Development and Characterization of Inorganic Materials with Energy Sector Applications

Samuel J. Frueh
University of Connecticut - Storrs, sam.frueh@gmail.com

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Four classes of materials with energy sector applications have been developed or characterized herein. Processing requirements that lead to a toughened carbon fiber reinforced silicon carbide ceramic matrix composite with a compliant and oxidation resistance boron nitride interface coating were developed. Preliminary experiments resulted in highly brittle composites when BN was applied by CVD to as-received fiber. This led to a requirement of heat treating the carbon fiber to favorably modify the fiber surface prior to BN deposition. The compound ammonia borane was investigated as a potential chemical hydrogen storage material for hydrogen fuel cell applications. Two known thermal decomposition steps which yield hydrogen gas, borazine impurities, and residual B-N inorganic polymers were corroborated by several techniques. A high temperature decomposition step leading to boron nitride, and an unreported gaseous impurity from the two known decomposition steps were identified. The reactivity of a γ-alumina supported, fcc cobalt (Co/Al₂O₃) catalyst was evaluated in a CO₂/H₂ feedstock for activity towards CO, methane, C₂+ hydrocarbons and methanol. Comparable methane selectivities were obtained at low and high pressures. At low pressures the balance was composed mostly of CO while at high pressures the balance was composed mostly of C₂ hydrocarbons. This suggest CO₂* is preferentially hydrogenated at higher pressures instead of dissociating to CO* and O*. The evolution of the catalyst composition and structure during fabrication was tracked by a several techniques. The acid/base character of CO₂(g) specifically towards exterior framework surfaces (to the exclusion of tunnel sites) on the manganese oxide octahedral molecular sieve OMS-2, was measured using synchrotron based soft X-Ray photoelectron spectroscopy. In addition to fundamental interest, the
adsorption of CO$_2$ on OMS-2 has direct relevance to several energy sector applications. CO$_2$ is often considered to be a Lewis acid probe for surface basicity, but may also exhibit basic character towards acidic surface sites. Measurements of surface acidity and basicity aid in the determination of how these properties dictate the activity and selectivity of a heterogenous catalyst towards any given reaction.
Development and Characterization of Inorganic Materials with Energy Sector Applications

Samuel John Frueh

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A Dissertation
Submitted in Partial Fulfillment of the
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Doctor of Philosophy Dissertation

Development and Characterization of Inorganic Materials with Energy Sector Applications

Presented by
Samuel John Frueh.

Major Advisor
__________________________________________
Steven L. Suib

Associate Advisor
__________________________________________
Raymond Joesten

Associate Advisor
__________________________________________
Edward Neth

University of Connecticut
2018
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I thoroughly enjoyed and benefited from my experience as a graduate student in the chemistry department at UConn. This resulted in no small part from the efforts of my major advisor, Dr. Steven L. Suib, to secure resources and foster high level collaborative efforts with outside researchers. This went a long way towards ensuring that success was limited only by imagination and investment, and provided an immensely rich educational experience. The confidence that Dr. Suib placed in me to operate in this environment was received with gratitude.

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CHAPTER 1

Introduction

1.1 GLOBAL OVERVIEW

The research reported herein regards the fabrication and characterization of four different classes of inorganic materials that have applications in the energy sector. An *energy vector* may be defined as “a tool that allows the transportation and/or storage of energy”.\(^1\) The overarching motivations of this effort are to advance means of making more effective use of existing energy vectors, to diversify the sourcing of existing energy vectors for environmental and economic reasons, and to promote development of new energy vectors that simplify diversification or have niche applications.

Operating gas turbine engines at higher temperatures allows some combination of improved efficiency (greater work per unit of heat input) or improved specific work (greater work per unit of airflow) to be obtained. The efficiency and compactness of a turbine engine depends on the temperature limitation of the materials which are used to construct it. In general, this has led to considerable investigation into means of toughening ceramic materials which have a high thermal tolerance but are inherently brittle.\(^2,3\) Accordingly, a method of protecting carbon fiber from oxidation in a carbon fiber reinforced ceramic matrix composite has been developed which also imparts the necessary interfacial properties between fiber and matrix that are required to promote toughening.

The conversion of CO\(_2\) into hydrocarbon fuels through reactions with H\(_2\) or H\(_2\)O is of interest due to the diversification of energy sources that may be used to produce hydrocarbon fuels to include renewables, biofuels, nuclear, coal, and natural gas. CO\(_2\) is
an untapped resource that might become profitably used as a feedstock for hydrocarbon fuels if sufficient advancements are made in carbon dioxide capture and conversion chemistry. This study characterizes the structure of a baseline Fischer-Tropsch type alumina supported cobalt catalyst and its activity in a CO$_2$/H$_2$ feed towards the conversion of CO$_2$ to carbon monoxide, methane, C2+ hydrocarbons, and alcohols.

Advancing the use of hydrogen as a transportation fuel is of interest because, like CO$_2$ conversion, it has the potential to diversify energy sources away from liquid petroleum. The associated challenge is finding a means of safely delivering and storing it onboard a vehicle in sufficient capacity. The molecular solid, ammonia borane, H$_3$BNH$_3$, has sufficient gravimetric and volumetric hydrogen density to be a viable candidate for chemical hydrogen storage, and so the thermal decomposition reactions of ammonia borane that lead to hydrogen release are characterized in detail.

The final topic of investigation is a fundamental characterization of the interaction between carbon dioxide and specific surfaces of the cryptomelane type manganese oxide octahedral molecular sieve (OMS-2). The primary focus is determining the acid/base character between the carbon dioxide adsorbate and the OMS-2 surfaces, however, the interaction between these two species is also of direct relevance to several energy sector applications. OMS-2 is known as a heterogeneous catalyst. Iron doped OMS-2 and OMS-2 supported iron have been found to be active towards the conversion of CO$_2$ to hydrocarbons.$^4$ CO$_2$ has been found to re-oxidize oxygen depleted OMS-2 surfaces in-situ when delivered as a reactant along with ethane during the catalytic dehydrogenation to ethene at 800°C.$^5$ And lastly, OMS-2 or its variants have potential as inexpensive
emissions control catalysts for the total oxidation of volatile organic compounds and carbon monoxide to carbon dioxide.\textsuperscript{6-8}

\section*{1.2 \textbf{Carbon Fiber Reinforced Ceramic Matrix Composites}}

\textbf{1.2.1 CVD-BN for Oxidative Protection of Carbon Fiber}

Carbon fibers are used in high temperature thermo-structural materials because they retain their mechanical properties well at high temperature\textsuperscript{9} and are a small fraction of the cost of ceramic fibers with comparable properties. For applications above roughly 1000\textdegree C the cost of ceramic fibers tolerant to such temperatures increases dramatically. By 1300\textdegree C creep rates become problematic in nearly every case, and above roughly 1600\textdegree C almost all ceramic fibers will suffer significant strength losses\textsuperscript{10-13} However, high performance (HP) carbon fibers can retain their mechanical integrity at temperatures exceeding 2000\textdegree C\textsuperscript{9,14,15}

The obvious drawback of using carbon fibers at high temperature is that they must be protected from oxidation starting at about 400\textdegree C or less, otherwise the fibers will be destroyed. Oxidative protection is less critical for most non-oxide ceramic fibers as these usually have a degree of intrinsic oxidation resistance. Likewise, refractory oxide fibers cannot be further oxidized and do not require oxidative protection. Various schemes are employed to protect carbon fibers which have been integrated into a thermostructural ceramic matrix composite (CMC) from destructive oxidation.\textsuperscript{16-18} The research reported here describes a new category of scheme to protect carbon fibers from oxidation: a boron nitride fiber coating which imparts toughening characteristics to the composite and oxidative protection to the fibers.
Typically, carbon fibers intended to serve as the reinforcement phase in a CMC receive a carbon coating up to several hundred nm thick by chemical vapor deposition (CVD). This soft, easily cleavable interface coating ensures a mechanically weak bond between the fiber and the matrix which promotes toughening in a brittle-matrix fiber reinforced composite. This chemical vapor deposited carbon (CVD-C) and the carbon fiber substrate are susceptible to oxidation if a matrix crack exposes a route of ingress for oxygen from the air. Once air reaches the CVD-C, oxidation usually proceeds most rapidly along the CVD-C coating, ahead of oxidation of the fiber. Therefore an interface coating that protects against oxidation and also imparts the appropriate mechanical properties to the composite is desired.

The available sealing interfaces are boron nitride or boron doped carbon. The boron level requirement in boron doped carbon is too high to provide the necessary mechanical requirements. This leaves boron nitride as the desired sealing interface. Preliminary research revealed that processing steps and conditions that have been used to fabricate SiC/BN/SiC composites result in weak and brittle C/BN/SiC composites (the notation used here refers to the makeup of fiber/interface/matrix). Processing steps that are required to generate a compliant chemical vapor deposited BN (CVD-BN) interface coating, and reasons for compliance (or lack thereof), are investigated. The BN polymorph of interest is the hexagonal form, or its turbostratic cousin with stacking disorders of the 2-D BN layer sheets. BN is oxidation resistant in dry air to the range of about 800°C or 1000°C at which point it will react to yield boria according to Equation 1.1.
\begin{equation}
4\text{BN}(s) + (3+2x)\text{O}_2(g) \rightarrow 2\text{B}_2\text{O}_3(s,l) + 4\text{NO}_x(g)
\end{equation}

Eq. 1.1

Boria is a viscous crack filling glass between about 450°C and 1200°C. At higher temperatures, boria is volatile, but the presence of certain other oxides with solubility in boria such as silica or titania extend the upper working temperature of the melt.\textsuperscript{24}

1.2.2 Gas Turbine Engines

The temperature limitation of structural materials is the major design limitation for a number of aerospace and non-aerospace applications. Advancing these technologies depends on developing structural materials with increased temperature capabilities. This is perhaps most readily apparent for the gas turbine engine.

Gas turbine engines are based on the Brayton cycle. An analysis of the thermodynamics of the Brayton cycle reveals that higher use temperatures afford greater thermal efficiency and specific work. That is, the net work obtained per unit of heat input and the net work done per unit mass of airflow, respectively, can be improved by operating at higher temperatures. A major design limitation of a turbine engine is therefore the thermochemical tolerance of materials with the requisite mechanical properties that comprise the components. The development of materials tolerant to higher temperatures in oxidizing atmospheres and combustion environments which possess the requisite mechanical properties should lead to engines with better performance. The P-V diagram of an ideal Brayton cycle helps illustrate this concept in Figure 1.1.
In the Brayton cycle, when traveling along A-B, air passes through the inlet and is compressed adiabatically by a compressor. At B, the compressed air enters a chamber called the burner. Along B-C, an amount of heat $Q_1$ is added to the air through the combustion of fuel in the burner, and the air expands at constant pressure. The amount of fuel added is a small mass percentage of the airflow rate. At C, the air enters the power turbine. Along C-D, the air is adiabatically expanded through the power turbine and then through a nozzle. The power turbine drives the compressor along A-B. The work done on the turbine is equal to the work done by the compressor because the two components are on the same shaft. After passing through the turbine, a nozzle affects the flow of the gas, returning the air to free stream pressure, increasing the air velocity and generating thrust. At D, the air is exhausted from the nozzle to the atmosphere. Along D-A an amount of heat, $Q_2$, is expelled outside the engine to the environment and flow is fully returned to free stream conditions.
The ideal Brayton cycle thermal efficiency $\eta$ is the fraction of heat, $Q_1$, that is converted to useful work $w$. $\eta$ depends on the ratio of the atmospheric temperature ($T_A$) to the compressor exit temperature ($T_B$) as

$$\frac{w}{Q_1} = \eta = 1 - \left(\frac{T_A}{T_B}\right).$$  \hspace{1cm} \text{Eq. 1.2}

where $w$ and $Q_1$ are specified to a unit of mass of the working fluid, air. Thermal efficiency can therefore be increased by increasing the compression ratio.

The specific work $w$ generated by a turbine engine is given by

$$w = \eta Q_1.$$  \hspace{1cm} \text{Eq. 1.3}

Specific work can be improved by increasing either the compression ratio, which increases $\eta$, or increasing $Q_1$. An allowed increase in $T_c$, perhaps due to a materials advancement, allows for an increase in $Q_1$, an increase in compression ratio, or some combination of both. Depending on the exact nature of the change to the thermal efficiency and $Q_1$ parameters, some combination of improved specific work and improved efficiency is obtained. Advanced high temperature thermostructural materials are thus an enabling technology for turbine engines.

Another benefit of materials with enhanced temperature capabilities is that cooling schemes which add bulk, weight, complexity, and cost to an engine can be minimized. Advanced thermostructural materials may also find applications as leading edges of hypersonic vehicles, atmospheric re-entry surfaces of space vehicles, rocket engine nozzles, aircraft and high-performance brakes, cutting tools, heat-exchanger tubes, exhaust ducts, hot gas filters, and high temperature hot pressing molds.\textsuperscript{25}
1.2.3 Ceramic Matrix Composites

Metals and alloys are currently used almost exclusively to form the hot section components of turbine engines. Stainless steel has a maximum operating temperature of about 750°C. Creep rupture strengths of most Ni based superalloys makes them unserviceable when temperatures approach 1000°C, but some can operate up to 1150°C. This is the approximate current limitation of metals technology. These alloys are also very dense.

To find possible materials with increased use temperatures we turn to ceramics. Silicon carbide and silicon nitride are thermochemically stable in air to about 1400°C. Alumina has use temperatures of about 1500°C. Transition metal borides, carbides and nitrides, particularly of Ti, Zr, Hf, Ta, and Zr are thermally stable to temperatures well in excess of 2000°C because they have melting points above 3000°C and because they form protective stable oxide scales which also have high melting points. The obvious problem associated with using ceramics as structural components is that they are brittle and subject to catastrophic failure. Ceramics do not deform plastically like metals, and instead the propagation of a single flaw renders the entire body useless.

The mechanical strength, toughness, and tolerance to damage of a ceramic body can be improved with the use of a fibrous ceramic or carbon reinforcement phase embedded within the ceramic to form a CMC. The objective is to cause matrix cracks advancing under a remotely applied stress to slip against the fibers rather than to continue to propagate through the fibers. If the matrix in an advancing crack slips against the fibers, the crack will become bridged by the fibers, maintaining the mechanical integrity of the body.
Conversely, if the matrix crack propagates through the fibers, the body is susceptible to catastrophic failure from even a single crack as if the body were a monolith.\textsuperscript{27,29}

In order for this slippage to occur, the strength of the bond between the ceramic matrix and the ceramic fibers must not be too strong.\textsuperscript{30} Usually this is achieved by uniformly coating the fibers in an easily deformed refractory material such as carbon, or boron nitride and forming a ceramic matrix around the coated fibers. This coating is termed the “interface”.

Fibers in a CMC can be comprised of continuous fibers, randomly oriented short fibers, or randomly oriented short single crystal whiskers. Non-fibrous carbon or ceramic foams may also be used as a reinforcement phase. Composites using continuous fibers typically have better strength and toughness than composites reinforced by whiskers or short fibers.\textsuperscript{27,30} Fibers will typically have a diameter on the order of 10μm. In the case of continuous fibers, a manufacturer will bring together several thousand fibers into a unidirectional single strand, called a tow, which can be wound onto a spool. The tows can then be used to weave a fabric that can be rolled onto a bolt. A 2-D CMC can be fabricated using the woven fabric. A 3-D CMC can be formed from multiple plies laid up on one another or from a 3-dimensional weave. For the laboratory evaluation of a given fiber/interface/matrix system, a 1-D unidirectional single strand composite can be fabricated using a segment of a single tow. Such a specimen is termed a mini-composite. In this study, mini-composites using a carbon fiber reinforcement, a BN interface coating, and a SiC matrix (C/BN/SiC) were evaluated. Processing steps required to obtain tough
composites, and data isolating reasons for the presence or absence of toughening were identified.

The BN was applied by chemical vapor deposition (CVD) to variously heat-treated samples of woven carbon fiber. Single tows were extracted from the coated weave and a SiC matrix was fabricated into the tow volume by chemical vapor infiltration (CVI) from methyltrichlorosilane (MTS) in hydrogen gas.

![Diagram of an advancing matrix crack in a CMC](image)

**Figure 1.2** Diagram of an advancing matrix crack in a CMC

The primary categories of toughening mechanisms in a CMC are those that provide an increased resistance to damage and those that provide an increased tolerance to damage. In Figure 1.2, an advancing matrix crack is diagramed in a 1-D composite under tensile load parallel to the fiber direction. Three different mechanisms that may serve to increase the resistance to damage, i.e. the matrix cracking stress, are depicted. First, bridging fibers in the crack wake serve as tractions which resist opening and propagation of the crack.\(^{30,31}\) Second, in the region ahead of a crack tip, tensile forces perpendicular to the remote stress...
arise which debond the fiber from the matrix if there is a sufficiently weak bond between the fiber and matrix.\textsuperscript{25,32} This effectively generates cracks running perpendicular to the main crack and along the fiber matrix interface. These perpendicular cracks open as the primary crack advances. This mixed mode fracture increases the energy, and thus the stress, required to drive a matrix crack due to the creation of additional surface area per unit of crack extension. Third, these perpendicular cracks between the fiber and matrix blunt the curvature of an advancing crack tip at the site of the fiber/matrix debond. This significantly reduces the stress intensity factor present at the location of the crack tip. The magnitude of remote stress required to propagate the crack is consequently increased.

Perhaps the more important category of toughening mechanisms in fiber reinforced CMCs is that of tolerance to damage. In real, and aggressive CMC applications such as a gas turbine engine, situations will inevitably arise where an applied stress or strain exceeds the cracking limit for at least one component of the composite. These events could occur during fabrication of the material (thermal residual stress), machining or shaping of the final part, assembly of the part into a device, or during the intended use of the part. It is not a reasonable expectation to design a ceramic material, composite or otherwise, so highly resistant to fracture that it will never occur. A composite must be able to tolerate inevitable damage. As discussed above, fibers bridging a matrix crack under tensile stress can continue to carry an applied stress. The proviso is that the fiber volume fraction must be large enough to support the additional load that was being carried by the matrix at the matrix cracking stress. If the fiber volume fraction is not high enough, the fibers within a
through crack will fail in load control as soon as the crack propagates. Specifically, matrix cracks will be supported by the fibers under the condition that

\[ \sigma_{fu}V_f \geq \sigma_{mu}V_m + \sigma'_f V_f \]  

Eq. 1.4

Where \( \sigma_{fu} \) and \( \sigma_{mu} \) are the fiber and matrix failure stress respectively, \( V_f \) and \( V_m \) are the volume fractions of the fiber and matrix, and \( \sigma'_f \) is the stress supported by the fibers at \( \sigma_{mu} \).

If the inequality in Eq. 1.4 is met, crack bridging and multi-cracking of the matrix will occur as described below. If the inequality in Eq. 1.4 is reversed, the fibers will fracture immediately following a single matrix fracture under load control.

We can define a length \( X_c \) in a 1-D composite under uniaxial load such that multi-cracking will occur to a saturation spacing whereby the distance between any two adjacent cracks falls between \( X_c \) and \( 2X_c \). The cracks run perpendicular to the direction of the applied tensile stress and divide the matrix into segments as depicted in Figure 1.3. Also depicted in Figure 1.3 is another mechanism of damage tolerance: fiber fracture within the matrix which requires that fibers pull out of the matrix with friction under additional strain.

\( X_c \) is determined by the shear stress \( \tau \) that the interface can sustain. A balance of forces requires, for \( N \) fibers per unit cross section,

\[ \sigma_{mu}V_m = 2\pi r N \tau X_c. \]  

Eq. 1.5

A segment of length shorter than \( X_c \) cannot form because the shear stress transferred to the matrix from the fiber over such a length could never be large enough to reach the matrix cracking stress. Therefore, any segments with spacing larger than \( 2X_c \) will crack until every new segment is shorter than \( 2X_c \). When this condition is met, additional strain will result
in fiber sliding against the matrix segments. Fiber failure will ultimately occur at sufficient stress. If the fiber breaks within segments, fiber pull-out will occur.

![Matrix multi-cracking and fiber failure in a CMC](image)

**Figure 1.3** Matrix multi-cracking and fiber failure in a CMC

Table 1 summarizes possible toughening mechanisms that may occur during the failure of a ceramic matrix composite. All mechanisms listed depend upon a weak bond between the fiber and matrix such that advancing matrix cracks do not proceed through fibers but rather proceed around them. It is not necessary to observe all mechanisms in a CMC system for toughening to be observed. But inasmuch that a weak fiber/matrix bond is required for any and all of the mechanisms, the properties of the interface largely determine the properties of the entire composite system.
The failure and toughening mechanisms of 2-D or 3-D CMC’s formed from woven fabric and under various types of stress from various directions will be more complicated than the case of a tensile load applied parallel to the direction of fibers in a 1-D composite. However, the above discussion suffices to indicate the role and importance of the interface.

### 1.2.4 Structure and Properties of Carbon Fiber

As previously mentioned, low cost and the retention of mechanical properties to temperatures in excess of 2000°C make high performance (HP) carbon fiber an attractive choice for the fiber reinforcement in a CMC. Properties of HP carbon fibers derived from polyacrylonitrile (PAN) and from pitch are listed in Table 2 and compared to common types of ceramic fibers. The high performance (HP) carbon fibers equal or surpass other inorganic ceramic fibers in their mechanical properties at room temperature. The type of carbon fiber used in this study was PAN derived T300 manufactured by Toray.

<table>
<thead>
<tr>
<th><strong>Toughening mechanisms that may occur during composite failure</strong></th>
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<tr>
<td>Increased resistance to damage</td>
<td>Increased tolerance to damage</td>
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<tr>
<td>Closure traction by bridging fibers</td>
<td>Multicracking</td>
</tr>
<tr>
<td>Crack tip blunting</td>
<td>Crack bridging</td>
</tr>
<tr>
<td>Mixed mode fracture</td>
<td>Fiber pull out</td>
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**Table 1.1** Summarized tabulation of toughening mechanisms
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<tr>
<th>Type</th>
<th>Fiber designation</th>
<th>Tensile strength (MPa)</th>
<th>Tensile Modulus (Gpa)</th>
<th>Elongation %</th>
<th>Density (g/cm³)</th>
<th>Diameter (µm)</th>
<th>Manufacturer</th>
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<td>HP Carbon</td>
<td>T300</td>
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<td>230</td>
<td>1.5</td>
<td>1.76</td>
<td>7</td>
<td>Toray</td>
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<td>(PAN)</td>
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<td>1.8</td>
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</table>

Table 1.2  Selected Fiber Properties Data
The IUPAC has designated different classes of carbon fiber based on their physical properties.\textsuperscript{33}

- **UHM** - (ultra-high modulus) modulus greater than 500 GPa
- **HM** - (high modulus) modulus greater than 300 GPa and strength to modulus ratio less than 0.01
- **IM** - (intermediate modulus) modulus less than 300 GPa and strength to modulus ratio greater than 0.01
- **LM** - (low modulus) modulus as low as 100 GPa and low strength
- **HT** - (high strength) strength greater than 3000 MPa and strength to modulus ratio between 0.015 and 0.02.

