required hydrothermal treatment to achieve these nanostructures. However, this showed that the production of these structures is not limited only to primary amine templates. Conversely, the mechanochemical synthesis of ZrSi$_2$ was carried out without the need of a secondary technique. In this case, size control was carried out. By changing the amount of the diluent, CaCl$_2$, nanocrystalline powders were synthesized with crystallite sizes ranging from 9 to 30 nm. Removal of the salt produced polydisperse nanoparticles without a passivating oxide layer.

Calcium and sodium tantalates were studied via high-energy ball milling. This method allowed for the study of the kinetics of the synthesis of Ca$_2$Ta$_2$O$_7$. This revealed that an intermediate, Ca$_4$Ta$_2$O$_9$, is formed after 1 h and reacted after 5 h to form the desired product, which is complete after 10 h. If prolonged milling is carried out, Ca$_2$Ta$_2$O$_6$ is formed. Analysis
was carried out using RIR method, which revealed the production of nanocrystalline $\text{Ca}_2\text{Ta}_2\text{O}_7$ powders.

Rhenium and osmium diborides were successfully synthesized mechanochemically from the elements. This required prolonged milling of up to 80 h in the case of ReB$_2$, versus 18 h for OsB$_2$. This method eliminated the need for excess boron to be used in the case of ReB$_2$. In both cases, the analysis of the powders by SEM, TEM and STEM revealed large agglomerates composed of smaller crystallites, which ranged from 1 to 10 nm for OsB$_2$. In addition, OsB$_2$ was determined to be the hexagonal phase. Annealing under vacuum at 1050ºC over 6 days resulted in increase crystallinity without phase change, which suggested $h$-OsB$_2$ is very stable.

Mechanical activation was carried out to reduce the particle size of the desired material, which in turn leads to lower reaction conditions. This was mentioned earlier for spinels and kaolinites, but was also utilized for the deposition of germanium. Copper (I) iodide and germanium powders were ground and intimately mixed in a high-energy SPEX mill to decrease the particle size. This mixture was used to synthesize GeI$_2$ under vacuum at 400ºC. We showed that disproportionation of this material occurred at 210 ºC, which is the lowest reported.

Balling milling can also be utilized in catalysis. The input of mechanical energy can be used to activate the catalyst through the formation of defects and reduction of particle size. The depolymerization of cellulose was carried out under mild conditions without the generation of waste, making the process green. The use of kaolinite significantly reduces the cost of the process and can be reused several times without deactivation. This process is also insensitive to the biomass source and does not require the sole use of corn for ethanol production. On the other
hand, mechanocatalysis was used for the hydrogenation of olefins over defect-laden h-BN. Mechanical activation was carried out to induce defects into the structure, which resulted in a catalytic material. DFT calculations showed that the carbon double bond in ethene is weakened over B_N, V_N, V_B, and Stone-Wales defect sites. The binding energies at these sites are on par with those of metals currently used for catalytic hydrogenation.

Mechanochemistry is not limited exclusively to solids. Liquid reagents can also be utilized. The synthesis of trisubstituted pnictides was carried out using alkali metal pnictides with aryl halides or alkyl halides, the latter two being liquids. Triphenylstibine and triphenylbismuthine were produced as the major products, but side products due to Wurtz-type coupling were also present. Triphenylbismuthine acted as a catalyst for this type of coupling, which led to a higher formation of coupling products. The trialkylated analogues were also produced, but to a lesser extent.
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