The T300 carbon fiber used in this research can be classified as both IM and HT.

Clearly, processing details have an effect on the properties and thus the structure of carbon fiber. There is no universally agreed upon detailed structure of carbon fiber. It is reasonable to presume this is because carbon fibers processed under different conditions have different structural details and studies into the structure of carbon fibers have been made on a number of different, sometimes unspecified, fiber types.\textsuperscript{34} Nonetheless, there are similarities among the models and some trends between processing, structure, and properties can be established.

In the production of carbon fibers from PAN,\textsuperscript{24,34} the acrylonitrile monomer is first polymerized to the PAN polymer. A solution of the polymer dissolved in a solvent is wet spun or dry spun into filaments. Often a co-monomer is used during polymerization. The PAN fibers are rendered infusible during a stabilization step consisting of heat treatment.
in air or other oxidizing gas under tension between 200°C and 300°C for several hours. The stabilization step cyclizes and partially oxidizes the PAN fiber. The evolution of chemical structure during the polymerization and stabilization steps is diagramed in Figure 1.4.

**Figure 1.4.** Polymerization and thermo-oxidative stabilization of PAN

The cyclization and dehydrogenation steps during the stabilization of PAN result in a ladder polymer. Oxidation then promotes cross linking of the ladder polymer during carbonization at higher temperatures by providing sites for the formation of carbon-carbon bonds through hydrolysis between H atoms on one chain and oxygenated functional groups on another. Cross linking may also occur through dehydrogenation. The application of tension during stabilization elongates and orients the uncyclized PAN along the fiber axis. A similar orientation of the ladder polymer along the fiber axis is locked in, promoting
preferential orientation of graphitic planes that form during carbonization at higher temperatures.

Carbonization is the pyrolysis of the stabilized PAN at temperatures ranging from 1000°C to 1600°C in nitrogen or argon. Hydrogen, nitrogen, and oxygen compounds are evolved and the oriented cyclized structures coalesce through cross-linking to form graphitic structures with layer planes largely oriented parallel with the fiber axis.\textsuperscript{24,34} The heating rate during carbonization is initially low to prevent overly rapid release of volatiles, and is increased above about 1000°C. The residence time at temperatures below 1000°C may be on the order of an hour, but above 1000°C may be on the order of minutes. To obtain fibers with a high modulus (above roughly 300 GPa), a subsequent graphitization heat treatment between 2000°C and 3000°C is required, with the use of argon alone above 2000°C because nitrogen will react with the carbon to form cyanogen. Graphitization increases the modulus by increasing the preferential orientation and crystallinity of the fiber but can have a deleterious effect on strength. The decrease in strength on graphitization could be a result of structural changes within the fiber, however it has been reported that graphitized fibers fabricated in clean room conditions result in a tensile strength increase. Dust reacting on the surface of carbon fibers might react and degrade the fiber strength at graphitization temperatures.\textsuperscript{34}

The types of carbon which compose carbon fiber can be described along a continuum marked by three different structures. Carbon can be graphitic, turbostratic, or amorphous.\textsuperscript{24} Highly crystalline graphitic regions are uncommon. Turbostratic carbon is similar to crystalline graphite, but successive layer planes are randomly rotated or
translated. Amorphous carbon is less ordered than turbostratic carbon. Layer stacking is not precisely parallel, and the layers can undulate and fold. The layer planes in the graphitic, turbostratic and amorphous graphite, to the extent they occur, preferentially align parallel to the fiber axis.

Most models of carbon fiber structure do not include distinct grains or crystallites. These models are largely based on neutron, electron and X-Ray diffraction as well as optical and electron microscopy. Perret and Ruland\textsuperscript{35} proposed a model of undulating ribbons 5 to 7 nm in width generally running along the fiber axis. In this model, layer planes branch off and join adjacent parallel ribbons every 6 to 13 nm with longer unbranched sections corresponding to fibers with increased orientation. The gaps between ribbons give rise to needle shaped voids. Oberlin\textsuperscript{36} proposed that a structure of wrinkled sheets that are folded and entangled but not connected better describes the carbon fiber. Diefendorf and Tokarsky\textsuperscript{37} proposed a model similar to the ribbon model of interweaving and undulating microfibrils 4 to 30 nm in thickness as the major structural unit, and where the thickness increases with modulus. The amplitude of the undulation is large for high strength fibers and smaller for high modulus fibers. This is supported by an increased orientation of the 002 planes with ultimate heat treatment temperature. Bennet and Johnson\textsuperscript{38} drew a schematic showing that the layer planes are preferentially oriented along the fiber axis but are folded, entangled, connected and enclose void spaces. In this model, the extent of curvature of the layers increases and the length of the layers decreases moving from the skin to the core. Knibbs\textsuperscript{39} used polarized light microscopy to report a gradient in radial texture from a circumferential orientation in a sheath to a more isotropic core. Under
some processing conditions a circumferential orientation can be obtained through the entire cross section. Other investigators have identified a skin core heterogeneity in high modulus fibers from SEM images of fractured fibers.\textsuperscript{37,40,41} This skin core heterogeneity is more pronounced in HM (high modulus) fibers, which have undergone a high temperature graphitization step, than in HT (high strength) fibers for which this step was omitted.

The formation of a circumferentially oriented sheath structure in high modulus fibers observed by imaging techniques is consistent with two chemical observations:\textsuperscript{33} that the proportion of “active” surface area is greater in HT fibers than in HM fibers, and that heat treating fibers lowers their rugosity factor. The rugosity factor is the ratio of actual surface area (measured by Brunauer Emmet and Teller (BET) techniques) to the geometric surface area calculated from the dimensions of the fiber. Typical rugosity factors for carbon fiber are between 1 and 50 and actual surface area is typically less than 1 m\textsuperscript{2}/g. The active surface area is a measure of the amount of graphite-like basal plane edge carbons at the surface of the fiber\textsuperscript{42}. Active surface area is determined by measuring thermal desorption of CO or CO\textsubscript{2} at high temperatures (950°C) after chemisorbing O\textsubscript{2} at low temperature (300°C). O\textsubscript{2} chemisorbs on edge carbon surfaces resulting in a chemical reaction that desorbs CO or CO\textsubscript{2} at elevated temperatures while no such conversion to CO or CO\textsubscript{2} occurs on layer plane surfaces. In one study,\textsuperscript{43} the active surface area of an HT carbon fiber was about 11% of the total surface area. In a HM fiber the active surface area was only 4% of the total surface area. Heat treatment reduces the amount of edge carbon comprising the fiber surface.
1.2.5 Oxidative Protection of Carbon Fiber Reinforced Composites

Various means may be used to protect carbon fibers from oxidation. In C/C composites, protection of the matrix as well as the fibers is usually accomplished by multi-layered coatings on the surface of the entire composite. Two concepts are described here.24

There is a four-part approach to oxidation protection in C/C composites that may be used up to 1700ºC. The first part is to incorporate oxygen getters and glass formers into the matrix. Compounds between titanium, boron, silicon, titanium, and zirconium such as SiC, Ti₅Si₃, TiB₂, Si₂TiB, and ZrB₂ may be used. The second part is to apply a SiC coating to the outside of the composite body. A glassy coating on top of the SiC is applied to fill cracks and voids. The glassy coating may be comprised of boria with silica and titania added to increase viscosity and reduce volatility. Lastly an outer SiC or Si₃N₄ coating, denser than the first inner coating, is applied.

Above 1700ºC, a different 4-layer method may be used. The outermost layer on the composite body is a refractory oxide. Underneath the oxide is silica, which is a crack sealant and oxygen barrier. Another refractory oxide layer beneath the silica layer acts as a barrier to reactivity between the silica layer and a refractory carbide layer applied directly to the C/C substrate.

Using a ceramic matrix rather than a carbon matrix is another way to protect carbon fiber from oxidation. However, matrix cracking still provides a route of ingress for oxygen to attack the carbon fiber. Matrix cracking can result from mechanical or thermal stress. Thermal stresses arise from mismatches to the coefficient of thermal expansion (CTE) between the carbon fiber and ceramic matrix. Given the low CTE of graphite in the “a”
direction, much less than $1 \times 10^{-6}$ K$^{-1}$, and the preferential orientation of layer plane structures in carbon fiber, the CTE of carbon fibers along their axis is substantially lower than most materials which might comprise a ceramic matrix. For example, the CTE of silicon carbide averages about $4.3 \times 10^{-6}$ K$^{-1}$ from 0°C to 1000°C.\textsuperscript{44} A SiC matrix will typically be processed into the fiber preform at high temperatures of 1000°C or more. Significant tensile thermal stress may develop in the matrix along the fiber direction as the composite cools from its fabrication temperature because contraction of the matrix is constrained by the presence of the carbon fibers. The stress can be enough to cause a SiC matrix to crack. 2-D or 3-D composites using woven fiber will have more complicated thermal stress fields than a 1-D composite, but the issue of thermal stress induced microcracking remains. It is imperative to obstruct oxygen ingress through matrix microcracks in carbon fiber reinforced CMC’s

Lamouroux et. al.\textsuperscript{17} addressed the issue of matrix microcracking in carbon fiber reinforced CMC’s with a multicomponent and multilayer matrix. The CMC’s consisted of a carbon interface coating on the carbon fibers followed by alternating and progressively thickening layers of SiC and $B_{13}C_2$ separated by a 100 nm carbon coating. This accomplished several objectives. Matrix cracks deviated at the carbon interfaces forcing a circuitous path for the ingress of oxygen. Oxygen was forced to move along the carbon layers, a pathway which was readily closed by the presence of silica and boria oxidation products of SiC and boron carbide. Oxidation protection provided by the oxidation of boron carbide and silicon carbide occurs at differing temperature ranges so the incorporation of both materials extended the range of protection to the fiber. The French
firm, Snecma (now Safran Aircraft Engines), commercially produces a carbon fiber reinforced CMC based on the structure described by Lamouroux. Snecma also manufactures a carbon fiber reinforced silicon carbide CMC which uses an outer coating to improve oxidation resistance.

1.3 HYDROGEN STORAGE AND SYNTHETIC FUELS FROM CO/CO₂ FEEDSTOCKS

Investigations into practices and technologies capable of diversifying the resources used to manufacture energy products are motivated by environmental, economic, logistical and availability considerations. There are a number of means at various stages of implementation, from the laboratory bench to full commercial operation, that use reactivity in the CO₂/CO/H₂/H₂O system to produce synthetic hydrocarbon fuels, oils, waxes, alcohols, ethers and other hydrocarbon products. The Fischer-Tropsch synthesis, reacting CO and H₂, is robust, producing about 2% of the worldwide fuel supply.⁴⁵ Considerable efforts have also been made to develop systems that effectively use hydrogen gas as a fuel for transportation fuel cells because hydrogen is readily producible from a wide variety of resources.

Using reactivity in the CO₂/CO/H₂/H₂O system to produce hydrocarbons and adopting the use of hydrogen as a fuel have reciprocal drawbacks and benefits. The challenges associated with exploiting reactivity in the CO₂/CO/H₂/H₂O system relate to fabrication of the fuel products, while means of their delivery, storage and use are well entrenched into the existing fuels infrastructure. The challenges associated with using hydrogen gas as a fuel relate to delivery and storage of the fuel, while vigorous means of
producing H2 are known. In order to advance the goal of diversifying the resources used to manufacture energy products, this study evaluates the hydrogenation of CO\textsubscript{2}(g) from a CO\textsubscript{2}/H\textsubscript{2} mixture using a baseline Fischer-Tropsch type heterogeneous catalyst, and characterizes a means of storing (and releasing) hydrogen chemically using the compound ammonia borane (H\textsubscript{3}NBH\textsubscript{3}).

1.3.1 The CO\textsubscript{2}/CO/H\textsubscript{2}/H\textsubscript{2}O system

The primary reactions of practical consequence towards the synthesis of hydrocarbons from the CO\textsubscript{2}/CO/H\textsubscript{2}/H\textsubscript{2}O system are given below. Alcohols, ethers and other oxygenated hydrocarbons are also potential products for the Fischer-Tropsch (FT) reactions of Eq.1.6 but just the alkane products are given for brevity.

The Fischer-Tropsch Synthesis (FT)
\[ n\text{CO}(g) + (2n+1)\text{H}_2(g) \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}(g) \]  
\[ \Delta H^\circ_{298} = -206 \text{ kJ/mol (for } n=1) \]  

The Reverse Water-Gas-Shift Reaction (RWGS)
\[ \text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{CO}(g) + \text{H}_2\text{O}(g) \]  
\[ \Delta H^\circ_{298} = 41.1 \text{ kJ/mol} \]

The Methanol Synthesis
\[ \text{CO}_2(g) + 3\text{H}_2(g) \rightarrow \text{H}_3\text{COH}(g) + \text{H}_2\text{O}(g) \]  
\[ \Delta H^\circ_{298} = -53.3 \text{ kJ/mol} \]

The Sabatier Reaction
\[ \text{CO}_2(g) + 4\text{H}_2(g) \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}(g) \]  
\[ \Delta H^\circ_{298} = -166 \text{ kJ/mol} \]

Thermodynamically Coupled Splitting (TCS)
\[ \text{CO}_2(g) + \text{H}_2\text{O}(g) \xrightarrow{\Delta \text{ couple}} \text{CO}(g) + \text{H}_2(g) + \text{O}_2(g) \]  
\[ \Delta H^\circ_{298} = 525 \text{ kJ/mol} \]
The manner in which these reactions integrate or could potentially integrate into a fuels infrastructure is diagrammed in Figure 1.5. The reverse water-gas shift (RWGS) and thermodynamically coupled splitting (TCS) reactions in Eq. 1.7 and Eq. 1.10 are both methods of producing syngas. Syngas is a mixture of CO(g) and H_2(g) that can be used, when appropriately proportionated, as the feedstock for the Fischer-Tropsch reaction of Eq. 1.6 to produce hydrocarbons. TCS reactions between CO_2 and H_2O are highly non-spontaneous and require thermodynamic coupling with another spontaneous process. Thermolysis, thermochemical cycles, electrolysis and photoelectrolysis methods are among the possible means of splitting CO_2 and H_2O to CO and H_2. Currently, coal and natural gas are the nearly exclusive sources of syngas.

Figure 1.5 Means by which activity in the CO_2/CO/H_2/H_2O system may be integrated into a fuels infrastructure. Adapted from ⁴⁶.
Carbon dioxide is an abundant resource which, in theory, can be collected from the atmosphere by sorbents or captured from point sources. Eq. 1.7, Eq. 1.8, and Eq. 1.9 illustrate that CO$_2$ can be converted to methane, methanol or syngas through reaction with hydrogen. This study outlines the CO$_2$ conversion reactions involving CO$_2$/H$_2$ mixtures at variable temperatures, pressures, and flow rates over a baseline Fischer-Tropsch alumina supported cobalt catalyst. The evolution of structure in the catalyst is also examined. Selectivity towards C2+ hydrocarbons is not typically reported from CO$_2$/H$_2$ mixtures but was found to occur appreciably on this catalyst at some conditions of temperature and pressure. From the outline of activity presented here, regions of conditions can be specified for more targeted testing, and some initial postulates about mechanism can be put forward.

1.3.2 The Fischer-Tropsch Process

An understanding of some of what is known about the FT process may help to explain catalytic behavior observed in the CO$_2$/H$_2$ reactor examined in this work under conditions similar to an FT reaction with an FT type catalyst. Interest in and development of FT technology has waxed and waned with the price of petroleum and extent of oil reserves in the century since discovery of the reaction in the early 20$^{th}$ century.$^{47,48}$ Most commercial FT operations currently use syngas sourced from the steam reforming or dry reforming of coal or natural gas. The decision to convert natural gas or coal deposits to hydrocarbons via an FT reaction has been motivated in part by difficulties transporting coal and natural gas resources away from remote locations with little local demand.
The FT reaction is carried out using syngas with an H\textsubscript{2}:CO ratio of about 2:1, corresponding to the stoichiometry of the reaction with alkane products. The reaction proceeds in the presence of a heterogeneous catalyst, at temperatures between 475 K and 625 K, and up to several tens of bars of pressure. Longer hydrocarbon chains are usually favored at low temperature. The only materials that have been found to have any appreciable FT activity are iron, cobalt, nickel and ruthenium. Only iron and cobalt have been adopted for commercial use. Ru is the most active FT catalyst but its extreme scarcity and high cost make it unreasonable to use outside of lab scale experimental settings. Nickel forms volatile carbonyls which deactivate the catalyst and contribute to loss of the active phase. Nickel also results in high methane yields. Cobalt is more expensive than iron, but iron deactivates more readily.

Typical FT catalysts are comprised of an active metal supported on a metal oxide. A typical support might consist of a high surface area powder of alumina, silica, or titania. To fabricate the catalyst, a metal nitrate may be precipitated onto the support, then oxidized at elevated temperature to a metal oxide followed by reduction to the metal in hydrogen. Structural promoters such as the oxides of Zr or La (from co-precipitated nitrates) affect the structure of the metal phase due to their proximity to the oxide of the active metal phase before reduction in hydrogen. Noble metal promotors, usually less than 5 wt.% , increase the reduction behavior of the oxide of the active metal by spillover of dissociatively adsorbed H* from the noble metal to the oxide of the active phase. An alkali promoter at levels as low as 0.01 wt.% changes the bonding behavior of the active metal in a manner that increases selectivity away from methane and towards higher hydrocarbons. Alkali
oxide promoters seem to work by increasing adsorption of CO at the expense of hydrogen due to the electropositive nature of the alkali promoter. In an examination of mechanism below, we see that this preferential adsorption limits the rate of methanation, increasing selectivity towards higher hydrocarbons.

There is still some debate about aspects of the mechanism of the Fischer-Tropsch reaction. In particular, whether the first hydrogenation step occurs before or after C-O bond scission is debated and mechanistic details probably vary on different surfaces. The reaction proceeds through a CH* intermediate as in Figure 1.6, where the asterisk indicates that the species it is associated with is bonded to a surface in some manner. The CH* intermediate is stepwise hydrogenated to CH2* and CH3* intermediates in reactions 1 and 2. CH3* can initiate a chain with CH2* as in reaction 5, and CH2* can be incorporated into a chain as in reaction 4. CH3* can also hydrogenate to methane as in reaction 3. Selectivity towards higher hydrocarbons by the reactions 4 and 5, and away from the methanation in reaction 3 is achieved by a principle of selective inhibition. The methane formation rate is selectively inhibited by increased CO partial pressures due to increased occupation of H* sites by CO*. The probability that CH2* or CH3* will incorporate into a chain rather than hydrogenate is increased at higher CO partial pressures due to lower coverages of H*. This principal is also responsible for the effects of alkali promoted catalysts mentioned above. The effect of the alkali is to increase the extent of CO adsorption at the expense of H adsorption thereby increasing selectivity towards higher hydrocarbons.
1.3.3 Reactions in the CO$_2$ and H$_2$ system

Mixtures of CO$_2$ and H$_2$ may typically be reacted to form methanol, methane or CO. The extent to which each of these reactions occurs depends on the catalyst, temperature and pressure. The precious metals Pt$^{56}$, Pd$^{57}$, Rh$^{58}$ and Au$^{59}$ the non-precious metals Cu$^{60}$, Fe$^{61}$ and Ni$^{62}$ and molybdenum carbide$^{63}$ have been found to be active towards RWGS, CO forming activity. This is an important reaction because it can generate syngas for higher hydrocarbon synthesis by the Fischer-Tropsch reaction. Cu is active and the most studied RWGS catalysts.$^{64}$ Selectivity towards CO is primarily determined by the binding energy of the surface adsorbed CO* that forms from the dissociation of CO$_2^*$.$^{56,65}$ A weakly bound CO* will tend to desorb before hydrogenating. Metal/support interfaces which weakly bind CO* yield higher selectivity toward CO. The binding energy of CO* at the metal/support interface is support dependent. ZnO, MgO, Nb$_2$O$_5$, ZrO$_2$, TiO$_2$, CeO, and Al$_2$O$_3$ are among the supports that have been investigated.$^{64}$ CO yields are limited by thermodynamics.$^{62}$ CO yields become thermodynamically favorable over about 600$^\circ$C. Below this temperature the thermodynamically favored CO$_2$ conversion product is

---

**Figure 1.6** Chain growth, chain initiation, and methanation pathways in the Fischer-Tropsch reaction (H* omitted for clarity).
methane. RWGS reactions carried out near 300°C will typically have CO₂ conversions around 5% while reactions carried out near 600°C will have conversions near 50%.\textsuperscript{66} RWGS reactions may be carried out at temperatures exceeding 900°C in order to avoid coke formation which becomes thermodynamically unfavorable above this temperature.\textsuperscript{62}

Cu,\textsuperscript{67} Pd,\textsuperscript{68} and Au\textsuperscript{69} have been found to be active towards methanol synthesis from CO₂/H₂ mixtures. A major difference between catalysts used for methanol synthesis and the RWGS reaction is thought to be the strength of the bonding of intermediate CO* species. CO* needs to bond more strongly to a surface to prevent desorption to CO\textsubscript{(g)} and undergo hydrogenation to HCO*, however not so strongly that the active sites are poisoned.\textsuperscript{64,65,69} In practice, CO and methanol are usually both obtained. A Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst is used industrially to prepare methanol from CO₂/CO/H₂ syngas. Pressures from 50-100 bar and temperatures between 250°C and 300°C are used.\textsuperscript{66,67} Elevated pressures are used because this drives the reaction towards the products according to Le Chatelier’s principal because there are a fewer number product molecules than reactant molecules (in RWGS chemistry, the number of reactants and products are the same so that conversion is less dependent on pressure). The understanding and basis for optimization of methanol catalysts is largely phenomenological, but an emerging trend is the requirement for the existence of non-planar surface features such as steps or the interface of a metal grouping on the oxide support, and the presence of partially reduced metal oxide in atomically close proximity to the metal. Reduced metal sites stabilize the oxygenate intermediates HCO*, H₂CO*, and H₃CO*. The reducibility of some oxides such as ZnO, ZrO\textsubscript{2}, and CeO\textsubscript{2} is large enough to allow partial reduction at reaction conditions but not large enough for full
reduction to the metal and subsequent bulk alloying with copper. Zn substitutions at stepped sites on copper lead to high methanol activity. Likewise when copper is supported on zirconia, the methanol selectivity and activity is increased compared to when copper is supported on titania because the zirconia is more reducible than the titania and stabilizes oxygenated intermediates adsorbed at the metal/oxide interface. In another study, Ce$^{3+}$ sites from a partially reduced CeO$_2$ support at the metal/oxide interface were found to enhance CO$_2$ adsorption which lead to higher conversion rates.

In comparison to the RWGS and methanol synthesis reactions, the formation of methane from CO$_2$ in the Sabatier reaction is not as widely studied. Yields are thermodynamically limited at high temperature (above 500°C – 600°C) and kinetically limited at low temperature. Conditions similar to the methanol synthesis are used; temperatures below 500°C and up to several tens of bars of pressure (to drive the reaction towards products according to Le Chatelier’s principal). Methane is obtained by using different metal based catalysts than what is used for methanol synthesis. Ni and Ru based catalysts supported on metal oxides have been the most widely studied. CO or methanol evolution is typically observed in parallel to methane selectivity. Methane selectivity is shown to be affected by the loading of the metallic phase and the synergistic presence of more than one type of metal. The possible pathways that lead to methane formation pass through one or more of the intermediates represented by the formula H$_x$COH$_y$* where the value of y may be 0 or 1, and the value of x may be 0, 1, 2 or 3. At some point before hydrogenation to methanol, the intermediate undergoes C-O bond scission leading to a CH$_x$* intermediate which is hydrogenated to methane. Promotion of C-O bond scission
over the hydrogenation of this intermediation to methanol is a critical factor for methane catalysts compared to methanol catalysts.

Conversions to hydrocarbons above methane (C2+) is not frequently observed or reported from CO₂/H₂ feeds. In the research reported here using a baseline Co/Al₂O₃ Fischer-Tropsch type catalyst, appreciable C2+ yield was observed at some conditions of temperature and pressure. A Co based catalyst was chosen because it is FT active and if CH* and/or CH₂* intermediates are involved in methanation, then C2+ hydrocarbon chain initiation and lengthening might occur according to the FT mechanism of Figure 1.6. In the FT reaction, Co is more active than Fe, and Ni has a high selectivity toward methane and it was judged that C2+ yields might be most likely to be observed from Co.

### 1.3.4 Chemical Hydrogen Storage

The U.S. Department of Energy has issued targets for performance metrics of total on-board hydrogen storage systems. This has directed research towards chemical hydrogen storage systems because some appear able to meet volumetric hydrogen capacity and volumetric energy density targets. In Tables 1.3 and 1.4, hydrogen capacity and energy density targets are compared to hydrogen based and hydrocarbon based fuels. The targets are specified to include the entire on-board system that is used to store and deliver the hydrogen to a fuel cell, so the capacity of the chemical component of any system must exceed these targets to account for mass and bulk of components used for storage and delivery. Volumetric hydrogen capacity and volumetric energy density targets are not met by physically compressing, or cryogenically condensing hydrogen to a liquid, however the

[32]
compound ammonia borane (AB), \( \text{H}_3\text{N-BH}_3 \), meets these targets, and the facile release of hydrogen from ammonia borane above its melting temperature of about 110°C is examined extensively in this research.

<table>
<thead>
<tr>
<th>System or Fuel</th>
<th>Volumetric Hydrogen Density (g/L)</th>
<th>Gravimetric Hydrogen Density (wt.% Hydrogen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE total system level target for on-board hydrogen storage</td>
<td>81</td>
<td>9</td>
</tr>
<tr>
<td>163 bar ( \text{H}_2 )</td>
<td>12</td>
<td>100</td>
</tr>
<tr>
<td>700 bar ( \text{H}_2 )</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>Liquified cryogenic ( \text{H}_2 ) at 1 bar</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>Neat ammonia borane (3 mol equivalents ( \text{H}_2 ) in AB compact at 100% theoretical density)</td>
<td>147.3</td>
<td>19.6</td>
</tr>
</tbody>
</table>

**Table 1.3** Volumetric and gravimetric hydrogen capacity of various systems.

<table>
<thead>
<tr>
<th>System or Fuel</th>
<th>Volumetric Energy Density (kJ/L)</th>
<th>Gravimetric Energy Density (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE total system level target for on-board hydrogen storage</td>
<td>9,720</td>
<td>10,800</td>
</tr>
<tr>
<td>Gasoline</td>
<td>31,834</td>
<td>44,288</td>
</tr>
<tr>
<td>Diesel</td>
<td>35,848</td>
<td>42,748</td>
</tr>
<tr>
<td>Methanol</td>
<td>15,973</td>
<td>20,201</td>
</tr>
<tr>
<td>Ethanol</td>
<td>21,296</td>
<td>26,934</td>
</tr>
<tr>
<td>Liquified propane</td>
<td>23,506</td>
<td>46,716</td>
</tr>
<tr>
<td>163 bar compressed natural gas</td>
<td>5,625</td>
<td>42,682</td>
</tr>
<tr>
<td>163 bar ( \text{H}_2 )</td>
<td>1,425</td>
<td>{ \text{108,020} }</td>
</tr>
<tr>
<td>700 bar ( \text{H}_2 )</td>
<td>4,750</td>
<td></td>
</tr>
<tr>
<td>Liquified cryogenic ( \text{H}_2 ) at 1 bar</td>
<td>8,510</td>
<td></td>
</tr>
<tr>
<td>Neat ammonia borane (LHV of 3 mol equivalents ( \text{H}_2 ) from AB compact at 100% theoretical density)</td>
<td>16,793</td>
<td>114,238</td>
</tr>
</tbody>
</table>

**Table 1.4** Volumetric and gravimetric energy density of various systems.
Given that ammonia borane has among the highest hydrogen storage capacity of any material, we also see in Table 1.4 the tremendous advantage of using liquid hydrocarbons as a transportation fuel in terms of volumetric energy density. Developing means of producing hydrocarbons from CO₂/CO/H₂/H₂O feeds might ultimately be a more effective means of diversifying fuels production than a widespread adoption of hydrogen fuel because the volumetric energy density that can be obtained from hydrocarbons is inherently greater than what can be obtained from hydrogen. Both avenues merit investigation due to their potential for widespread and niche applications.

A number of chemical hydrogen storage schemes have been researched. Hydrogen can be released rapidly from imidazole compounds such as 1,3-dimethylhydrobenzimidazole through reaction with a weak acid in an organic solvent and in the presence of a divided platinum catalyst. A benzimidazole salt is formed. The hydrogen release is facile but only quantities near 1 wt. % have been obtained.

Magnesium methoxide evolves H₂(g) and CO₂(g) in the presence of water vapor. A composite system of Mg(OCH₃)₂ and MgO evolves hydrogen and captures CO₂ forming magnesium carbonate according to:

\[
\text{Mg(OCH₃)}₂(\text{s}) + \text{MgO}(\text{s}) + 3\text{H}_₂\text{O}(\text{g}) \rightarrow 2\text{Mg(CO}_₃\text{)}(\text{s}) + 6\text{H}_₂(\text{g}).
\]

Since the independent steps of H₂ evolution and CO₂ capture are respectively exothermic and endothermic, investigators sought to leverage this into a near thermoneutral hydrogen release and uptake process. However, the magnitude of heat adsorption from CO₂ capture is much greater than the magnitude of heat evolution, the gravimetric
hydrogen capacity of the system is only 1.1 wt. %, and the release temperature is over 200°C.

Sodium borohydride, NaBH₄ (SBH) is stable in aqueous solution. By passing an SBH solution over a catalyst bed, pure hydrogen is released via hydrolysis and the borohydride is converted to sodium metaborate (NaB(OH)₄).⁷⁶

\[
\text{NaBH}_4(\text{aq}) + 4\text{H}_2\text{O}(l) \rightarrow \text{NaB(OH)}_4(\text{aq}) + 4\text{H}_2(\text{g})
\]

At room temperature the solubility limit of SBH in water is 30 wt. % corresponding to 6.5 wt. % hydrogen. An experimental car using the aqueous storage and hydrolytic release of hydrogen from SBH was developed and road tested by DaimlerChrysler.⁷⁷ In order to maximize the volumetric density of the hydrogen storage system, a movable bladder is required to adjust to changing volumes of liquid in the supply and collection tanks during operation. The possibility of precipitation of the SBH and sodium metaborate, and the use of large amounts of water on-board a vehicle are problematic.⁷⁸ Initial reports of an economical electrochemical method of recycling sodium metaborate into BSH have not been able to be reproduced.⁷⁷ Hydrolytic hydrogen release from metal polyhedral boranes occurs similarly to the process involving SBH, and similar concerns likewise occur.⁷⁷ Hydrolytic chemical hydrogen storage systems are not likely to be practical for transportation systems, but may be so for applications with less demanding criteria.

Nanoparticulate silicon clathrates were investigated.⁷⁹ An SiH₂ stoichiometry corresponds to a 6.5 wt. % hydrogen storage capacity. The largest hydrogen content that could be obtained by these investigators was 4.5 wt. % at a desorption temperature of 180°C.⁷⁹ Other systems that have been investigated as hydrogen storage materials include
metal hydrides, complex hydrides, and sorbents such as carbon nanotubes, inorganic nanotubes, and metal-organic frameworks.

A specific long-term goal of this research is to produce a fuel element that contains solid reactants for the generation of H₂ fuel. Under development is the use of ammonia borane as a hydrogen source. The ammonia borane is to be held in a housing where electrical leads are used to ignite a small pyrotechnic charge which initiates a self-propagating thermal decomposition reaction throughout the fuel element, releasing the hydrogen. When a number of these elements are brought into a contained assembly, the overall rate of hydrogen release can be controlled by initiating each element individually. Such an arrangement addresses the issue of very slow hydrogen evolution from ammonia borane below its melting point at about 110°C and rapid hydrogen evolution above its melting point. It is observed that roughly 2 mole equivalents of hydrogen may be evolved within seconds upon exposure of AB to temperatures between about 150°C and 200°C. As will be discussed in detail, hydrogen is released along with impurities at two low temperature steps initiating at about 110°C and 130°C and in a high temperature step above 1000°C.

1.4 The Adsorption of CO₂ on Specific OMS-2 Surfaces

The interaction between carbon dioxide and exterior framework surfaces of the cryptomelane type manganese oxide octahedral molecular sieve (OMS-2) will be examined using synchrotron based soft X-Ray photoelectron spectroscopy (sXPS). The surface specificity will be achieved using a crystallographically oriented thin film of OMS-2 on a
strontium titanate (STO) single crystal surface that excludes participation of tunnel sites in the analysis. In addition to being of fundamental interest, the manner of CO$_2$ adsorption to the OMS-2 surface has implications in several areas directly or indirectly related to energy sector applications.

Iron doped OMS-2, and OMS-2 supported iron have been observed to act as CO$_2$ hydrogenation catalysts towards CO and light hydrocarbons with selectivities towards C2-C6 hydrocarbons as high as 68%. A possible intermediate species proposed for metal oxide supported metal catalysts that promote CO$_2$ conversion is a bent, and therefore activated, CO$_2$ adsorbate on the metal oxide which reacts with H* spillover from the adsorption of molecular hydrogen on the supported metallic phase. CO$_2$ has been demonstrated to be a mild oxidant that can replenish the oxygen depleted surfaces of OMS-2 that occur during the dehydrogenation of ethane to ethene at 800°C, without oxidizing the reactant or product hydrocarbon. OMS-2 may have emissions control applications. OMS-2 may be viable as an effective low cost and low temperature carbon monoxide oxidation catalyst. Surface specific determinations concerning the manner in which the CO$_2$ product binds to OMS-2 could be useful in developing more effective variants of the material or in explaining observed trends in behavior of the different variants. OMS-2 has also been proposed as a catalyst for the low temperature total oxidation of volatile organic compounds to carbon dioxide.

The presence of acid sites or base sites on a heterogeneous catalyst surface is often a primary factor determining the reactivity and selectivity for a given set of reactants. Often however, acidity/basicity is less determinative than other factors. In either case, a
determination about the influence of acidity and basicity is largely made from the correlation, or lack thereof, between activity and selectivity with the manner of desorption of an acidic or basic probe molecule, usually as determined by temperature programmed desorption analysis.

The concern here is to fundamentally investigate the manner of binding between carbon dioxide and specific surfaces of OMS-2 to determine the Lewis acid and Lewis base character of the molecule towards these surfaces. CO$_2$ is often used as an acidic probe to determine the basicity of a surface in temperature programmed desorption studies.$^{86,88-93}$ However, as will be discussed, it is reasonable to expect that CO$_2$ may behave as a Lewis base, Lewis acid or both at the same time towards any given surface.$^{92}$ This analysis will determine the validity of CO$_2$ as a probe for surface basicity on the OMS-2 surfaces under examination and identify which surface species of the material are involved in electron transfer.
CHAPTER 2

Development of a Compliant BN Interface Coating for Carbon Fiber Reinforced CMC’s

2.1 INTRODUCTION

This research proceeds from a preliminary observation that carbon fiber reinforced SiC CMC’s with a BN interface coating (C/BN/SiC) exhibited very weak and brittle behavior when these composites were fabricated using conditions\textsuperscript{94,95} that have produced toughened SiC/BN/SiC composites. Specifically, a 100 nm BN coating applied to Toray T300 carbon fiber by low pressure chemical vapor deposition (CVD) at 1 torr and 800°C from BCl\textsubscript{3} and NH\textsubscript{3} precursors yielded very brittle composites after the chemical vapor infiltration (CVI) of a SiC matrix from methyltrichlorosilane. This investigation seeks to identify processing parameters that result in toughened C/BN/SiC composites and address reasons for toughening or lack thereof.

Possible causes of weak and brittle behavior that will be distinguished in this study include a strength degrading chemical attack to the fibers during the CVD-BN or CVI-SiC fabrication steps, bulk interactions with the carbon fiber that result in undesirable phases such as boron or a boron carbide, and interactions with fiber surface functionalities that result in a poorly compliant interface coating. In this latter case, reactive surface functionalities that may occur and cause strong bonding between the fiber and the BN are oxygen or nitrogen containing functional groups,\textsuperscript{96} defect sites, and reactive “edge” carbon
surfaces.\textsuperscript{33,42} Edge carbons on the surface of a graphitic structure are distinguished from basal plane surface carbons within a surface graphene layer.

In order to process the T300 carbon fiber into toughened SiC matrix composites, the approach evaluated, and which was ultimately successful, was to subject the fiber to heat treatments in argon to temperatures up to 1600$^\circ$C before the CVD-BN step. In the event that brittle behavior resulted from interactions restricted to carbon fiber surface regions, heat treatments could potentially rearrange the fiber surface to contain less edge structure, heal defects, and evolve off reactive surface functionalities. Since carbon fibers which have experienced greater temperatures during their manufacture will typically have a lower surface edge carbon content,\textsuperscript{33} heat treatments performed here reasonably have the same effect.

Within the boron nitride CVD reactor, any number of intermediate species could potentially react with carbon and lead to strength loss or poor interface compliance. At a minimum, the compounds intended to comprise a CMC should not be reactive in bulk at processing or use temperatures. In the C/BN/SiC composite of interest here, the combinations that must be stable are the C/BN interaction and the BN/SiC, interaction. C and BN might react according to Eq. 2.1 while BN might react with SiC according to Eq. 2.2.

$$C_{(s)} + 4BN_{(s)} \rightarrow B_4C_{(s)} + 2N_{2(s)} \quad \text{Eq. 2.1}$$

$$3SiC_{(s)} + 4BN_{(s)} \rightarrow Si_3N_4_{(s)} + B_4C_{(s)} + 2C_{(s)} \quad \text{Eq. 2.2}$$
B-C-N and Si-B-C-N phases exist but thermodynamic and compositional information on them is not as reliable or readily available. The Gibbs free energy change of Eq. 2.1 & Eq. 2.2, calculated from JANAF thermochemical data, is large and positive across the temperature range of interest as plotted in Figure 2.1. The occurrence of these reactions is therefore not expected during processing of the BN interface or the SiC matrix at 800°C and 1050°C respectively. However these calculations refer to bulk behavior and do not account for surface reactivity between two contacting components which might be an important factor in regards to interface compliance.

![Figure 2.1](image)

**Figure 2.1** Gibbs free energy change for (A) interface-matrix and (B) interface-fiber chemical interactions.
2.2 EXPERIMENTAL

2.2.1 Materials

PAN derived T300 type carbon fiber in a plain weave was obtained from Toray. The fabric was woven from 3K tows (3000 filaments per tow). The filament diameter value given by Toray was 7 μm. All gasses used for heat treatments, BN chemical vapor deposition, and SiC chemical vapor infiltration were obtained from Airgas. The Ar, N₂, and H₂ gasses were of Ultra High Purity grade (99.999%). The NH₃ gas was Anhydrous grade (99.99%) and the BCl₃ was Chemically Pure grade (99.9%). Air was Ultra-Zero grade. Methyltrichlorosilane (MTS) (99%) liquid was obtained from Sigma-Aldrich.

2.2.2 Composite Fabrication

1-D, unidirectional, single strand, composites were examined at this stage in order to minimize the introduction of variables associated with fabricating 2-D composites. However, 2-D composites must ultimately be fabricated to best establish the practicability of the BN interface coating. In order for the behavior of the 1-D composites to be as predictive as possible towards the behavior of a 2-D system, the CVD-BN step was carried out on woven fiber with dimensions that would be used to fabricate a 2-D layup about 7 inches in width. This necessitates the use of a low-pressure CVD reaction to achieve coating uniformity and a reactor tube of sufficient diameter to accommodate the fabric.

Sections of woven carbon fiber measuring 7 inches along the warp direction, and 21 inches along the weft direction were cut from the weave and ramped at 2°C/min in flowing argon to temperatures of 1000°C, 1200°C 1300°C, 1400°C, and 1600°C for a 4
hour hold in an alumina tube. The as-received and heat-treated fibers are given the designations $C_{AR}$, $C_{1000}$, $C_{1200}$, $C_{1300}$, $C_{1400}$, and $C_{1600}$ respectively.

Boron nitride was deposited by low pressure CVD onto the as-received and variously heat-treated woven carbon fiber at 1 torr and 800°C in a fused silica tube. The N$_2$(g), NH$_3$(g), and BCl$_3$(g) gas flow rates were 400, 500, and 125 standard cubic centimeters per minute (sccm) respectively.$^{94,95}$ The deposition time was 60 minutes. The 4:1 NH$_3$:BCl$_3$ ratio corresponds to the stoichiometry of the reaction

\[
4\text{NH}_3(g) + \text{BCl}_3(g) \rightarrow \text{BN}(s) + 4\text{NH}_4\text{Cl}(s).
\]

A diagram of the hot walled reactor used to deposit BN is depicted in Figure 2.2. An 11 inch inner diameter fused silica tube was lined with a graphite insert tube and capped at both ends by a vacuum flange plate. Gases were delivered and exhausted through fittings joined to the plates. The gas flow was controlled by MKS mass flow controllers (MFCs) interfaced to an MKS 647C readout. The BCl$_3$(g) and N$_2$(g) were pre-mixed into the same delivery tubing. An alumina injection tube was used to deliver the BCl$_3$(g) into the hot zone of the furnace to prevent formation of the BCl$_3$-NH$_3$ adduct in the cool portion of the tube outside the furnace. The carbon fiber weave was wrapped around a cylindrical graphite mandrel in a single layer and fixed in place using carbon cordage. The 7 inch warp direction of the fabric was aligned with the cylindrical axis. The mandrel had an open construction so gases could diffuse into the weave from interior and exterior directions. The mandrel was rotated at 8 revolutions per minute along its cylindrical axis by an electric
motor acting on the central shaft via a mechanical feedthrough in the front-end vacuum flange plate.

Figure 2.2 Diagram of the low pressure chemical vapor deposition reactor for boron nitride.

The system was warmed to deposition temperature at 1 torr under flowing nitrogen and ammonia after establishing a base pressure of 5 mtorr and leak checking. The deposition was initiated and terminated by switching the BCl\(_3\) flow on and off. After flowing ammonia for an additional 10 minutes to react with any remaining BCl\(_3\) at the end of the reaction, the furnace was allowed to cool under flowing nitrogen.

Figure 2.3 Diagram of the chemical vapor infiltration reactor for silicon carbide
Coated tows along the warp direction were extracted from the weave. A silicon carbide matrix was applied to these tows by chemical vapor infiltration (CVI) from methyltrichlorosilane (MTS) entrained in flowing $\text{H}_2(g)$ at 1050°C and atmospheric pressure in order to fabricate unidirectional single strand composites. The CVI-SiC reactor is depicted in Figure 2.3. $\text{H}_2(g)$ was bubbled through the liquid MTS to carry vapors to the reactor. SiC was formed from the decomposition of the MTS according to the reaction:

$$\text{H}_3\text{CSiCl}_3(g) \xrightarrow{\text{H}_2} \text{SiC}(s) + \text{HCl}(g).$$  \hspace{1cm} \text{Eq. 2.4}

The reaction was initiated and terminated by initiating and bypassing $\text{H}_2(g)$ flow through the MTS bubbler. The reactor was a 1 inch outer diameter fused silica tube, internally lined with graphoil sheet and heated by a tube furnace 17 inches in length. The tows were supported on graphite tooling in the middle of the furnace. The partial pressure of the MTS was approximately equal to its vapor pressure at 20°C, (167 mm Hg) with $\text{H}_2(g)$ comprising the balance of composition. The $\text{H}_2(g)$ flow rate was 150 sccm and the infiltration time was five hours.

### 2.2.3 Characterizations of the Fiber and Composites

The composition and thickness of the coating resulting from the CVD-BN process was experimentally gauged by depth resolved elemental analysis using scanning Auger microscopy (SAM). SAM spectra were obtained between $\text{Ar}^+$ ion sputtering steps that progressively removed material from the surface of the fiber. A Physical Electronics PHI 610 scanning Auger microprobe was used. The spot size analyzed by SAM was about 1μm.
in diameter so information on individual fibers was obtained. Composition to a depth of 500 nm was obtained. A depth profile was obtained for C_{AR}/BN, and C_{1600}/BN systems before and after they had been heat-treated at 1500°C for 4 hours under flowing argon in order to determine phase stability. The energy of the e⁻ beam was 5.0 keV. The e⁻ beam current was 70 nA. The tilt angle was 75°. The Ar⁺ ion beam energy was 4.0 keV. The Ar⁺ ion beam current was 1.0 μA. The area rastered by the Ar⁺ ion beam was 7.5 mm². The confinement of the e⁻ beam was about 1 μm in diameter. The peak intensity for any transition was taken as the difference between the maximum and the minimum of the derivative plot. Atomic percent concentrations were obtained by applying a correction factor to the normalized peak height.

The tensile strengths of the fiber tows were evaluated at points along the processing chain: before heat treatment, after the various heat treatments, after BN deposition on the variously heat-treated fibers, and after heating coated tows at 1050°C or 1500°C. The strength of mini-composites was determined as they were fabricated and after their exposure to air at 1000°C for 12 and 100 hours. Multiple samples of each type of specimen were tested and their strengths averaged. An Instron 1011 mechanical analyzer was used to obtain the tensile data. A 100 lb. load cell was used and calibrated with weight standards. The paper frame method was used to mount the samples into the analyzer grips. The tow or mini-composite was laid across a cardboard frame with a cut out as in Figure 2.4. Epoxy was applied at either end of the paper frame to affix the sample between the frame and an overlaid cardboard square, providing a site for gripping with even force transfer to the specimens. The portions of fiber tows within the cutout window were painted with an
acrylic binder to promote even loading of the fibers. The distance between the grips was 1 inch. The two sides of the paper frame were then cut after gripping so that only the fiber would be strained during the extension. The crosshead speed was 0.05 inches/min. The total cross section of fibers in a tow was calculated assuming 3000 filaments per tow and a circular cross section for each 7 μm diameter fiber. For mini-composite samples, ultimate tensile strength (UTS) and stress vs. cross-head displacement curves were obtained. Optical micrographs of the fracture surfaces were used to measure the cross-sectional area of each composite at the site of fracture.

The effect of the carbon fiber heat treatments on atomic scale structuring was monitored by powder XRD and by a Raman microprobe. Powder XRD patterns were obtained using a Scintag model XDS 1000 diffractometer using CuKα radiation. A glass sample holder was used. The differently treated carbon fibers were finely chopped to a
powder with a razor blade for XRD analysis. The diffraction pattern of chopped C$_{1600}$ fibers was also compared to native unchopped segments of C$_{1600}$ tows laid flat in the sample holder to qualitatively gauge preferential orientation within the fiber. The Raman spectra in the D and G peak region was obtained using a 514 nm laser source focused to a 1 μm spot on single fibers using the microscope optics. The spectra of as-received fibers were compared to selected heat-treated fibers.

FESEM was used to observe structural details of the fibers, the BN fiber coatings, the SiC matrix, and composite tensile fracture surfaces. A Zeiss DSM 982 Gemini with a Schottky emitter and a secondary electron detector was used. The electron beam energy was 2 kV. As-received, heat-treated and BN coated fibers were fractured by razor blade to observe the fiber and the coating in cross section.

TGA, DSC, and TPO-MS experiments in dry air were conducted on heat-treated C$_{1600}$ fibers with and without a CVD-BN coating. The temperature was ramped at 15°C/min from room temperature to 1200°C in each experiment. TGA and DSC data were collected simultaneously in a TA Instruments Q600. About 10 mg of sample was loaded into a weight tared alumina pan and ramped to temperature. TPO-MS experiments were conducted using an MKS Cirrus model residual gas analyzer (RGA) with a 70 ev electron impaction ionization source. Samples (25 mg) were loaded into a 9 mm outer diameter (O.D.) and 7 mm inner diameter (I.D.) quartz tube. Temperature was controlled by a resistively heated tube furnace and a type K thermocouple at the location of the sample. Dry air was delivered through PFA tubing connected to the quartz tube via compression fittings. The vacuum system of the RGA continuously sampled the gasses present at a “T”
in the exit gas line from the quartz tube. The fibers were cut to length in order to be introduced to the sample holders used in each experiment. As a result, the BN coated fibers still contained carbon exposed to air, unprotected by the BN, but less extensively than the neat fibers.

C\textsubscript{1600}/BN/SiC mini-composites were also subjected to air oxidation treatments at 1000\textdegree C for durations of 12 hours and 100 hours. After this exposure the mini-composites were subjected to tensile testing and FESEM imaging of the fracture surface to gauge oxidation resistance.

2.3 Results

2.3.1 C/BN/SiC CMC Tensile Strengths

The data of most immediate interest are the tensile strengths of the mini-composites. The UTS data in Figure 2.5 are for C/BN/SiC composites fabricated from the differently heat-treated types of carbon fiber. Also depicted are the UTS of the C\textsubscript{1600}/BN/SiC composites that had been treated in air at 1000\textdegree C for 12 or 100 hours. C/BN/SiC composites fabricated from T300 carbon fibers heat-treated between 1200\textdegree C and 1600\textdegree C had tensile strengths between 350 and 500 MPa. On the other hand C/BN/SiC composites fabricated from as-received T300 carbon fibers were so extensively weak and brittle that a strength measurement could not be obtained. The slight stresses involved in gripping the composites into the mechanical analyzer consistently and immediately fractured these composites. Fully formed C\textsubscript{1600}/BN/SiC composites that had been
oxidation tested in air at 1000°C for both 12 and 100 hours retained strengths very similar to their as fabricated condition.

Figure 2.5 UTS of C/BN/SiC CMCs as fabricated and after 1000°C air oxidation tests.

(Error bars indicate one standard deviation)

2.3.2 Carbon Fiber Structure and Temperature Induced Changes

The T300 carbon fibers have a crenulated surface. This is observed in the FESEM image of Figure 2.6A where the crenulations are apparent on the fiber surface and in Figures 2.6B and 2.6C at the edge of a razor blade cut cross section. The topology of the material within the razor blade fractured cross-section is more granular than the topology
of the fiber surface. There are no obvious microstructural differences between $C_{AR}$ and $C_{1600}$ in the FESEM images of these fibers.

The XRD peaks of the carbon fiber are broad and overlapping but correspond to the location and relative intensity of the reflections from graphite [Figure 2.7]. Increasing heat treatment temperatures progressively narrowed the FWHM of the (002) peak and shifted the peak position to higher $2\theta$ values [Figure 2.8]. The FWHM of the (002) reflection for $C_{1600}$ is nearly half that of $C_{AR}$. The $2\theta$ peak position shift is appreciable for heat treatments above 1000°C.

![FESEM micrographs of the surface and cross-section of $C_{AR}$ and $C_{1600}$](image)

*Figure 2.6* FESEM micrographs of the surface and cross-section of $C_{AR}$ and $C_{1600}$. 
Figure 2.7 Powder XRD patterns of as-received and heat-treated T300 carbon fiber.

Figure 2.8 (002) peak position and FWHM of the differently treated carbon fibers.
Differences between the XRD patterns of chopped C$_{1600}$ fibers and native unchopped C$_{1600}$ fibers laid flat in the sample holder were observed [Figure 2.9]. The intensity of the (101) peak relative to the (002) and (004) peaks was significantly greater in the XRD pattern of the chopped fibers.

Changes to the Raman spectrum of the carbon fiber occur with sufficient heat treatment. The solid lines in the spectra of Figure 2.10 are a seven-point floating average of the raw data points. The peaks commonly termed as the D and G peaks in graphitic materials are indicated. A distinct D’ on the high wavenumber shoulder of the G is not evident. In this case, the D peak is very broad and overlaps the G peak in the C$_{AR}$ and C$_{800}$ samples so the usual comparison of D/G ratios is an unreliable indicator of disorder.
However it is clear that the width of the D peak is significantly decreased in $C_{1600}$ compared to the cases of $C_{AR}$ and $C_{800}$.

![Raman spectra](image)

**Figure 2.10** Raman spectra of $C_{AR}$, $C_{800}$, and $C_{1600}$. Solid lines are a 7-point floating average.

### 2.3.3 Characterizations of BN Coated Carbon Fibers

The presence and extent of a coating on the woven carbon fiber resulting from the CVD-BN process was quantified by mass changes given in Table 3. Visually the fibers were color banded and there was no visible evidence of powder formation from homogenous nucleation. The weave remained drapable during handling. The mass increase for the $C_{AR}$ fiber was 4.8% and the mass increases for the heat-treated fibers was clustered around 6.5%. The thickness of the coatings determined by FESEM observation [Figure 2.11] was about 50 nm on $C_{AR}$ but was 150 nm on the heat-treated fibers. The increased coating thickness on the heat-treated fibers occurs with an increased mass gain,
however the C\textsubscript{AR} fiber has a 1-2 wt.% sizing which is volatilized off while the fiber is heated to the deposition temperature. Accounting for this, the actual weight increase on the C\textsubscript{AR} is closer to 6%.

<table>
<thead>
<tr>
<th>Fiber Designation</th>
<th>Treatment Temp (celsius)</th>
<th>Fabric Dimension</th>
<th>CVD run time (min)</th>
<th>% Mass Increase</th>
<th>BN Thickness Observed by FESEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{AR}</td>
<td>Not Treated</td>
<td>7&quot; X 21&quot;</td>
<td>60</td>
<td>4.8</td>
<td>~50nm</td>
</tr>
<tr>
<td>C\textsubscript{1200}</td>
<td>1200</td>
<td>7&quot; X 21&quot;</td>
<td>60</td>
<td>6.79</td>
<td>~150nm</td>
</tr>
<tr>
<td>C\textsubscript{1300}</td>
<td>1300</td>
<td>7&quot; X 21&quot;</td>
<td>60</td>
<td>6.35</td>
<td>~150nm</td>
</tr>
<tr>
<td>C\textsubscript{1400}</td>
<td>1400</td>
<td>7&quot; X 21&quot;</td>
<td>60</td>
<td>6.91</td>
<td>~150nm</td>
</tr>
<tr>
<td>C\textsubscript{1600}</td>
<td>1600</td>
<td>7&quot; X 21&quot;</td>
<td>60</td>
<td>6.54</td>
<td>~150nm</td>
</tr>
</tbody>
</table>

**Table 2.1.** Mass increase due to CVD-BN and BN thickness.

The FESEM micrographs of BN coated fibers in Figure 2.11 demonstrate a microstructural change to the BN coating induced by heat treatments. Additional FESEM images in Figure 2.12 of C\textsubscript{AR}/BN and C\textsubscript{1600}/BN are included to more comprehensively demonstrate this change. In the C\textsubscript{AR}/BN system the boundary between the fiber and the coating is difficult to identify [Figures 2.11A and 2.12A-D]. The boundaries on C\textsubscript{1200}/BN, C\textsubscript{1300}/BN, C\textsubscript{1400}/BN, and C\textsubscript{1600}/BN, are sharp and easy to identify [Figures 2.11B-E and 2.12E-H]. The BN coating on the heat-treated fibers tended to decohere and break away from the fiber near the site of the razor blade fracture. On the as-received fibers, the BN coating tended to remain adherent near the site of the razor blade fracture.
Figure 2.11 FESEM of C/BN on differently treat fibers (continued on next page).
Figure 2.11 (Continued from previous page) FESEM of C/BN on differently treated fibers.
Figure 2.12 Multiple FESEM images of $C_{AR}/BN$ and $C_{1600}/BN$
When the surfaces of BN coated fibers are observed via FESEM, the topology of the coating on the as-received and heat-treated fibers is similar [Figure 2.13]. The coating uniformly and evenly covers both types of fiber.

![A](image1.jpg) ![B](image2.jpg)

**Figure 2.13** Surface of BN coated fibers.

The composition of the coating is confirmed to contain equal parts B and N by SAM analysis of C\textsubscript{AR}/BN and C\textsubscript{1600}/BN in Figures 2.14A and 2.14B. A few atom % of oxygen was found in all the samples. The BN thickness observed by the depth profile is about 50 nm greater in C\textsubscript{1600}/BN than C\textsubscript{AR}/BN, consistent with FESEM observations. In an artifact due to surface crenulations, the transition from BN to C appears to occur over a much greater distance than what would be expected from FESEM observations of Figures 2.11 and 2.12. Heat treating the BN coated fibers to 1500°C in flowing argon did not result in any identifiable change to the compositional depth profile. The B:N ratio remained constant though the transition region from BN to carbon in all samples [Figures 2.14A-D].
Figure 2.14 SAM depth profiles of C/BN samples before and after heat treatments in argon at and above CVI-SiC processing temperatures.

The strength of the fibers after different processing steps is charted in Figure 2.15. The average measured tensile strength of the as-received fiber tows was about 2.15 GPa and heat treating the C\textsubscript{AR} fiber had little effect on the strength. The strength of both the as-received and C\textsubscript{1600} fibers were not adversely affected by the CVD-BN process. The C\textsubscript{AR}/BN fiber retained its strength after heating to both 1050\degree C and 1500\degree C in argon, temperatures at and above what is experienced during the CVI-SiC process.
TGA, DSC, and TPO-MS experiments conducted to gauge the oxidation resistance provided by the BN coating evidenced a delayed onset of detectable oxidation for BN coated fibers. Carbon was exposed at the ends of the cut segments in the C$_{1600}$/BN system.

In the TPO-MS experiment [Figure 2.16] using the uncoated C$_{1600}$ fiber, CO$_{2(g)}$ was detectable starting at 650°C. Mirroring the CO$_{2(g)}$ peak was a decrease in the O$_{2(g)}$ content of the flowing air. When coated C$_{1600}$/BN was used, detectable CO$_{2(g)}$ evolution and a dip in the O$_{2(g)}$ levels was delayed by 100°C to a temperature of 750°C. NO$_{(g)}$ evolution occurred from the coated sample at about 950°C.
Figure 2.16 TPO-MS of uncoated (A) and coated (B) carbon fiber in air at a 15°C/min ramp rate

In the TGA and DSC experiments [Figure 2.17] onset of mass loss and the onset of an exothermic peak was also delayed by 100°C for the coated C1600/BN system compared to the uncoated C1600 system. The onset temperatures of these effects were close to those

[62]
measured by TPO-MS. An exothermic bump initiating at 950°C from the coated fiber sample corresponds to the evolution of NO(g) in the TPO-MS experiments. The broad, low temperature, exothermic hump centered around 400°C in both DSC measurements is likely an artifact of the instrument rather than a reflection of physical or chemical change to the sample. The C_{1600}/BN sample retained 35% of its weight in the TGA/DSC experiment. After cooling the oxidized C_{1600}/BN sample, the specimen pan was found to contain intact carbon fibers embedded within a clear hard material.

![Graph](image)

**Figure 2.17** Simultaneous TGA and DSC of uncoated and BN coated C_{1600} carbon fiber in air ramped at 15°C/min.
Figure 2.18  Tensile fracture surfaces of C/BN/SiC mini-composites fabricated from differently heat-treated fiber.
2.3.4 Characterization of C/BN/SiC Composites

As previously mentioned, the composites fabricated from as-received fiber were immeasurably weak and brittle, while composites fabricated from heat-treated fibers had appreciable strengths. The tensile fracture surfaces of the C/BN/SiC mini-composites observed by FESEM changed markedly as a result of the fiber heat treatments. [Figure 2.18] Composites fabricated from the as-received fibers had a smooth, planar fracture surface as in Figure 2.18A. There were no fiber pullout holes or fibers extending from the matrix in these samples. Conversely the C_{1200}/BN/SiC, C_{1300}/BN/SiC, C_{1400}/BN/SiC, and C_{1600}/BN/SiC composites in Figures 2.18B-F had irregular fracture surfaces. Fiber extensions, pull-out holes, cracks perpendicular to the main fracture surface, and the physical detachment of fibers from the matrix are observed. The appearance of these features was significantly more pronounced in the C_{1600}/BN/SiC composites than in composites fabricated from fibers heat-treated to lower temperatures.

A carbon fiber extending from the tensile fracture surface of a C_{1600}/BN/SiC composite is observed in Figure 2.19A and a fiber pull-out hole is observed in Figure 2.19B. Viewing the fracture surface at this level of detail elucidates the microstructure of the composite and the behavior of the component phases. FESEM micrographs of the C_{1600}/BN/SiC composite surface [Figure 2.20] reveal multicracking perpendicular to the fiber direction. The width of the cracks was approximately 300 nm. The tensile stress vs. crosshead displacement curve for a C_{1600}/BN/SiC composite in Figure 2.21 was mostly linear to fracture, but with a number of non-linear, stress relieving events during the extension. A qualitative, but highly illustrative, demonstration of the mechanical
properties of C$_{1600}$BN/SiC involved bending a unidirectional single strand composite by hand to a high degree of flexure multiple times, after which the material returned to its approximate original state [Figure 2.22].

**Figure 2.19** FESEM micrograph at a tensile fracture surfaces detailing the microstructure and behavior of component phases in a C$_{1600}$/BN/SiC composite. **Image A:** (a) SiC matrix fracture surface, (b) carbon fiber extending from fracture surface, (c) 150-200 nm BN fiber coating, (d) fiber-BN debonding, (e) matrix-BN debonding. **Image B:** (a) SiC matrix fracture surface, (b) fiber at base of pull-out hole, (c) BN lining the pull-out hole, (d) fiber-BN debonding.
Figure 2.20 Multicracking of the C/BN/SiC composite surface

Figure 2.21 Tensile stress vs. crosshead displacement curve for a C_{1600}/BN/SiC composite.
2.3.5 Characterizations of Air Oxidized Composites

The C_{1600}BN/SiC mini-composites retained their strength after oxidation in air for 12 and 100 hours at 1000°C [Figure 2.5]. These oxidized composites exhibited tensile stress vs. strain curves with features similar to those of composites obtained prior to the oxidation tests [Figure 2.23]. The curve was mostly linear to failure with several non-linear stress relieving events during the extension. FESEM imaging of the 100-hour air oxidized composite fracture surface [Figure 2.24] also revealed irregular features, fiber
extensions and pull-out holes similar in character and extent to those found in the as-fabricated C_{1600}BN/SiC mini-composites. A color change of the oxidized mini-composite is observed in a photograph in Figure 2.25. A 625 nm outer layer of oxidized SiC matrix at the edge of the fracture surface is observed by FESEM in Figure 2.25.

Figure 2.23 Stress vs. crosshead displacement of a C_{1600}BN/SiC mini-composite after being treated at 1000°C in air for 100 hours.
Figure 2.24 $C_{1600}/\text{BN/SiC}$ tensile fracture surface after air oxidation at $1000^\circ\text{C}$ for 100 hours.

Figure 2.25 Color change of mini-composite due to air oxidation. As fabricated composite (A) and green hued oxidized composite (B).
2.4 DISCUSSION

Features of the fiber, the BN coated fiber, the fully formed composite, and changes caused to these elements by the fiber heat pre-treatments are discussed below. In summary, heat treating T300 carbon fiber prior to the deposition of a boron nitride interface coating resulted in significant changes to the nature of the CVD-BN and consequently to the mechanical behavior of the final composite. Composites fabricated from as-received fibers were immeasurably weak and brittle while composites fabricated from fibers which had been heat pre-treated in argon had tensile strengths between 350 MPa and 500 MPa. The weak and brittle behavior of the C_AR/BN/SiC composites was due to a poorly compliant interface rather than a loss of fiber strength or development of unwanted phases during processing. Heat treating the fibers prior to BN deposition resulted in a compliant interface and toughened composites.

Figure 2.26 625 nm layer of oxidized SiC matrix at the outer edge of the tensile fracture surface due to air oxidation.
2.4.1 Features of the T300 Carbon Fiber

The tensile strength of the T300 carbon fibers in this study was measured at 2175 MPa. This is somewhat less than the value reported by Toray, the manufacturer. There could be several reasons for this, including the performance of tensile tests on tows rather than single fibers, or systematic error in the calculated total cross-sectional area of fibers in a tow resulting from the assumption of a circular cross-section 7 µm in diameter. However, the results are reproducible and valid for comparative purposes. Heat treating the fibers in argon at temperatures up to 1600°C did not result in loss of strength to the fiber, a prerequisite for the methods employed in this study.

Raman spectra and XRD patterns reveal a disordered structure based on graphite with a preferential orientation. The XRD peak positions [Figure 2.7] index to graphite and the peaks in the Raman spectrum [Figure 2.10] are at positions consistent with graphitic materials. Broad XRD peaks are attributable to either small crystallite size or disorder. The shift of the maxima of the (002) 2Θ peak position to higher values of 2Θ on heat treatments in excess of 1000°C [Figure 2.8] indicates that the broadening is at least in part due to disorder, because size broadening does not shift peak position.

The strong and broad D band in the Raman spectrum indicates a significant degree of disorder. The D/G peak intensity ratio in Raman spectra of graphitic materials is often used as a comparative indicator of disorder between different samples because the D band only occurs in the presence of disorder. In this case, the D band overlaps and contributes to the G band in C_{AR} and C_{300} so the D/G ratio is not a good figure of merit. However, the FWHM of these peaks are approximately inversely proportional to the
crystallite size,\textsuperscript{99} often interpreted as an average interdefect distance.\textsuperscript{98} The width of the D band decreases as a result of heat treatment to 1600°C, indicating a relaxation of disorder, consistent with the shift of the (002) peak in the XRD pattern. The fiber structurally reorders above the 800°C BN deposition temperature used in this study.

 Preferential orientation in the fibers was qualitatively observed through differences in the X-Ray diffraction patterns from C\textsubscript{1600} fibers which had been finely chopped into a powder with a razor blade and from continuous C\textsubscript{1600} fiber tows which were laid flat in the sample holder [Figure 2.9]. The relative intensity of the (101) peak in the diffraction pattern of finely chopped C\textsubscript{1600} fibers is increased compared to the relative intensity of the same peak from continuous C\textsubscript{1600} fibers laid flat in the sample holder plane. When fibers are laid with their axis in the sample holder plane, Bragg diffraction can only occur from planes which are parallel to the fiber axis. The random orientations induced by chopping the fiber into a powder allows planes which do not lie parallel to the fiber axis to be represented in Bragg diffraction. Thus, the relative increase of the (101) peak relative to the (002) peak when chopped fibers are examined results from a preferential orientation of graphitic basal planes lying parallel to the fiber axis.

 Whatever structural details were changed by the heat treatments, they were not evident in observations of morphology by FESEM [Figure 2.6]. C\textsubscript{AR} and C\textsubscript{1600} fibers had a cross section that appeared more granular than the fiber surface. This is also evident in the FESEM micrographs of heat-treated fibers coated with BN in Figures 2.11 and 2.12. It is not known if this granularity is truly a reflection of a less contiguous structure within the fiber compared to the skin, or if the granularity is an artifact of fracturing the fiber with
a razor blade. If an interruption to the microstructural pattern within the fiber does occur at the skin, such as a circumferentially oriented sheath that is described in some studies,\textsuperscript{39-41,43} then such a skin microstructure is present with a sub-10 nm thickness in both the as-received and heat-treated fibers. Since atomic scale rearrangement in the bulk due to heat treatment is evident from XRD patterns and Raman spectra, structural rearrangement at the surface during heat treatments is very likely.

### 2.4.2 Features of Boron Nitride Coated Fibers

The presence and amount of a BN coating is first indicated by the weight change to the fibers onto which the deposit was applied. The weight increase of the heat-treated fibers clustered near to 6.5 wt.%. The slightly lower increase of 4.8 wt.% for the as-received fiber is expected due to the presence of a 1-2 wt. % sizing on the fiber that volatilizes off in the CVD reactor prior to initiating deposition. The thickness of the coatings observed by FESEM was greater among the heat-treated fibers and smaller for the as-received fibers. SAM depth profiles also measured a greater coating thickness on the heat-treated fiber as compared to the as-received carbon fibers. The reason for the apparent difference in coating thickness is unknown but reflects the fact that heat treatment induced a change to the surface of the fiber on which the BN was deposited.

The SAM depth profiles indicate an apparent transition region of about 300 nm between the carbon and BN that is artificially broadened due to surface crenulations. Deviation from the stoichiometric B:N ratio may occur undetectably if sufficiently limited to the near surface region of the carbon fiber. Clearly, BN alone comprises the bulk of the
coating, but such near surface reactivity cannot be ruled out as a factor influencing interface compliance.

The strengths of the as-received and heat-treated fiber were not degraded by the chemical vapor deposition of boron nitride. Compositional analysis does not indicate that any phase other than BN, such as a boron carbide, was formed during the CVD-BN process with as-received or heat-treated fibers [Figure 2.14A-B]. No interactions were observed between the BN coating and the fiber during the infiltration of the SiC matrix that resulted in degraded fiber strength or unwanted phases. The compositional depth profile and tensile strengths of coated fibers was unchanged by heat-treating C\text{AR}/BN and C\text{1600}/BN fibers at 1050°C and 1500°C in Argon.

Since the strength of as-received fibers was not degraded by processing them into a C/BN/SiC composite, and no extensive reactivity involving the fiber or unwanted phases are evident in SAM profiles, the poor strength and brittleness of the composites using C\text{AR} fiber is due to a poorly compliant interface. This is consistent with FESEM observations of microstructural changes to the C/BN phase boundary induced by heat treatments, and with the tendency for the BN coating to decohere from the fiber at the site of razor blade fractures in heat treated fiber systems [Figure 2.11 and 2.12]. The result of a compliant BN interface was accompanied by a change to the phase boundary microstructure and behavior of the BN coating.

TGA, DSC, and TPO-MS experiments in air [Figures 2.16 and 2.17] demonstrate that the BN coating provides oxidation resistance to the fiber. In each experiment, the onset of detectible oxidation in the C\text{1600}/BN system occurred about 100°C above the onset of
detectible oxidation in the uncoated C_{1600} system. However, the temperature at which fiber oxidation was detected from C_{1600}/BN should not be considered the ultimate temperature at which the fiber is protected from oxidation by the BN coating. The fibers were cut to fit into the sample holder so the ends of the fibers were not protected by BN and oxidation could proceed down the fiber from that point. The effect observed is that oxidation was slowed by the presence of the coating owing to the significantly smaller surface that was available for oxidation. A higher temperature was required to cause oxidation of the coated fibers at the same rate as the uncoated fibers. Additionally, fiber sizing effects were not present because heat treated fiber was used.

Other evidence of oxidation protection is given by the TGA of the coated system where mass loss was halted at 1000°C. At this temperature, NO$_{(g)}$ was detected in the TPO-MS and a small exothermic peak was detected in the DSC due to the oxidation of BN. In the TGA, the boria at this point flowed around the remaining fiber protecting it from further weight loss by oxidation. At the end of the experiment, fiber was observed embedded within a clear hard material which could only be solidified boria.

### 2.4.3 Features of the Composites

As already mentioned, a compliant interface was developed by heat treating the fibers prior to BN deposition. These composites possessed uneven fracture surfaces, fiber extensions, fiber pull-out holes, ultimate tensile strengths in excess of 400 MPa, and non-linear matrix cracking events in their tensile stress vs. displacement curves. These characteristics demonstrate the ability to accumulate damage through matrix crack bridging
without catastrophic failure of the entire body. Advancing matrix cracks slipped against the fibers rather than propagating through the fibers due to the weak fiber-matrix bond provided by the BN interface coating.

The appearance of composites with appreciable tensile strengths and with evidence for toughening mechanisms in their fractographs occurred when fiber heat treated at 1200°C and above was used. This coincides with the appearance of a more sharply demarcated microstructure to the phase boundary between carbon fiber and BN that indicates a modification to the nature of interaction between the two phases.

The final microstructure of the C_{1600}/BN/SiC composite consisted of carbon fiber coated with 150 nm of BN followed by a SiC matrix that was infiltrated into the fiber volume by direct growth off the BN coating. This microstructure and the role of the BN component in determining the stress response of the composite is observed in Figure 2.19. The BN coating is seen to separate the fiber and the SiC in Figure 2.19A, where an extended fiber emerges from a fracture surface. The BN is observed to be debonded from the carbon fiber. Some less extensive debonding is observed between the BN and SiC. Outside the matrix, the BN has either fallen away from the fiber or remained in the pull-out hole. In Figure 2.19B, we see a pull-out hole that is lined with BN, indicating the latter possibility does occur. The fiber at the base of the pull-out hole has debonded from the BN. We conclude from this microstructure and behavior that the fiber-matrix debonding required for toughening to occur is largely facilitated through weak interactions between the fiber and BN.
During the CVI-SiC process, the composites canned off near the end of the process limiting the growth of the matrix on interior fibers to about 7-10 µm. Interior regions not within 7-10 µm of a fiber resulted in porosity. This can be observed in Figure 2.18. The prevalence and distribution of this type of porosity was related to how tightly the fibers were drawn while supported on the tooling during the CVI-SiC process and was independent of the heat treatment step.

A number of factors indicate that the surface properties of the carbon fiber strongly influenced the mechanical properties of the final composite. These factors include the lack of a clear demarcation to the microstructure of the phase boundary in the Car/BN system, the clear demarcation at the phase boundary in the heat-treated fiber systems, the tendency for the BN to debond from heat-treated fiber during tensile failure of composites and at razor blade fracture sites, the absence of evidence for bulk reactivity in the SAM profiles, and the absence of significant change to fiber strength during processing. These factors suggest a modification to the fiber surface occurred during heat treatment which prevented a strong bond from forming with the BN, yielding a compliant interface. The heat treatments could have restructured the surface to contain less edge carbon and fewer defect sites or evolved off reactive oxygen and nitrogen containing surface functional groups. Edge sites on graphitic surfaces are reactive because they contain unbonded electrons and should therefore be expected to participate in some form of stable covalent bonding with boron or nitrogen atoms in the BN coating. In contrast, basal plane surfaces are more inert and so their interaction with the BN coating is probably limited to weak intermolecular forces that allow for fiber-matrix debonding.
There was not a significant difference in the ultimate tensile strength of composites fabricated from fiber heat treated to different temperatures, but the greater degree of fiber extension and pull-out behavior in the C$_{1600}$/BN/SiC system compared to C$_{1200}$/BN/SiC suggests the C$_{1600}$/BN/SiC system was more effectively toughened. This may be due to a progressive restructuring at the fiber surface associated with the progressive restructuring in the bulk observed by XRD across temperatures used in this study. There are not as yet direct observations associating surface edge carbon, surface defects, or surface functional groups with strong bonding between the fiber and BN, however the data generated here serve to highlight these factors and justify future research towards testing them. Some limited qualitative data exist to suggest that strength degradation of the fibers may occur under different precursor flow conditions than what was used during the CVD of BN in this study. This is something to consider during attempts to extend this research.

FESEM observation of the surface of the composites revealed microcracks running perpendicular to the fiber direction [Figure 2.20]. The fiber coefficient of thermal expansion (CTE) along its length is small compared to the matrix CTE, so matrix contraction on cooling is impeded, resulting in tensile strain in the matrix along the fiber direction that can cause matrix cracking. This is evidence of damage tolerance by crack bridging, and the ability of the composite to support multi-cracking.

The high degree of flexure which can be applied to the C$_{1600}$/BN/SiC mini-composites and from which the composites can recover [Figure 2.22] is further evidence of the ability of the composite to tolerate damage. Such a high degree of flexure could

[79]
only be obtained if the matrix were extensively microcracked into segments and if all the cracks were bridged by the fibers.

The combination of the silicon carbide matrix and the BN interface coating provided effective oxidation protection to the fibers in the $C_{1600}/BN/SiC$ composites. When these mini-composites were treated in air at 1000°C for 12 and 100 hours, they did not suffer any strength degradation [Figure 2.5]. The composite color changed from black to a green hue as a result of the oxidation [Figure 2.25]. An FESEM image in Figure 2.26 of the outer edge of the SiC matrix at a fracture surface shows a layer of oxidized SiC. The stress-strain curves of the oxidized mini-composites were similar to the pre-oxidized sample. A typical stress-strain curve of a $C_{1600}/BN/SiC$ composite treated in air at 1000°C for 100 hours is depicted in Figure 2.23. Non-linear matrix cracking events occurred after which the composite was still able to support a load. Evidence for the occurrence of toughening mechanisms are apparent in the FESEM fractograph of the oxidized composite in Figure 2.24. Fiber extension, pullout holes, and an uneven fracture surface are observed.

2.5 CONCLUSIONS

Processing requirements that lead to an oxidation resistant BN interface coating for Toray T300 carbon fiber reinforced ceramic matrix composites have been established. This processing is important for providing a means of enhancing the properties of carbon fiber reinforced CMC’s. This procedure also supports a more general conclusion that fiber surface properties can be as important as the bulk properties of component phases toward dictating the stress response of a CMC. Modifications might sometimes be
processed into a fiber surface, before component phases of the CMC are added, which promote favorable changes to properties of the final composite.

The BN coating imparts mechanical properties to the carbon fiber reinforced composites that are usually achieved with a carbon coating, and also provides oxidation protection that a carbon coating does not. These data isolate the reason for toughening or lack thereof to surface or near surface interactions involving the carbon fiber and the BN or other species present during the CVD of BN. The heat treatment plausibly reduces the amount of edge carbon, defect sites or functional groups on the surface of the fiber not removed by the 800°C BN deposition temperature. These factors have not yet been directly observed experimentally as the reason for toughening, but the data generated here suggest targeted testing of these hypotheses. The weak and brittle behavior of composites fabricated using as-received fiber results from a poorly compliant interface, rather than from a degradation of the fiber strength or reactivity during processing that results in unwanted phases.
CHAPTER 3
Pyrolytic Decomposition of Ammonia Borane to Boron Nitride

3.1 INTRODUCTION

Ammonia borane (H\textsubscript{3}N-BH\textsubscript{3}) is molecular solid currently being investigated as a chemical hydrogen storage material because of its high hydrogen content (19.6 wt. %) and favorable hydrogen release characteristics. Two temperature dependent pyrolysis steps that each release about 1 mol equivalent of H\textsubscript{2} per mole of ammonia borane (AB) are generally accepted to occur at 110 and 130\textdegree C\textsuperscript{101-105}. A third mass loss onset temperature has not been well-defined. Here we report a third major mass loss event beginning at 1170\textdegree C in a nitrogen atmosphere that results in a semicrystalline hexagonal boron nitride (hBN) after treatment at 1500\textdegree C for 24 hours in N\textsubscript{2}.

Empirical formula determinations, vibrational spectroscopy and \textsuperscript{11}B magic angle spinning–nuclear magnetic resonance (\textsuperscript{11}BMAS-NMR) studies performed by other researchers have provided evidence that a complex, branched form of polyaminoborane (PAB), -[NH\textsubscript{2}-BH\textsubscript{2}]\textsubscript{n}-, is formed in the solid phase during the first hydrogen release step\textsuperscript{102,106}. In separate studies, preparations of PAB decompose over a broad range of temperatures to form structures approximating polyiminoborane, (PIB) -[NH=BH]\textsubscript{n}-\textsuperscript{105}. Quantities of gas phase species which form in addition to hydrogen, such as borazine (N\textsubscript{3}B\textsubscript{3}H\textsubscript{6}) account for mass losses observed in TGA experiments that cannot be solely attributable to hydrogen evolution. Baitalow et. al. demonstrated constant hydrogen
production, and variable mass loss at different heating rates,\textsuperscript{102} suggesting that reaction kinetics are an important factor in dictating the formation of impurity gases.\textsuperscript{101-105}

A number of recent studies have focused on chemical analogues of ammonia borane.\textsuperscript{107-109} The compounds LiNH$_2$BH$_3$ and NaNH$_2$BH$_3$ were reported by Xiong, et al. to evolve hydrogen in a single exothermic step near 90$^\circ$C, without detectable evolution of borazine.\textsuperscript{107} Wu et al. have determined the crystal structure of these metal amidoboranes.\textsuperscript{108} Sneddon and Yoon have examined ammonia triborane as a potential hydrogen storage material.\textsuperscript{109}

In this study, the thermal decomposition of ammonia borane was studied using a variety of methods to qualitatively identify gas and remnant solid phase species after thermal treatments up to 1500$^\circ$C. Attenuated total reflectance Fourier transform infrared spectroscopy, (ATR-FTIR) is used to determine chemical structures in the residual solid phase material present after each of the three known decomposition steps. The residual boron nitride was characterized by powder X-ray Diffraction (XRD) scanning Auger microscopy (SAM) to determine structure and composition. The boron nitride was also characterized by field emission scanning electron microscopy (FESEM) to determine morphology. Gas evolution and thermochemistry were quantified by vacuum line techniques, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The temperature dependence of hydrogen and impurity gas evolution was studied using mass spectroscopy.
3.2 EXPERIMENTAL

3.2.1 Materials

High purity Ammonia borane powder was obtained from Ensign Bickford Aerospace and Defense. Samples were stored in desiccators or an argon drybox. Ultrahigh purity (UHP) grade Helium, Argon, and N₂ were obtained from Airgas. Anhydrous ammonia (99.99%) was also obtained from Airgas. Borazine was obtained from Borosciences Canada. Hexagonal boron nitride was obtained from Alfa Aesar (99.5%, lot F09P16).

3.2.2 Thermal Analysis and Measurements of Gaseous Decomposition Products

Thermogravimetric Analysis

Because of the tendency for AB to significantly expand in volume during pyrolysis, sample mass was limited to less than 2 mg for all TGA experiments. Thermogravimetric analyses were conducted on three instruments. The first instrument, a TA Instruments TGA Q500, was enclosed within an argon filled glovebox to eliminate the presence of trace atmospheric gases in the thermobalance during analysis. The second instrument, a TA Instruments TGA 2950, was housed in the open atmosphere on a benchtop. These two instruments have nearly identical furnace and balance configurations. Samples were loaded into weight tared platinum pans and the temperature was ramped at 5 °C/min from 23 °C to 450 °C under flowing Argon.

The third instrument, used for high temperature studies, was a TA Instruments TGA Q600. The sample was loaded into a weight tared alumina pan and ramped at 25 °C/min
to 1500 °C under flowing nitrogen. A 25 minute isothermal period at 98 °C was included to prevent excessively rapid mass loss at the melting point due to the otherwise high heating rate. Operational parameters of the Q600 instrument required a heating rate of 5 °C/min above 1485 °C.

**Thermogravimetric Analysis-Mass Spectroscopy (TGA-MS) and Temperature Programmed Desorption-Mass Spectroscopy (TPD-MS)**

TGA-MS experiments were carried out using the TA Instruments TGA Q500, enclosed within an argon filled glovebox. Mass spectroscopic analysis of gases exiting the thermobalance was carried out with an MKS model quadrupole residual gas analyzer (RGA) using a 40 ev electron impact ionization source. The quadrupole was used to scan all m/z ratios from $m/z = 1$ to $m/z = 90$ approximately every 30 seconds.

TPD-MS experiments were conducted on a home-built apparatus which could accommodate a larger sample size than the TGA-MS instrument, thus allowing detection of impurity level gases. An MKS E-Vision+ model RGA was used with a 40 ev electron impaction ionization source. Samples (50 mg) were loaded into a 9 mm outer diameter, (O.D.) and 7 mm inner diameter (I.D.) quartz tube reactor. Helium carrier gas (50 sccm) was delivered through PFA tubing connected to the quartz tube via Swagelock and Ultra-Torr brand compression fittings. The vacuum system of the RGA continuously sampled from species present at a “T” in the exit gas line from the quartz tube. Temperature was controlled by a resistively heated tube furnace and a type K thermocouple in thermal contact with the external surface of the quartz tube at the location of the sample.

[85]
The sample was heated at 25°C/min, held at 114 °C for 120 seconds, and then heated again at 25°C/min to 135°C where the temperature was held for another 120 seconds. At least 3 scans from m/z=1 to m/z= 90 were recorded during both isothermal periods, averaged, and plotted after a baseline subtraction.

*Borazine Mass Spectrum*

Borazine vapor was introduced into a lecture bottle along with helium and in the absence of air. The lecture bottle was connected to a “T” in a helium carrier gas line. The borazine vapor was entrained by the flowing helium carrier gas, and this mixture was carried to the inlet of the MKS e-vision residual gas analyzer to obtain a mass spectrum for comparison to spectra of gaseous AB thermal decomposition products.

*Differential Scanning Calorimetry.*

Differential scanning calorimetry (DSC) experiments were carried out on a TA Q100 system. Ammonia borane was weighed in an aluminum pan which was then crimped closed. A pinhole allowed the escape of evolved gases. Ramp rates of 5°C/min to 400°C were used with an N₂ purge gas after an initial 30-minute isothermal period at 40°C to remove atmospheric gases and adsorbed moisture.

*Vacuum Experiments*

Ammonia borane was decomposed under high vacuum conditions in a closed vacuum line of known, constant volume for quantitative measurements of H₂ evolution.
Attachments of the different components to the manifold were made with standard ground glass joints. The volume of the entire system was determined by using ideal gas law calculations. The base pressure was 1 mtorr. The system was isolated by closing the vacuum stopcock. The reaction flask containing ammonia borane was then heated to 240 °C by immersion in a silicone oil bath. Gases generated in the reaction flask passed through a liquid nitrogen trap before entering the manifold. Borazine and any other condensable gases remained in the trap. The number of mols of H₂ evolved was calculated from the final pressure and volume of the vacuum line with a small experimentally determined correction factor applied due to the cooling effect of the liquid N₂.

**Figure 3.1** Vacuum system for quantification of H₂ evolution from ammonia borane: (1) manifold constructed of 9 mm (outside diameter) pyrex tubing; (2) mercury monometer; (3) 2000 mL pyrex vacuum chamber; (4) 100 mL sample holder heated by immersion into a 240°C silicone oil bath; (5) liquid nitrogen trap to condense non-hydrogen gas phase species; (6) vacuum stopcock; (7) Pirani vacuum gauge; (8) mechanical vacuum pump.
3.2.3 Characterizations of Solid Phase Decomposition Products

Preparation of Solid Phase Ammonia Borane Pyrolysis Products

Under controlled atmospheres, AB was thermally treated at three different temperatures, 120, 210 and 1500°C, referred to as AB-120°C, AB-210°C and AB-1500°C respectively. AB-120°C and AB-210°C were generated by immersing Pyrex vessels containing the compound into heated oil baths for 5 minutes under UHP Helium carrier gas. The materials generated were stored in helium atmosphere until immediately prior to analysis by ATR-FTIR. A third sample was prepared by treatment of AB at 1500°C for 24 hours in a high temperature tube furnace in an alumina sample holder under UHP Nitrogen carrier gas.

ATR-FTIR Spectroscopy

A Spectra Tech IR Plan model, micro-attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectrometer with a Nicolet Magna 560 light source and detector was used to obtain IR spectra. The spectra of ammonia borane and the three solid phase pyrolysis products prepared as described above was obtained. In addition, the spectrum of the hexagonal phase boron nitride (hBN) from Alfa-Aesar was obtained.

Powder X-Ray Diffraction

Powder XRD patterns of AB-1500°C and commercially available hBN were obtained using a Scintag model XDS 1000 X-Ray diffractometer. The scan rate was 0.5 deg 2θ/min. An aluminum sample holder was used.
Auger Spectroscopy

Auger spectra were acquired using a Physical Electronics PHI 610 scanning Auger microprobe. The powdered AB-1500 °C and commercial hBN samples were embedded into In foil. The samples also were sputtered with Ar ions. The following conditions were used: Tilt = 45° WRT incident electron beam, energy analyzer resolution = 0.6 %. $P_{\text{Base}} \leq 8.2 \times 10^{-9}$ mm Hg, $E_{\text{p}} = 3.0$ keV, $I_{\text{e-}} = 10$ nA, $E_{\text{Ar+}} = 4.0$ keV, $I_{\text{Ar+}} = 1.0$ µA, $A_{\text{Raster}} \approx 7.5$ mm$^2$, $\text{Time}_{\text{Sputter}} = 20.0$ minutes [6]. The symbol $P_{\text{Base}}$ is the system pressure during data acquisition (excluding $P_{\text{Ar}}$ while sputtering with Ar$^+$), $E_{\text{p}}$ is the energy of the incident electron beam, $I_{\text{e-}}$ is the electron beam current measured at sample with +90 V bias applied, $E_{\text{Ar+}}$ is the energy of the incident Ar$^+$ beam, $I_{\text{Ar+}}$ is the Ar$^+$ beam current measured at the sample with +90 V bias applied, $A_{\text{Raster}}$ is the area rastered by the ion beam, and $\text{Time}_{\text{Sputter}}$ is the Total Ar$^+$ sputtering time. A lower electron beam energy was not used since the calculated concentrations tend to be less accurate. Detailed spectra as well as survey spectra were acquired. Peak intensities in detailed spectra are defined as the difference between the maximum and minimum values of the derivative plot.

Field Emission Scanning Electron Microscopy

FESEM images of AB-1500 °C and the crystalline hBN from Alfa Aesar were obtained using a Zeiss DSM 982 Gemini with a Schottky emitter and a secondary electron detector. The electron beam energy was 2kV. The powders were mounted onto the sample
stub using double sided carbon tape. Excess powder was gently blown off the tape with compressed air.

3.3 RESULTS

3.3.1 Thermal Analysis and Mass Spectroscopy

TGA-MS

The mass loss profiles of ammonia borane and the $m/z=2$ signal recorded by the mass spectrometer during the TGA-MS experiment to 400°C are overlaid in Figure 3.2. These data were collected with the TGA system in a glovebox under argon gas. At a heating rate of 5°C/min in Ar atmosphere there is an onset temperature at 108°C and a second onset is initiated at about 130°C. Around 210°C, mass loss stabilizes at 50 wt. %. Mass loss and H$_2$ evolution were tightly associated. Ammonia borane contains 19.3% hydrogen by mass, however, no other gas phase species were detected. Presumably, the small, 1.5 mg sample size did not evolve nitrogen and boron containing molecules into the carrier gas at detectable levels. Nitrogen or boron species have a greater per molecule effect on mass loss than H$_2$ and are also more likely to form condensed phases in the tubing prior to reaching the mass spectrometer sampling inlet. Larger sample sizes were used for TPD-MS experiments, and nitrogen and boron containing molecules were detectably evolved.
Figure 3.2. TGA-MS mass loss and $H_2(g)$ evolution profile

**TPD-MS**

Baseline subtracted mass spectra of pyrolysis gases obtained during isothermal periods at 114°C and 135°C clearly indicate $H_2$ is the most abundant gas phase pyrolysis species but that other species are also present in both cases. After rapid heating to 114°C [Figure 3.3A] the presence of species at 27, 28, and 29 amu is identified. After rapidly heating this sample again to 135°C, mass fragments consistent with those obtained from pure borazine [Figure 3.3C] and increased levels of the 27, 28, and 29 amu species were detected [Figure 3.3B]. A small peak at 87 amu was also detected. The 2 amu signals are at least an order of magnitude larger than signals produced by any other mass. Typically, a white coating formed the interior walls of the quartz tubing at the exit of the tube furnace. This coating evolved additional hydrogen, borazine, and molecular aminoborane when gently heated with a Bunsen burner flame.

[91]
Figure 3.33. Mass Spectrum: (A) pyrolysis gases generated at 114°C scaled to impurity levels; (B) pyrolysis gases generated at 135°C scaled to impurity levels; (C) pure borazine. The m/z = 2 signal intensities in A and B are each about 2 orders of magnitude above their respective y-axis scales.

Borazine Mass Spectrum

The isotopic distribution of boron causes molecular ion and deprotonation peaks to overlap. The most intense peak of the pure borazine mass spectrum at 80 amu [Figure 3.3C] corresponds to the mass of the 80 amu molecular ion, and deprotonation of the most abundant 81 amu molecular ion. The 81 amu borazine species is statistically the most
abundant molecular weight for borazine. Other fragment clusters were observed around 67 amu, 63 amu, 53 amu and 28 amu. There was no contribution at 29 amu, and only small contributions at 26, 27, and 28 amu.

Figure 3.4. TGA curves: The glovebox effect. Three TGA curves obtained from an instrument housed in an argon filled glovebox (shaded area) are stacked against five TGA curves obtained from an instrument housed in the open atmosphere (unshaded area). Horizontal line spacing corresponds to a 20 wt. % change. The heating rate was 5°C/min in Ar carrier gas to 450°C.
**TGA: The Glovebox Effect**

When the thermobalance was not housed within a glove box, mass loss curves typically deviated at the second mass loss step. [Figure 3.4] A thermobalance housed within an argon filled glovebox was able to eliminate these deviations and mass increases.

**TGA to 1500 °C**

TGA data in Figure 3.5 for ammonia borane heated to 1500°C in nitrogen atmosphere at a 25°C/min ramp rate record the mass loss associated with the first two well known decomposition steps. A 25 minute isotherm was included at 98°C, and mass loss was observed during this period. A third major mass loss event was initiated at 1170°C and decomposition was still occurring at 1500°C, the maximum operating temperature of the instrument.

![Figure 3.5. TGA to 1500°C in N2. Heating rate was 25°C/min. Above 1485°C the heating rate was 5°C/min. A 25 minute isotherm was included at 98°C.](image-url)
Differential Scanning Calorimetry

DSC data for pure ammonia borane in nitrogen are shown in Figure 3.6. The heat flow per gram of starting mass of sample is -0.68 W/g at 110°C; -9.61 W/g at 116°C; -1.45 W/g at 170°C; and -0.56 W/g at 397°C. An endothermic transition initiates at 110°C followed by an exothermic transition at 120°C followed by another endothermic transition at 135°C.

![DSC curve: Ammonia Borane, 5°C/min in N₂ to 400 °C.]

Figure 3.6. DSC curve: Ammonia Borane, 5°C/min in N₂ to 400 °C.

3.3.2 Vacuum Line Hydrogen Quantifications

Rapidly heating ammonia borane to 240°C released an amount of hydrogen equal to 10.5% of the original sample mass, or 1.61 mol equivalents. Roughly 95% of the hydrogen evolved in less than one minute. After 5 minutes, no more hydrogen evolution could be observed. When the sample holder was immersed in silicone oil, the ammonia borane melted within several seconds. Vigorous bubbling occurred immediately within the melt. Within seconds, the melt solidified to a white material. In similarity to TPD-MS

[95]
experiments, a white film coated the inside walls of the Pyrex tubing between the sample holder and the liquid nitrogen trap, (between points 4 and 5 in Figure 3.1). This material was found to produce additional hydrogen when gently heated with a Bunsen burner flame.

If stored in an argon drybox at atmospheric pressure, the white coating persisted for several months. If exposed to room air, the white coating visibly decomposed within minutes. A protected environment would be required to obtain spectral data for this material.

3.3.3 Solid Phase Characterizations

ATR-FTIR

Band positions in the ATR-FTIR spectra [Figure 3.7] of untreated, room temperature ammonia borane match well with those from previously published vibrational spectroscopy studies of the compound. The absorbance peaks at 3302 cm\(^{-1}\) and 2278 cm\(^{-1}\) in ammonia borane are shifted to a slightly lower wavenumber in AB-120°C. A small peak at 3435 cm\(^{-1}\) also appears in AB-120°C. These bands shift position again to 3437 cm\(^{-1}\) and 2498 cm\(^{-1}\) in AB-210°C and also exhibit a decrease in their relative intensity. In AB-1500°C, and the commercial hBN sample, no bands are present above 1700 cm\(^{-1}\). There are a number of overlapping, complex bands present in each spectrum below 1700 cm\(^{-1}\).
**Figure 3.7.** ATR-FTIR spectra of solid phase decomposition products and hexagonal boron nitride: (A) room temperature ammonia borane; (B) ammonia borane treated at 120°C; (C) ammonia borane treated at 210°C; (D) ammonia borane treated at 1500°C; (E) hBN.
Powder X-Ray Diffraction

The Powder XRD pattern [Figure 3.8] obtained from the commercial hBN sample was closely indexed to the JCPDS card file 34-0421 for space group P63/mmc hBN. All reflections arising from the AB-1500°C material are weak and broad but occur in coincidence with the locations and relative intensities of the sharp peaks in the commercial hBN sample. Reflections arising from the aluminum sample holder are identified in both patterns.

![Powder X-ray diffraction of hexagonal phase boron nitride and ammonia borane treated at 1500°C (AB-1500°C). Sample holder peak positions, indicated by bullets (●), and by dashed lines.](image)

Figure 3.8. Powder X-ray diffraction of hexagonal phase boron nitride and ammonia borane treated at 1500°C (AB-1500°C). Sample holder peak positions, indicated by bullets (●), and by dashed lines.
Scanning Auger Microscopy

Two Samples, AB-1500°C and a commercial hBN were subjected to elemental analysis by SAM to compare atomic composition. Representative survey spectra of the two samples are displayed in Figure 3.9. Attempts to obtain SAM spectra after Ar+ sputtering were unsuccessful due to sample charging. The adventitious carbon may have provided a conductive pathway for charge dissipation. Spectra without a carbon signal were not possible to obtain. Oxygen, nitrogen, boron, and carbon were found in each sample by the presence of KLL transitions from each atom. Relative peak intensities obtained from detailed spectra at multiple spots are listed in Table 3.1.

Figure 3.9. B, C, N, and O KLL Auger Electrons in SAM survey spectra: (A) AB-1500°C; (B) the commercially available hBN powder.
Table 3.1  Normalized, B, N, C and O, KLL scanning Auger microscopy peak intensities at three different spots on both AB-1500°C and the commercially available hBN powder. Intensity was taken as the difference between the maximum and minimum in the derivative plot.

The composition of ammonia borane powder treated at 1500°C is nearly identical to the hBN reference powder. Three spots from each sample were examined. Spectra could not be obtained after the sample was Ar⁺ sputtered to remove adventitious carbon due to charging. Carbon impurity is the likely explanation for variation in spot 3 of AB-1500°C. The sums of peak intensities from each spot are normalized to a value of 100. N:B is the nitrogen to boron peak intensity ratio.

**Scanning Electron Microscopy**

The crystalline hBN sample [Figure 3.10a] is composed of micrometer sized platelets typical of highly crystalline hBN. The topology of AB-1500°C [Figure 3.10b] is

<table>
<thead>
<tr>
<th>Sample</th>
<th>AB-1500 °C</th>
<th>P63/mmc hBN</th>
</tr>
</thead>
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<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>25</td>
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<td>N</td>
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<td>C</td>
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<tr>
<td>O</td>
<td>6</td>
<td>6</td>
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<tr>
<td>N:B Intensity Ratio</td>
<td>1.19</td>
<td>1.23</td>
</tr>
</tbody>
</table>
non-uniform and discontinuous at a 100 nm scale. The AB-1500°C particles have not adopted a uniform, regular shape. The AB-1500°C particle size ranges from 1 micron to over 100 microns.

**Figure 3.10.** Secondary electron FESEM images: (A) commercially available hexagonal boron nitride; (B) AB-1500°C; (C) AB-1500°C, the enclosed area in panel B.
Decomposition Under Anhydrous Ammonia

A second sample of ammonia borane was ramped to 1500°C under a pure anhydrous ammonia carrier gas and held at that temperature for 24 hours in an alumina tube and alumina sample boat. There was no significant difference in the XRD pattern or the ATR-FTIR spectrum of the resultant material in comparison to AB-1500°C, prepared under identical circumstances with a nitrogen carrier gas.

3.4 DISCUSSION

3.4.1 Thermal and Evolved Gas Analysis

High Temperature TGA: Towards Boron Nitride

According to TGA data of Figure 3.5, a major mass loss event was initiated at 1170°C, and was still occurring at 1500°C, the maximum operating temperature of the instrument. This is in agreement with a report that a polyamnioborane pre-ceramic polymer undergoes hydrogen loss at an unknown point between 1000°C and 1400°C. The kinetics of the third mass loss step are significantly slower than either of the first two mass loss steps. The high onset temperature and slow rate of the third mass loss effectively limits the amount of hydrogen available from ammonia borane by thermal pyrolysis. The 2%-3% mass gain initiating at 500°C, is probably due to slight mass measurement error at elevated temperatures.

TGA-MS
A mass of 2 mg was used in the TGA-MS experiments. The TGA-MS data of Figure 3.2 demonstrate the first two well-known onset points at 108°C and 125°C occur in coincidence with an increase in hydrogen evolution. The two mass loss events are not completely separated at the 5°C/min heating rate used in this experiment although the occurrence of a second onset strongly implies the existence of two distinct temperature dependent chemical events. On the basis of peak areas, roughly equal amounts of hydrogen were evolved in each of the two steps.

A 50% total weight loss can not be accounted for entirely by hydrogen evolution alone; however, the mass spectrometer did not detect any other species. This is presumably because impurities occurred below detection limits. The evolution of nitrogen and boron containing species has a greater per molecule effect on weight loss than the evolution of H₂. TPD-MS experiments using larger sample sizes detected the evolution of multiple nitrogen and boron containing species at low levels.

**TPD-MS and the Pure Borazine Spectrum**

Comparison of the mass spectrum of non-hydrogen pyrolysis gases, generated during the TPD-MS experiment to the mass spectrum of pure borazine, clearly identify a temperature dependent evolution of impurity gases and the evolution of molecular aminoborane, in addition to borazine. [Figure 3.3] Pyrolysis gases generated at 114°C contain molecular aminoborane at low levels, as evidenced by the presence of a peak at 29 amu, due to molecular aminoborane with a ¹¹B isotope. The relative intensities of the peaks at 26-29 amu match a previously obtained electron impact ionization mass spectrum of
aminoborane.\textsuperscript{110} The peak at 87 amu could be an aminoborane trimer. During TPD-MS experiments a white particulate film consistently coated the interior walls of the reactor exit tubing. On gentle heating with a Bunsen burner, this film was found to evolve hydrogen, borazine and molecular aminoborane, but was not completely volatilized off the tubing wall. In light of this information, the most plausible sources of this white film are physically and chemically condensed low molecular weight volatile with a stoichiometry of $\text{NBH}_x$ where $x>2$. This includes species such as ammonia borane, molecular aminoborane, and low polymers of PAB. At the low temperatures outside the furnace, gas phase molecular aminoborane could polymerize to a PAB type structure, or the molecule could physically condense to a solid and then polymerize. Similar results obtained with the vacuum line experiments are discussed elsewhere in this chapter.

\textit{Glove-Box TGA and DSC}

The presence of trace atmospheric gases influenced the TGA curves in relation to the reproducible results obtained from UHP argon conditions. Adsorbed species like $\text{H}_2\text{O}$ and $\text{O}_2$ could suppress desorption of $\text{H}_2$ by interacting with surface sites on the decomposing ammonia borane. The two major effects of the glovebox are to prevent water and oxygen from adsorbing onto the sample and onto the surfaces of the cell during loading and preparation of the sample, and to prevent exchange of the pure delivery gases with room air during the analysis. The extent of delivery gas exchange with room air depends on the configuration and condition of the instrument. However, only a glove-box or dry-
box can prevent the adsorption of moisture and oxygen onto the surfaces of the sample and analysis cell.

The DSC data [Figure 3.6] were not collected with the instrument housed in a glovebox. Measures were taken to reduce the amount of adsorbed H$_2$O within the DSC cell itself. The first large endothermic transition is consistent with the melting of ammonia borane. The rapid transition to an exothermic process corresponds with the rapid desorption of H$_2$ that occurs immediately on melting. The DSC data indicate an endothermic step corresponding with the second mass loss event initiating at about 135°C. This event has been reported as an exothermic transition in other DSC studies$^{102}$ with the same heating rate and carrier gas. We have repeated our experiments several times and obtained highly consistent results. Minute differences in conditions clearly have an effect on the chemical pathways and heat effects which occur during pyrolysis. This result highlights some areas of urgently needed research if ammonia borane is to be commercialized as a fuel cell hydrogen source. Future investigations may be designed to identify and quantify the influence of variables such as trace levels of atmospheric gases, purity, preparation method, grain size, agglomeration, bulk configuration, heat transfer kinetics, presence of additives, container geometry, and gas flow dynamics.

3.4.2 **Solid Phase Characterizations**

**ATR-FTIR**

Changes in the fundamental N-H, B-H, and B-N stretching frequencies are particularly diagnostic of chemical state as decomposition proceeds because these
frequencies tend to increase as the $\pi$ bond character between nitrogen and boron atoms increase.\textsuperscript{111-118} Table 3.2 lists selected assignments from infrared spectra of several molecular compounds with different nitrogen-boron bond orders.

The bond orders of nitrogen and boron atoms present in ammonia borane, AB-120°C, AB-220°C and AB-1500°C can be identified by the position of the NH, BH and BN stretching frequencies in each of the materials. A determination of chemical structure of each material follows from knowledge of hydrogen loss and the bond orders present. Table 3.3 lists selected assignments from the infrared spectra we have obtained. A more detailed discussion of structural determinations obtained from the spectra follows below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ref</th>
<th>BO</th>
<th>NH$^\nu$(cm$^{-1}$)</th>
<th>BH$^\nu$(cm$^{-1}$)</th>
<th>BN$^\nu$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$B-NH$_3$</td>
<td>a,d,e</td>
<td>1</td>
<td>3167-3316</td>
<td>2279-2375</td>
<td>784-800</td>
</tr>
<tr>
<td>H$_3$B-NH$_2$-CH$_3$</td>
<td>b</td>
<td>1</td>
<td>3175-3374</td>
<td>2367-2415</td>
<td>667-726</td>
</tr>
<tr>
<td>H$_3$B-NH(CH$_3$)$_2$</td>
<td>b</td>
<td>1</td>
<td>3219-3236</td>
<td>2260-2384</td>
<td>659-708</td>
</tr>
<tr>
<td>H$_3$B-N(CH$_3$)$_3$</td>
<td>b</td>
<td>1</td>
<td>none</td>
<td>2270-2393</td>
<td>648-667</td>
</tr>
<tr>
<td>H$_2$B=NH$_2$</td>
<td>c</td>
<td>2</td>
<td>3451-3533</td>
<td>2495-2564</td>
<td>1337</td>
</tr>
<tr>
<td>H$_2$B=NH-CH$_3$</td>
<td>b</td>
<td>2</td>
<td>3447</td>
<td>2471-2561</td>
<td>1314-1322</td>
</tr>
<tr>
<td>H$_2$B=N(CH$_3$)$_2$</td>
<td>b</td>
<td>2</td>
<td>none</td>
<td>2369-2575</td>
<td>1148-1229</td>
</tr>
<tr>
<td>HB≡NH</td>
<td>f,g</td>
<td>3</td>
<td>3700-3712</td>
<td>2775-2820</td>
<td>1782-1822</td>
</tr>
</tbody>
</table>

**Table 3.2** Dependence of Stretching Frequencies on Bond Order for BNH compounds.

As bond order (BO) between the boron nitrogen bond increases, fundamental stretching mode frequencies increase. The wavenumbers listed cover the range of values assigned to stretching modes in the indicated references. a$^{111}$; b$^{112}$; c$^{113}$; d$^{114}$; e$^{115,116}$; f$^{117}$; g$^{118}$.  

[106]
Table 3.3 Bond Stretch and Bond Order (BO) Assignments. The bond order (BO) present between nitrogen and boron atoms can be ascertained by the IR absorbance peak positions of NH, BH, and BN stretching vibrations. The formation of nitrogen-boron double bonds (BO=2) begins to occur at about 120°C. Boron to nitrogen bonds of BO=1 and BO=2 are both present in AB-120°C. The NH\textsuperscript{st} and BH\textsuperscript{st} peak positions in this table include contributions from multiple fundamental stretching modes and are diagnostic of bond order. BN\textsuperscript{st} peaks overlap with other bending modes. (a) BO assumed from hBN structure. The BN\textsuperscript{st} in fully dehydrogenated BN species is not diagnostic of BO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N-B Bond Order</th>
<th>NH\textsuperscript{st} (cm\textsuperscript{-1})</th>
<th>BH\textsuperscript{st} (cm\textsuperscript{-1})</th>
<th>BN\textsuperscript{st} (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB-RT</td>
<td>1</td>
<td>3302</td>
<td>2278</td>
<td>781</td>
</tr>
<tr>
<td>AB-120°C</td>
<td>1</td>
<td>3250</td>
<td>2250</td>
<td>850</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3437</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AB-210°C</td>
<td>2</td>
<td>3455</td>
<td>2498</td>
<td>1344</td>
</tr>
<tr>
<td>AB-1500°C</td>
<td>1.33\textsuperscript{a}</td>
<td>none</td>
<td>none</td>
<td>1338</td>
</tr>
<tr>
<td>hBN</td>
<td>1.33\textsuperscript{a}</td>
<td>none</td>
<td>none</td>
<td>~1300</td>
</tr>
</tbody>
</table>

ATR-FTIR: Ammonia Borane

An early vibrational spectroscopy study of argon matrix isolated ammonia borane by Smith et al.\textsuperscript{114} was thorough, but has been somewhat updated and revised. Infrared absorbance data observed in AB-RT of Figure 3.7a can be assigned on the basis of currently accepted experimental and calculated vibrational spectra of ammonia borane.\textsuperscript{111,115,116,119} The absorbance data in Figure 3.7a, obtained from a pure, solid state powder, are therefore
assigned on the basis of calculated and experimental vibrational spectra of crystalline ammonia borane from other studies.

The position of stretching frequencies in ammonia borane is consistent with boron and nitrogen atoms in tetrahedral environments bonded by a single covalent single bond [Table 3.3]. The peaks near 3302 cm\(^{-1}\) are assigned to NH stretching modes and those near 2278 cm\(^{-1}\) are assigned to BH stretching modes. The B-N stretching mode is observed at 781 cm\(^{-1}\). The peaks at 1601 cm\(^{-1}\) and 1371 cm\(^{-1}\) are due to \(\text{NH}_3\) deformations, and a pair of partially resolved peaks at 1155 and 1180 cm\(^{-1}\) is assigned to \(\text{BH}_3\) deformations. The peaks at 1055 cm\(^{-1}\) and 727 cm\(^{-1}\) have been assigned to NBH rocking modes.

\textit{ATR-FTIR: AB-120^\circ C}

After the evolution of significant quantities of hydrogen by treatment at 120\(^\circ\)C, the stretching frequency positions in AB-120\(^\circ\)C [Table 3.3] indicate the material is composed mostly of tetrahedral, singly bonded nitrogen and boron atoms. This is strongly suggestive of a PAB, -(\(\text{NH}_2\)-\(\text{BH}_2\))\(_n\)-, based structure with an NBH\(_x\) stoichiometry, where \(x\leq 4\). A highly branched or cyclized PAB polymer, where \(x\) is less than 4, may have a very similar IR spectrum without significant shifts in stretching frequencies from the purely linear case.

A small peak at 3437 cm\(^{-1}\) appears in the AB-120\(^\circ\)C spectrum and is assigned to NH stretching modes involving nitrogen atoms pi bonded to adjacent boron atoms in short segments of a PIB, -(\(\text{HN}=\text{BH}\))\(_n\)-, type chemical structure, or to terminal \(=\text{NH}_2\) groups of a PAB polymer. The NH and BH stretching mode peak positions decreased slightly from the
ammonia borane case. This reflects the loss of the high symmetry stretching modes in ammonia borane that cannot exist in PAB.

Detailed ab-initio investigations by Jacquemin et al.\textsuperscript{120} on the vibrational structure of PAB predict the umbrella mode of terminal NH$_3$ groups to have a frequency of 1380 cm$^{-1}$ and the BN stretching mode to have a frequency 900 cm$^{-1}$. On this basis the strong peak at 850 cm$^{-1}$ in AB-120 °C was assigned to the BN stretching vibration involving tetrahedral nitrogen and boron atoms and the peak at 1394 cm$^{-1}$ is assigned to the -NH$_3$ umbrella vibration. Since the variation in dipole moment is very large with the -NH$_3$ umbrella mode, -NH$_3$ should be detectable in very small quantities. The peak centered at 1119 cm$^{-1}$ with a shoulder at 1035 cm$^{-1}$ is probably due to multiple unresolved bending modes possibly including a BH$_2$ deformation and a BH$_3$ umbrella.\textsuperscript{120,121} Absorptions near 1550-1600 cm$^{-1}$ reported elsewhere for cycloaminoborane species and the H$_3$B-NH$_2$-CH$_3$ adduct are assigned to NH$_2$ deformations in each case.\textsuperscript{120} The peak at 1556 cm$^{-1}$ in the AB-120 °C spectrum is thus explained by an NH$_2$ deformation.

Using the BN stretching frequency to assign a bond order between the Nitrogen and Boron atoms is complicated by its overlap with a number of peaks in the lower wavenumber fingerprint region of the IR spectra. Assignment of the BN stretching frequency instead follows from the assignment of bond order that can be unequivocally determined from the NH and BH stretching frequencies which do not overlap with other modes. The presence of a peak at the expected position for a BN stretch serves as a confirmation of the bond order assigned from the NH and BH stretching frequencies, but cannot be used for an assignment in isolation.
**ATR-FTIR: AB-210 °C**

The absorption bands at 3435 cm\(^{-1}\) and 2498 cm\(^{-1}\) and 1350 cm\(^{-1}\) in Figure 3.7c are each respectively consistent with NH, BH and BN stretching modes involving pi bonded nitrogen and boron atoms. This strongly implies a chemical structure approximating PIB, and an NBH\(_x\) stoichiometry where \(x\leq 2\). A highly branched or cyclized PIB polymer where \(x\) is less than 2 would have a very similar IR spectrum without significant shifts in the stretching frequencies in comparison to the pure linear case. An alternative structure that is not observed but might result after the second mass loss step is a highly branched or cyclized PAB polymer, or a mixture of a PIB and branched PAB structure. The occurrence of branched PAB can be definitively ruled out based on the NH and BH stretching frequencies.

Other than the NH, BH and BN stretching vibrations in this material, the remaining IR spectrum should be highly dependent on cis-trans isomerism, structural conformation, crystallinity, exact stoichiometry, degree of branching and degree of cyclization in the polymer.\(^{110}\) Unequivocal assignments to the remaining absorption peaks in this spectrum can not be made at this time because the effect of these multiple variables has not been well established.

**ATR-FTIR: AB-1500 °C**

The strong peak in AB-1500°C at 1344 cm\(^{-1}\) and the sharp transition at 790 cm\(^{-1}\) are respectively coincident with IR active stretching and out of plane bending vibrations in hexagonal phase boron nitride\(^{122,123}\) [Figure 3.7D]. The absence of NH and BH stretching
peaks in this spectrum indicates that the hydrogen has been removed from the system by treatment at 1500 °C under nitrogen for 24 hours.

**ATR-FTIR: Commercially Supplied hBN**

There are no active modes in the NH and BH stretching regions in the hBN spectra. There are a number of factors that could contribute to the different IR spectrum of AB-1500°C and hBN at low wave numbers, namely, differences in crystallinity and the anisotropy of pure phase hBN. Infrared reflectance studies using linearly polarized light have determined that the direction of the polarization vector with respect to the c axis of the crystal affects absorbance frequency positions in hBN by over 100 cm⁻¹ due to the splitting of transverse and longitudinal optical phonons.¹²³,¹²⁴ The spectrum of a powder using non-polarized light is therefore complicated. The complicating effect of anisotropy would be diminished in a material of low crystallinity. Lattice vibrations are expected to be more pronounced in a highly crystalline material.

**XRD, SEM and SAM Spectra: AB-1500°C**

Powder XRD and SEM data identify differences in crystallinity between AB-1500°C and the commercially supplied hBN. The powder diffraction pattern of AB-1500°C contains weak and broad reflections which coincide in position and relative intensity with reflections from a crystalline, P63/mmc hexagonal phase boron nitride. P63/mmc hBN has a graphitic structure where N atoms are stacked in-line between the B atoms of adjacent sheets, and vice versa. This stacking pattern was identified by Pease¹²⁵.
in 1952. The smallest discrete particles in AB-150°C are about 1μm, but most are larger than 5μm. These particles appear to be aggregates of partially sintered or interconnected particles about 100 nm in diameter. The XRD pattern of AB-150°C is similar to what has been termed turbostratic boron nitride (tBN). tBN is a specific type of defected hBN, where layers graphitic layers are stacked nearly parallel, but with random translation and rotational orientation. Highly crystalline samples of hBN cannot typically be obtained without annealing at 1600°C -1800°C. Other researchers have prepared tBN and hBN from compounds similar to ammonia borane, PAB and PIB.

Normalized peak intensities from SAM spectra of AB-150°C provide a measure of atomic composition by comparison with normalized peak intensities from SAM spectra of hBN powder. The commercially supplied hBN has a sharp, tightly indexed diffraction pattern and the material can be taken as stoichiometric. The AB-150°C and hBN samples have very similar nitrogen to boron peak intensity ratio [Table 3.1]. The instrument has a slightly different sensitivity to Auger electrons from each element so the peak intensity ratios are not expected to be 1:1. The carbon present on the surface of each sample is assumed to be adventitious. AB-150°C is therefore composed of nitrogen and boron in a 1:1 ratio. A small amount of oxygen impurity is present. Spot 2 from the AB-150°C sample has a slightly increased nitrogen to boron ratio probably caused by carbon based impurities.

Based on IR, XRD, and SAM data, the AB-150°C material can be characterized as a semi-crystalline boron nitride, structurally approximating the P63/mmc hexagonal phase species but lacking significant long-range order. Additionally, a second sample of
ammonia borane was heated to 1500°C under pure anhydrous ammonia. There was no significant change to the XRD pattern or ATR-FTIR spectrum in comparison to the AB-1500°C sample prepared under a nitrogen carrier gas. Ammonia performs a nucleophilic removal of carbon, oxygen, halogens and free boron impurities which may inhibit crystallization processes. The reason fully crystalline species were not obtained after 24 hours at 1500°C is therefore thermodynamic, or related to atomic scale disorder prior to the third decomposition step. Interestingly, Toury et al. have documented a so-called “precursor memory” effect in their explorations of hBN preceramic polymers. Polymers which adopt conformations and packing structures similar to hBN yield ceramic char with greater crystallinity.

### 3.4.3 Quantitative and Semi-Quantitative Assessments

ATR-FTIR data suggests that at least 2 mol equivalents of H₂ can be released from ammonia borane by pyrolysis at temperatures up to 210°C. However, only 10 wt. % hydrogen was typically obtained in our vacuum line measurements, corresponding to 1.61 mol equivalents of H₂. An important reason for this discrepancy is a white coating which formed on the tubing walls between the liquid nitrogen trap and the sample that evolved hydrogen on gentle with a Bunsen burner. Similar condensed species were found at the exit of the furnace in TPD-MS experiments, as discussed previously. The triple point temperature of borazine is 215.6°C, and borazine exists as a liquid at room temperature and atmospheric pressure. Therefore, the coatings cannot be solid phase borazine. Physically condensed and/or polymerized low molecular weight volatiles with an NBHₙ stoichiometry
where $x > 2$ must be major constituents in these coatings because hydrogen is not readily evolved from $\pi$ bonded nitrogen and boron atoms. The practical implication of these data are that reactor design could markedly influence hydrogen yield and hydrogen purity by controlling the amount of partially decomposed volatiles allowed to escape to cool areas.

### 3.4.4 Chemical Pathways

The pyrolytic decomposition pathways of ammonia borane that can be identified from this analysis are outlined in the scheme of Figure 3.11. This scheme corroborates the results of other researchers, (namely, Wolf et al.\textsuperscript{104} and Hess et al.\textsuperscript{111}) and includes the two major additions addressed below:

1) Molecular aminoborane evolves as a pyrolysis product concurrently with the evolution of hydrogen at about 110°C. A reversible condition between molecular aminoborane and PAB is inferred. At 110°C and above, the decomposition of PAB into molecular aminoborane is competitive with the hydrogen evolving reaction. At room temperature, the polymeric form is strongly preferred, and hydrogen evolving reactions do not occur while both types of reactions proceed from PAB, simultaneously, above 110°C. Chain length, degree of branching and cyclization of the polymer should affect the rate of molecular aminoborane formation.

2) Hydrogen is abstracted from the solid phase residue beginning at 1170°C, resulting in a semicrystalline P63/mmc (hexagonal) phase boron nitride after treatment at
1500°C for 24 hours in nitrogen and anhydrous ammonia. The concurrent evolution of molecular hydrogen is assumed.

Borazine and molecular aminoborane are unacceptable impurities in a fuel cell hydrogen stream. Neither mechanism of formation is precisely known. Baitalow et al. have proposed that desorbed molecular NH$_2$=BH$_2$ above 130°C undergoes dehydrogenation to form a reactive HN=BH (iminoborane) intermediate that rapidly trimerizes to form borazine. We are not aware of any physical evidence documenting the direct thermal conversion of molecular aminoborane to hydrogen and borazine. Another possibility is the direct evolution of iminoborane from the condensed phase pyrolysis residue after PIB structures begin to form above 130 °C, followed by rapid trimerization. The evolution and rapid association of diborane and ammonia to form borazine and hydrogen gas is unlikely.

3.5 Conclusions

Taken together, the TGA, DSC, TPD-MS, vacuum line, XRD, SAM, and ATR-FTIR data suggest hydrogen is lost from ammonia borane in three major stages in roughly equal amounts. Ammonia borane first decomposes into a material structurally approximating PAB, then PIB. The evolution of partially decomposed volatiles can affect the amount of hydrogen evolved during the first two decomposition steps. Subsequent higher temperature processes starting at 1170°C lead to the formation of a semicrystalline, hexagonal boron nitride. These pathways are shown in Scheme 1. Trace amounts of H$_2$O and O$_2$ can markedly influence the decomposition process, and reactor configuration can potentially have a significant effect on hydrogen yield. Infrared vibrational spectra of
thermally treated ammonia borane, at known temperatures, have provided information regarding pathways of decomposition.
CHAPTER 4
Structure and Reactivity of a Co/γ-Al₂O₃ Catalyst in a CO₂/H₂ Feedstock

4.1 INTRODUCTION

A primary purpose of this portion of research was to broadly map the structure and activity of a baseline FT heterogenous catalyst in CO₂/H₂ feeds for CO, methane, higher hydrocarbon (C2+), and methanol activity. A second purpose was to characterize the structure of the catalyst material. A cobalt-based catalyst was chosen for this study for the reasons discussed in chapter 1: C2+ activity is most likely to be observed on an FT active material such as cobalt if CH* and/or CH₂* occur as intermediates. In FT reactions, cobalt is more active than iron, and nickel tends to produce more methane. The goal was to broadly map the activity of the catalyst across temperature, pressure and flow rate variables in order to:

1) Determine the presence and extent of C2+ hydrocarbon evolution;
2) Discover the ranges of temperature, pressure and flow rates that yield conversions to CO, methanol, methane and C2+ hydrocarbons in order to select parameters for systematic studies;
3) Make initial postulates concerning mechanism.

If CO is observed as product along with hydrocarbons or alcohols, this means that at least some of the hydrocarbon or alcohol product passes through a CO* intermediate.
Those pathways that involve a CO* intermediate can be ruled out if CO\(_{(g)}\) is not detected as a product because some of the CO* will desorb. If methane evolves, a CH\(_3^*\) intermediate is strongly implied. If higher hydrocarbons evolve, this indicates CH* and CH\(_2^*\) intermediates may occur that participate in the chain initiation and chain lengthening reactions depicted in Figure 1.6. No promoters or additives were used here so that the baseline may be understood without regard to their effects on the system.

4.2 Experimental

4.2.1 Preparation of the Catalyst

A SCFa series Catalox brand, commercially-provided γ-alumina support produced by Sasol was used for this study. The d\(_{50}\) particle size was 25μm, the surface area was 120 m\(^2\)/g, the pore volume was 0.4 ml/g and the pore radius 4-10 nm. The cobalt phase was added to the support surface by incipient wetness impregnation. The volume of liquid water which could be added to the support per unit mass of support before free standing liquid DDW water could be visually observed was empirically determined. After calcination of the support at 350°C for 2 hours, a quantity of the support was impregnated by the volume of Co(NO\(_3\))\(_2\)·4H\(_2\)O\(_{(aq)}\) solution determined necessary for incipient wetness impregnation. The concentration of the solution was adjusted so that the final catalyst would consist of 20 wt. % cobalt assuming total reduction of the cobalt to the metal. The impregnated support preparation was dried in air at 70°C for 24 hours. The precipitated cobalt (II) nitrate was then decomposed to an oxide in flowing air by ramping the temperature at 0.5°C/min to 250°C and holding at that temperature for 16 hours. This
temperature was selected based on a thermogravimetric analysis (TGA) of Co(NO₃)ˑ4H₂O(s). The TGA was carried out in a TA Instruments Q600 in flowing air at a 10°C/min ramp rate. The TGA identified the temperature at which the decomposition of the nitrate to an oxide was complete and identified the stoichiometry of the oxide product by weight change to the sample. After cooling the impregnated and oxidized support, the atmosphere was changed to flowing hydrogen and the temperature was ramped at 0.5°C/min to 350°C and held at that temperature for 24 hours.

The phase evolution of the catalyst was tracked by ex-situ and in-situ powder X-Ray diffraction (XRD). In ex-situ tests, the synthesis was carried to various points and the resultant material was examined by a Scintag XDS 1000 X-Ray diffractometer with Cu Kα radiation. For the in-situ tests, XRD patterns were obtained after the air oxidation step of the preparation while the oxidized catalyst was reduced in flowing hydrogen gas at 350°C. A Thermo Electron ARL XTRA X-Ray diffractometer with Cu Kα radiation was used.

The support was examined by field emission scanning electron microscopy (FESEM) and compared to images of the fully fabricated catalyst to make morphological observations about the cobalt phase. A Zeiss DSM 982 Gemini with a Schottky emitter and a secondary electron detector was used. SEM-energy dispersive X-Ray spectroscopy (SEM-EDX) elemental maps of Co and Al were generated to determine the exclusivity of association between the cobalt phases and the alumina support phase.
4.2.2 Testing of Catalytic Activity

A diagram of the reactor used for catalytic tests is depicted in Figure 4.1. The reactor consisted of a ¼” outer diameter 316 type stainless steel tube within the 16-inch hot zone of a tube furnace. Roughly 0.2g of a massed, powdered catalyst was loaded into the tube and centered within the hot zone between two plugs of quartz wool. Since high pressure mass flow controllers were not available for this study, the following scheme was used. H₂ and CO₂ gases were charged into a single tank a with a 2:1 H₂/CO₂ molar ratio. Using a pressure reducing regulator, the outlet of the pressurized mixture was regulated to a pressure above the intended reactor pressure. A metering valve between the pressure reducing regulator and the reactor metered the flow rate to the reactor. A backpressure regulator downstream of the reactor regulated the reactor downstream from the metering valve to the desired pressure. A mass flow meter (MFM) at atmospheric pressure downstream of the backpressure regulator allowed the flow rate to be determined. Before
ramping the temperature, air was purged from the reactor with a flow of a 10 mole \% hydrogen mixture in helium.

Runs were conducted at temperatures between 150°C and 350°C, and at pressures between 2 bar and 14 bar. The flow rates used ranged from 3 to 12 L/hr/g cat., typical for laboratory examination of the FT and Sabatier reactions. The catalyst was treated at 350°C for 30 minutes in the H₂/He pretreatment mixture. When the temperature was cooled to the target value for a run, the gas feed was switched to the 2:1 H₂/CO₂ mixture.

The atmospheric pressure effluent gasses downstream of the backpressure regulator were sampled by the sample loop of a gas chromatograph with a thermal conductivity detector (gc-tcd) for quantitative determinations of CO₂ conversions and product selectivity. A 13X molecular sieve column was used to quantify the CO and methane levels. A HayseSep column was used to quantify alcohols and higher hydrocarbons. The levels of carbon dioxide, methane, C2+ hydrocarbons and alcohols were calculated from peak areas to determine the extent of conversion of CO₂ and the selectivity of the catalyst towards the various products at different conditions.

### 4.3 Results

In Figure 4.2, *ex-situ* diffraction patterns of the catalyst obtained after the various steps of the fabrication process are displayed. The first step in fabricating the catalyst, the calcination of the support at 350°C, did not result in changes to the XRD pattern of the support. The support peaks are broad but coincident with γ-alumina. After impregnating and drying the support, several peaks attributable to a cobalt (II) nitrate phase
appear in the diffraction pattern. After oxidizing the dry, impregnated catalyst material at 250°C in air, Co₃O₄ and γ-alumina peaks are observed in the XRD pattern [Figure 4.2]. Further treatment in hydrogen at 350°C for 24 hours resulted in the appearance of CoO, and fcc Co metal along with residual Co₃O₄. There is a small but present shoulder on the left side of the peak near 45° 2-theta in the patterns of the final product in Figures 4.2 and 4.4 which correspond to fcc cobalt. Multiple preparations of the catalyst resulted in slightly varying diffraction patterns in terms of the relative intensity of Co₃O₄, CoO, and fcc Co peaks [Figure 4.4]. For example, the fcc cobalt peak of catalyst #2 in Figure 4.4 is more apparent than from the other two preparations to which it is compared.

![XRD patterns of the Co/Al₂O₃ catalyst at various points during fabrication of the material.](image)

**Figure 4.2** XRD patterns of the Co/Al₂O₃ catalyst at various points during fabrication of the material.
Figure 4.3 TGA of Co(NO$_3$)$_2$·4H$_2$O in air.

Figure 4.4. XRD patterns of the support and three repeated preparations of the Co/Al$_2$O$_3$ catalyst.
Figure 4.5 *in-situ* XRD patterns obtained during the hydrogen reduction step of the catalyst preparation demonstrating the slow evolution of fcc cobalt metal.

The *in-situ* XRD measurements [Figure 4.5] also reveal that Co$_3$O$_4$ is the exclusive cobalt phase present after oxidizing the cobalt (II) nitrate impregnated support. The Co$_3$O$_4$ phase was found to partially convert to CoO during the 0.5°C/min temperature ramp to 350°C under flowing hydrogen. After reaching temperature, the Co$_3$O$_4$ and CoO peaks gradually reduced in intensity over the next 20 hours and the fcc Co peak became more prominent in each successive scan. The peak from fcc cobalt in the *in-situ* XRD is more prominent than the peak obtained from *ex-situ* measurements. The *ex-situ* samples were
exposed to air prior to obtaining the diffraction patterns while the in-situ samples were maintained in a hydrogen environment during measurement.

**Figure 4.6.** FESEM micrographs of the alumina Catalox support in the as received state (A), and after the final reduction step in the preparation of the catalyst (B).

**Figure 4.7.** SEM-EDX image and elemental map of aluminum and cobalt of a support particle loaded with cobalt after the final reduction step in the preparation, and of the blank support in the as received condition.
Table 4.1. CO$_2$ conversions and product selectivities as measured by gc-tcd across variables of temperature, pressure and flow rate for a 2:1 H$_2$/CO$_2$ feed on the Co/Al$_2$O$_3$ catalyst.

<table>
<thead>
<tr>
<th>#</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>GHSV (L/h/g)</th>
<th>CO$_2$ Conversion (%)</th>
<th>CO</th>
<th>CH$_4$</th>
<th>&gt;C2</th>
<th>R-OH</th>
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<tr>
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<td>150</td>
<td>12</td>
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<tr>
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<td>12</td>
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<td>20.7</td>
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<td>71.0</td>
<td>21.1</td>
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</tr>
</tbody>
</table>

In Table 4.8 quantitative conversions and selectivities from the 2:1 H$_2$/CO$_2$ feed are tabulated. Temperatures between 150°C and 350°C, and pressures between 2 bar and 14 bar were tested. The conversion and selectivity vary with temperature, pressure and space velocity. CO, hydrocarbons and alcohols are seen to evolve with the best conversion rates and selectivities towards hydrocarbons occurring at the upper range of these conditions. Temperatures at or above 275°C were required at all pressures and space velocities tested.
in order to obtain conversions in excess of 10%. Between 225°C and 350°C the methane selectivities fall between 65% and 88%, depending on the pressure and space velocity.

An increasing selectivity towards higher hydrocarbons is observed by increasing the pressure from 2 bar to 14 bar. Comparable methane selectivities can be obtained at both pressures, but at 14 bar, the balance is composed less by CO and more by C2+ hydrocarbons. At 14 bar, the selectivity towards C2+ hydrocarbons was as high as 26.3% while the CO selectivity was about 7% for all temperatures at this pressure. At 2 bar, the greatest C2+ selectivity observed was 4.0% while the CO selectivity varied from 16.0 to 46.0% with the balance comprised of methane.

Increasing the temperature increased the conversion rate. In tests 1, 2, 3, and 5 at 2 bar, the conversion rate increased incrementally with temperature from 3.0% at 150°C to 21.4% at 325°C. At 7 bar, conversion increased from 4.4% at 225°C in test 9 to 42.3% at 350°C in test 11, even though the space velocity was also increased by a factor of 2 in these tests. The same trend in conversion rate with temperature is also observed in the 14 bar tests with conversions increasing from 10% at 200°C in test 12 to 31% at 275°C in test 15.

At 14 bar, increasing the temperature from 200°C to 275°C shifted selectivity towards C2+ hydrocarbons and away from methane and methanol with little effect on the CO selectivity. At 2 bar, increasing the temperature from 225°C to 325°C shifted selectivity toward methane and away from CO. Further increase to 350°C at this pressure shifted selectivity toward back towards CO and away from methane.

The changes to CO₂ conversion by adjusting flow rates at 275°C were more pronounced at 14 bar than at 2 bar. At 2 bar, halving the flow rate from 12 L/h/g in test 3
to 6 L/h/g in test 4 only increased the CO\textsubscript{2} conversion from 13.1\% to 14.1\%. At 14 bar, the same reduction in flow rate increased the CO\textsubscript{2} conversion from 19.0\% to 31.0\%. Selectivities also exhibited a pressure dependent sensitivity to flow rate. At 14 bar, the CO selectivity was unaffected by the above flow rate change, while at 2 bar, halving the flow rate increased the CO selectivity from 16\% to 28\% at the expense of methane.

4.4 Discussion

4.4.1 Catalyst structure

The support phase and evolution of the cobalt phases during fabrication was tracked by XRD [Figures 4.2, 4.4 and 4.5]. The support phase was determined to be \(\gamma\)-alumina by XRD. Calcining the support in air at 350\(^\circ\)C, the greatest temperature to which it is exposed during fabrication, did not cause any phase change to the support or any structural modifications such as grain growth or crystalline ordering in a significant enough fashion to shift peak positions or peak width.

The 250\(^\circ\)C air oxidation of the support impregnated with cobalt (II) nitrate yielded Co\textsubscript{3}O\textsubscript{4} dispersed on the alumina. The presence of Co\textsubscript{3}O\textsubscript{4} after this step was expected, based on the air TGA of Co(NO\textsubscript{3})\cdot4H\textsubscript{2}O\textsubscript{(s)} [Figure 4.3] where the weight loss halted at 250\(^\circ\)C with the residual weight expected for the conversion of Co(NO\textsubscript{3})\cdot4H\textsubscript{2}O\textsubscript{(s)} to Co\textsubscript{3}O\textsubscript{4}. The Co\textsubscript{3}O\textsubscript{4} phase is known to be dispersed on the alumina because Co and Al occur in exclusive association after the final processing step as determined by SEM-EDX [Figure 4.7]

A pertinent question is whether it is possible to oxidize the nitrate less extensively to CoO rather than Co\textsubscript{3}O\textsubscript{4}, because this might increase the extent of reduction. From the
TGA, we see that CoO does not form during the decomposition in air because the conversion to CoO involves a greater weight loss than what is observed here. CoO is not an intermediate species in the decomposition of the cobalt (II) nitrate that can be obtained by oxidizing at lower temperatures.

$\text{Co}_3\text{O}_4$ fully reduces to metallic cobalt by 350°C under hydrogen.\(^{52}\) Here, when $\text{Co}_3\text{O}_4$ is supported on the alumina support, CoO and $\text{Co}_3\text{O}_4$ are retained even after 24 hours at 350°C under hydrogen [Figures 4.2, 4.4 and 4.5]. This is the result of an interaction between the support and the supported phases and a second indicator in addition to the SEM-EDX measurements that the cobalt phases occur exclusively as supported on the alumina. If the cobalt phases and alumina were not in close physical association, the interaction between the two phases would be negligible and the cobalt would have fully reduced to the metal.

The cobalt allotrope that results from the reduction in hydrogen at 350°C is the fcc phase. The hcp allotrope of cobalt metal is usually considered to be the stable phase below 425°C,\(^{131}\) transforming to the fcc phase above this temperature. The presence and composition of a support has elsewhere been reported to effect the phase of cobalt metal that is obtained from the reduction of $\text{Co}_3\text{O}_4$.\(^{132}\) The extent of conversion to metal was greater in the in-situ XRD measurement as compared to the ex-situ XRD measurement [Figures 4.2 and 4.5] probably due to exposure of the catalyst to air for the ex-situ experiment.

The in-situ XRD measurements reveal that reduction to CoO and Co occurred progressively over the course of 18-20 hours without evidence of further reduction in the
XRD pattern out to 24 hours. A soak time of at least 18 hours at 350°C in hydrogen is required to reduce the Co₃O₄ to the fullest extent possible. Carrying out the reduction beyond the time interval used in this preparation (24 hours) is not likely to yield a significantly greater extent of reduction.

The variation in the extent of reduction of Co₃O₄ to CoO and Co across multiple preparations of the catalyst [Figure 4.4] might reflect sensitivity to the details of the incipient wetness impregnation. The nature of the dispersity of the cobalt phases on the alumina could be sensitive to physical variables other than the ratio of solution volume to mass of support used during the impregnation, such as the manner in which the solution and the support are mixed.

The morphology of the catalyst as observed by FESEM is not remarkably distinguishable from the morphology of the neat support [Figure 4.6]. The absence of a clear new structure in the micrographs after synthesis qualitatively suggests the cobalt phases are highly dispersed on the support.

4.4.2 Activity and reactivity of the catalyst in CO₂/H₂ feeds

The fact of appreciable C2+ selectivity at reasonable conversion rates, and the pressure dependence of the C2+ activity, are unique data [Figure 4.8]. The observation of CO as a product means that at least a portion of the hydrocarbon products evolve from a CO* intermediate. The presence of methane indicates a CH₃* intermediate and the presence of higher hydrocarbons indicates a CH₂* intermediate. The CH₂* intermediate may induce chain initiation and growth by the mechanism depicted in Figure 1.6.
A greater selectivity towards higher hydrocarbons at greater pressures at the expense of CO selectivity may be explained by a variable competitive surface coverage between CO$_2$* and H*, which favors H* at higher pressures, and by the presence of two competing reaction pathways with relative rates that depend on the H*/CO$_2$* surface coverage ratios. Increased total pressure may enhance the kinetics of a pathway that proceeds through a chain forming CH$_2$* intermediate, but not a CO* intermediate as in pathway B of Figure 4.8, at the expense of a pathway that proceeds through a CO* intermediate, but not a CH$_2$* intermediate as in pathway A of Figure 4.8. Increased H* levels at higher total pressures may promote hydrogenation of CO$_2$* to HCOO* at the cost of CO$_2$* scission to CO*. If increased H*/CO$_2$* ratios do occur at higher pressure, this would account for the decreasing CO* selectivity at higher pressures.

Figure 4.8. Possible reaction pathways that account for observed reactivity where pathway A is favored at lower pressure (2 bar) and pathway B is increasingly favored at higher pressure (14 bar).

To explain the increased selectivity towards higher hydrocarbons at higher pressures, a change to the reactivity of the H$_x$CO* intermediate(s) common to both pathways in Figure 4.8 may be invoked. At low pressure, the common H$_x$CO* intermediate
species may preferentially hydrogenate to H₃CO*, subsequently yielding CH₃* without involvement of CH₂* so that chain initiation will not occur. At high pressures increased H* levels may preferentially hydrogenate the common H₂CO* intermediate to HₓCOH* from which C-O bond scission occurs yielding CH* or CH₂* which can participate in chain initiation and growth.

It is a reasonable assumption that increased H*/CO₂* ratios would result in a preferential hydrogenation of CO₂* over scission of CO₂* to CO*. There is less reason to assume that increased H*/CO₂* ratios would cause a preferential conversion of the HₓCO* intermediate to HₓCOH* (for x = 1 or 2) over the conversion to H₃CO*. However, doing so qualitatively links the model to the data.

The scheme suggests that modifications to the catalyst that promote H* coverage over CO₂* coverage may yield selectivity towards higher hydrocarbons by promoting reactions that lead to CH₂*. Note that increased coverage by H* would also tend to increase the rate of CH₃* hydrogenation to methane, so there may be a limit to the effectiveness of such a strategy. Assuming the validity of the proposed scheme, a better strategy might consist of a means of promoting C-O bond scission in the HₓCO* intermediate before hydrogenation to x=3.

The proposed scheme can be tested by carrying out the reaction from lean to rich partial pressures of H₂(g) at constant CO₂(g) partial pressure in order to vary coverage by H*. If the pathways of this scheme occur, and their relative rates shift due to increasing H* coverage as proposed, CO(g) selectivity will drop and C₂+ will increase with increasing H₂(g) partial pressure. The scheme can be disproved if increasing H₂(g) partial
pressures results in increased CO\textsubscript{(g)} selectivity, or decreased C2+ selectivity. Such an experiment should be carried out with a CO\textsubscript{2(g)} partial pressure at or above its partial pressure in the 14 bar experiment (4.66 bar) because this is the pressure at which C2+ hydrocarbons were seen to evolve. For the same reason the temperature should be 275°C, or possibly greater. The H\textsubscript{2(g)}:CO\textsubscript{2(g)} ratio should be varied from roughly 1:10 to 10:1.

The temperature dependence recorded for these reactions serve to outline the selected temperatures for any future analysis. A temperature of at least 225°C was required to achieve CO\textsubscript{2} conversions in excess of 10%, at all conditions tested, and conversion increased with temperature. Selectivity was also altered by temperature. Apart from stating the different responses to temperature at different pressures earlier stated, little can be postulated about mechanisms or intermediates from the changes to reactivity and selectivity with temperature. We can see that the selection of a space velocity between 3 and 12 L/h/g is a reasonable range of values from which to select for future studies of this system. Knowing this behavior, comparisons across different conditions can be made more readily using a consistent flow rate selected from this range.

4.5 Conclusions

The evolution of structure during the synthesis of a Co/Al\textsubscript{2}O\textsubscript{3} catalyst prepared by incipient wetness impregnation has been observed. The cobalt phases were seen to occur exclusively in association with the γ-alumina support. The cobalt (II) nitrate first oxidized to Co\textsubscript{3}O\textsubscript{4} in air and was then gradually reduced, partially, over 20 hours, to CoO and Co metal. Interactions with the support prevented full reduction to the metal. The influence
of the parameters of temperature, pressure and flow rates on conversions and selectivities have been broadly mapped and used to formulate an initial hypothesis concerning mechanism. More specific tests relating to the mechanism of formation of C2+ hydrocarbons have been proposed based on this initial postulate and knowledge of the parameters required to obtain the conversions and selectivities of interest.
5.1 Overview

In a traditional example where the acidity and basicity of a heterogeneous catalyst has been thought to direct catalytic activity and specificity, acidic catalysts have historically been thought to promote the dehydration of an alcohol to an olefin, while basic catalysts tend to promote dehydrogenation of an alcohol to an aldehyde or ketone\textsuperscript{86,133}. However, while some basic catalysts do in fact promote dehydration to an olefin, they result in a different placement of the double bond than what is obtained from acid catalysts. ZrO\textsubscript{2} has been industrialized as a basic catalyst in the dehydration of 1-cyclohexylethanol to vinylcyclohexane\textsuperscript{86}. Acidic Si impurities must be removed from this catalyst by treatment with NaOH in order to limit side products. The acid/base character of oxide catalysts also dictate cis/trans isomerism of double bond migration reactions. The basic catalyst of alumina loaded with NaOH and Na metal (Na/NaOH/Al\textsubscript{2}O\textsubscript{3}) is used industrially for selective double bond migration at low temperatures (under 300 K)\textsuperscript{134}. Acidic catalysts are used extensively in petroleum refining techniques including for decarboxylation, cracking, and isomerization among other reactions\textsuperscript{87,135}. 


CO₂ is frequently used as a Lewis acid probe for surface basicity in temperature programmed desorption (TPD) studies to relate the number and strength of Lewis base sites on different heterogenous catalysts to catalytic behavior.\textsuperscript{86,88-93} This procedure has resulted in a determination that the presence of acid/base pair sites, redox couples, and facile structural oxygen are more determinative than surface basicity alone towards the dehydrogenation of alcohols.\textsuperscript{88,89} Specifically, preparations of OMS-2 doped with copper have greater reactivity towards the conversion of 2-propanol to acetone than undoped native OMS-2 even though their basicity was similar as determined by CO₂ desorption. The copper doped OMS-2 also has greater specificity and reactivity towards 2-propanol conversion to acetone than MgO and γ-Al₂O₃ despite the fact that the Mg and Al oxides have more basic sites than OMS-2 as ascertained from CO₂ TPD measurements.

However, these conclusions partly depend on assuming that CO₂ behaves as a Lewis acid towards a surface, and it is not immediately obvious that this is always the case. A cursory examination of bonding in carbon dioxide extending from molecular orbital structure and valence bond theory, discussed in the next section of this chapter, illustrates plausible mechanisms by which the molecule can adsorb to an oxide surface as a Lewis acid or as a Lewis base or both. These descriptions make it clear that more detailed examination by experiment or calculation is required in order to determine the acid-base character of CO₂ adsorbing on any given oxide. This has been done experimentally, for example, on α-Cr₂O₃ where CO₂ adsorbs in structures with different acid/base character on different surfaces.\textsuperscript{90,92}
This research seeks to use experimentally determined binding energies of the C 1s, O 1s, and Mn 2p photoelectrons to identify the direction of charge transfer between the CO\textsubscript{2} and the surface. Binding energies from species which have accepted charge or are coordinated by a Lewis base will shift to lower values. Binding energies from species which donate charge or coordinate to a Lewis acid will shift to higher values.

The nominal composition of OMS-2 is KMn\textsubscript{8}O\textsubscript{16} and its structure is well described elsewhere\textsuperscript{136}. The average oxidation state of Mn is usually reported to be about +3.8. Most Mn cations have a 4+ oxidation state, and the K\textsuperscript{+} ion acts as charge balance for Mn\textsuperscript{3+} cations and, to the extent they exist, for Mn\textsuperscript{2+} cations. The structure consists of corner and edge shared MnO\textsubscript{6}\textsuperscript{δ−} octahedra arranged in a framework around tunnels that run along one crystallographic direction with a width of two edge shared octahedra (0.46 nm). The K\textsuperscript{+} ions occur within the tunnels.

As will be described in more detail, this study uses thin films of oriented nanocrystalline OMS-2 arrays to probe the adsorption of carbon dioxide onto specific OMS-2 surfaces. It is perhaps more accurate to say that the adsorption is probed onto OMS-2 surfaces except those surfaces which are specifically excluded. The orientation of the OMS-2 crystallites in the array exclude participation from tunnel sites which open to the surface. Photoelectrons will be ejected preferentially from surfaces which compose the framework surrounding the tunnels.
5.2 Predictions of CO$_2$ Bonding Behavior Towards a Metal Oxide Surface

Possible behaviors and geometric configurations of carbon dioxide acting as an acid or base towards a surface can be predicted or rationalized through an examination of the carbon dioxide molecular orbital (MO) structure and energy as a function of OCO bond angle in the Walsh diagram of Figure 5.1. The 8 orbitals occupied by the valence electrons up to the degenerate 1\(\pi_g\) HOMO orbitals, and the degenerate 2\(\pi_u\) LUMO orbitals in the linear case are depicted on the right-hand side. The ground state is linear because the net change in total energy of the occupied molecular orbitals is positive when the

![Walsh diagram for carbon dioxide](image)

**Figure 5.1** Walsh diagram for carbon dioxide. Energy scale is qualitative.
molecule is bent from the ground state. In the bent state, the LUMO degeneracy splits and the $6a_1$ orbital becomes the sole LUMO. The energy of the $6a_1$ orbital varies sharply with bond angle such that if coordinated by a surface species or populated with electrons to form a discrete $\text{CO}_2^{\delta-}$ anion, a bent configuration will result for the ground state structure.\textsuperscript{90} The nodal patterns predicted for the $6a_1$ LUMO of carbon dioxide in a bent configuration, the $6a_1$ HOMO for the $\text{CO}_2^{\delta-}$ anion, and the $2\pi_u$ LUMO of the linear ground state are depicted in Figure 5.2.

![Figure 5.2](image)

**Figure 5.2** Nodal pattern for the carbon dioxide ground state LUMO, the bent configuration LUMO and the ground state $\text{CO}_2^{\delta-}$ anion HOMO.

These patterns may be inferred from the Walsh diagram, and are consistent with calculations performed in the literature\textsuperscript{137} and by Kriz.\textsuperscript{138} The nodal pattern of the $6a_1$ LUMO in the bent state is more conducive towards $\sigma$ bonding interactions than are the $2\pi_u$ LUMOs in the linear condition. Additional stabilization might therefore be afforded to a bent $\text{CO}_2$ complex through coordination in a sigma configuration at the carbon atom to the $6a_1$ LUMO due to better overlap and less destructive interaction.
The above description predicts or rationalizes behavior of CO$_2$ as a Lewis acid, accepting electrons from the surface into the 6a$_1$ LUMO. Electrons may also plausibly be donated from occupied orbitals in the CO$_2$ to a surface. A pi interaction with a 1π$_g$ HOMO behaving as a Lewis base localized to one end of the molecule may occur. The molecule might also bind with two surface acid sites centered on the oxygen atoms in a bridging configuration. A greater degree of stabilization due to $\sigma$ bonding interactions can be envisioned through interactions involving one of the two degenerate 1π$_u$ molecular orbitals lying just below the 1π$_g$ HOMO orbitals due to its potential for more extensive constructive overlap based on the nodal pattern. The energy of the 1π$_g$ HOMO orbitals in linear charge neutral carbon dioxide increases as the molecule bends. If electrons in these orbitals coordinate to surface sites as a Lewis base, there is no energetic incentive for the molecule to adopt a bent ground state structure.

![Resonance structures for CO$_2$](image)

**Figure 5.3** Resonance structures and formal charges for carbon dioxide in a bent configuration (equivalent structures omitted).

Lewis structures based on valence bond theory can also be used to rationalize the behavior of CO$_2$ towards a metal oxide surface as a Lewis acid or Lewis base. The resonance structures in Figure 5.3 result for carbon dioxide in a bent configuration if it is
assumed that the carbon atom in the bent molecule is sp\(^2\) hybridized. The central carbon atom in this configuration has only one 2p orbital with which to participate in pi bonding, so the resonance structures contain a single pi bond, with the second pair of delocalized electrons written to occupy an atomic orbital either on the carbon atom or an oxygen atom, resulting in formal charges.

The sp\(^2\) atomic orbital on the bent carbon atom can plausibly become involved in bonding as either a Lewis acid or Lewis base with a surface species while the lone electron pairs on the oxygen atoms could behave as a Lewis base towards a surface species. Various combinations of these possibilities and the resulting net formal charges to the carbon dioxide adsorbate are depicted in Figure 5.4. Structure 1 may occur with two cations which do not possess an anion in line between them. Structures 2 and 4 correspond to species that behave as an acid and a base simultaneously where the sp\(^3\) orbital on the carbon atom is coordinated by a basic surface species and lone pairs on the oxygen atoms coordinate to acidic sites. In structure 3, the donation of two delocalized electrons from the molecule to a bond between the carbon atom and a metal cation has no obvious analogy to a bonding configuration in the MO treatment but is not forbidden in a VB treatment. Structures 5 and 6 in which the carbon sp\(^2\) orbital is coordinated by a basic surface site is analogous to a sigma coordination to the 6a\(_1\) LUMO in bent CO\(_2\) by a basic surface species.

Structures 4 and 6 are sometimes referred to as carbonates since the carbon is bonded with three oxygens. A surface oxygen is incorporated into the carbonate structures along with the two oxygens from the molecule. In structure 4, the carbonate is coordinated to a metal in a bidentate manner. IR studies indicate that the oxygens coordinated to the
metal in this structure are equivalent by symmetry. Structure 6 is said to be a carbonate that bonds to a metal cation in a monodentate manner. The discrete bent $\text{CO}_2^-$ anion that does not share electrons in a coordinate bond is also a possible structure.

![Diagram of Lewis type bonding structures](image)

**Figure 5.4** Lewis type bonding structures in which $\text{CO}_2$ exhibits behavior as a Lewis acid, a Lewis base, or both simultaneously towards metal cations (M) and oxygen anions (O) on a metal oxide surface. The resonance forms of structure 3 involve only 2 electrons in contrast to the other resonance forms of the other structures which involve 4 electrons.

This is not an exhaustive list of possible adsorbate structures but carbon dioxide may behave as a Lewis acid, Lewis base, or both at the same time towards a metal oxide surface so that experimentation is necessary to determine actual behavior. The structures in Figure 5.4 are listed in roughly increasing order of the Lewis acid character of the $\text{CO}_2$ adsorbate. As charge accumulates on the adsorbate, one might expect the C 1s binding energy to decrease. In practice though, these species are not all distinguishable from one another on the basis of C 1s binding energy alone. However, since structures 1-3 have a net positive formal charge resulting from basic, electron donating characteristics of the carbon dioxide, they will result in C 1s binding energies near or above what is found for
phytisorbed CO$_2$. Structures 5 and 6 have net negative formal charges resulting from the acidic, electron accepting character of the carbon dioxide so that these core level binding energies will occur below what is found in the physisorbed state. It has been reported that the bidentate and monodentate carbonates of structures 4 and 6 have the same C 1s binding energies on α-Cr$_2$O$_3$. Structure 5 is therefore also indistinguishable from the carbonate species. While the carbonate species cannot be distinguished from each other on the basis of the C 1s binding energy alone, they can be distinguished from anionic CO$_2$$\delta^{-}$, CO, graphitic carbon, and carbide. The expected binding energies resulting from these species and physisorbed CO$_2$ are tabulated in Table 5.1.

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<th>C$^0$</th>
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**Table 5.1** C 1s binding energies reported for different species that develop from CO$_2$ adsorption onto solid surfaces.

5.3 EXPERIMENTAL

5.3.1 The Oriented OMS-2 Thin Film Nanostructured Substrate

An oriented, nanostructured OMS-2 thin film array, prepared and described by Espinal, was used for this investigation. The OMS-2 was deposited onto the (111) surface of a strontium titanate (STO) single crystal square about 1 cm$^2$ in area by pulsed
laser deposition (PLD). Salient features of this process are that laser pulses impinging on an OMS-2 powder at reduced pressure deposited a nanocrystalline thin film array of OMS-2 onto a nearby STO target substrate which was heated to 875 K. The nanocrystals composing the OMS-2 thin film were preferentially oriented on the STO substrate. The nature of the preferential orientation could be controlled by depositing the OMS-2 onto different STO surfaces. The (111) STO surface resulted in a triangular net of OMS-2 nanofibers 50 -100 nm in width and 500 nm in length. The major axis of the nanofibers was parallel to the STO surface and colinear with the 1-D crystallographic tunnel direction. The tunnel direction was therefore parallel to the STO substrate. Using such a microstructure in an XPS analysis of adsorbates onto the OMS-2 surface provides a degree of surface specific information. A single surface is not isolated for analysis, but contribution from adsorbates onto tunnel sites is preferentially excluded. This XPS analysis is therefore effectively isolated to behavior on exterior framework sites that compose the tunnel walls.

The fact that the thin film was formed at 875 K is also an important factor for this analysis. The sample used for the sXPS analysis must be thermally annealed in the ultra-high vacuum (UHV) chamber to temperatures of 700 K to 800 K in order to prepare a clean surface free of adventitious carbon. Not all OMS-2 preparations are thermally stable to these temperatures, but this sample was prepared at temperatures above the requirement for removal of adventitious carbon.

5.3.2 The sXPS Analysis
The sXPS analysis was carried out at the experimental endstation of beamline U12a at the National Synchrotron Light Source (NSLS). C 1s, O 1s, and Mn 2p spectra were obtained at different photon energies to take advantage of the most luminous flux possible, eject photoelectrons with a kinetic energy most effectively counted by the analyzer, and to minimize the photoelectron escape depth. The C 1s spectra were recorded with a 400 eV photon energy, the O 1s spectra were recorded with a 600 eV photon energy and the Mn 2p spectra were obtained with a 720 eV photon energy. A fixed analyzer transmission energy (FAT) of 10 eV was used, and photoelectron counts were obtained at 0.1 eV increments.

The sample was mounted onto a tantalum foil sample holder. Tungsten wire was spot welded to the tantalum to mount the sample to a liquid nitrogen cold finger. The cold finger allowed the sample to be cooled to 180 K. Photoelectron spectra were recorded at this temperature. The sample could also be heated by electrical resistive heating. An electrical current was passed through the tantalum foil via the tungsten wires such that temperatures in excess of 900 K were attainable. A K type thermocouple was spot welded to the back surface of the tantalum sleeve to measure temperature.

The C 1s peak from adventitious carbon with a binding energy of 284.8 eV was used to reference the work function of the system in order to convert the kinetic energy of photoelectrons to accurate binding energies. After making this measurement, the adventitious carbon was removed from the sample surface by annealing the sample at 800 K under UHV in the beamline endstation. It is highly unlikely that the annealing changed the work function because the K2p peaks did not shift position. A small percentage (~3-
5%) of the original C 1s signal from adventitious carbon could not be removed by annealing, but using higher temperatures risked decomposing the sample, so the experiment proceeded from that point. Spectra were obtained to ensure that no contributions form tantalum, strontium, or titanium were present from the sample holder or the substrate. After obtaining spectra from the clean surface, it was exposed to CO$_2$ at 180 K using high precision leak valves. The number of Langmuirs (L) of exposure was metered. 1 L corresponds to an exposure which results in single molecular layer of adsorbate on the sample assuming a sticking coefficient of 1. Exposure to an adsorbate at $10^{-6}$ torr for 1 second is equivalent to 1 L, giving the magnitude and units of 1 L as $1E10^{-6}$ torr s. By metering the CO$_2$ exposure at much lower pressures, about $10^{-8}$ torr, sub Langmuir precision can be delivered accurately to the surface. Spectra were obtained at 180 K after various dosing levels from 0.5 L up to 50 L. CO$_2$ was then desorbed from the surface by annealing. Spectra were obtained at 180 K after incrementally annealing to temperatures up to 725 K.

5.4 Results

An XPS survey spectrum using a 600 eV photon energy did not evidence any strontium, titanium, or tantalum, ensuring that no interactions of the CO$_2$ adsorbate with the STO substrate or the sample holder contributed to the C 1s and O 1s photoelectron spectra. The binding energy of the C 1s electrons from carbon dioxide adsorbed to the OMS-2 framework surface after exposures from 0.5 L to 50 L was 288.6 eV [Figure 5.5]. The C 1s peak in Figure 5.5 did not increase significantly in intensity or shift position with
exposures from 0.5 L to 50 L, but beam intensity is variable so a comparison of the intensity of the C 1s peak after 1 L and 50 L exposures to the K 2p peaks in Figure 5.6 is useful. The intensity of the C 1s peak compared to the K 2p peaks was not significantly altered by additional exposure beyond the first ½ L. Figure 5.6 shows no additional peaks in addition to the peak at 288.6 eV. The CO$_2$ is seen to desorb progressively from the sample by annealing in Figure 5.7, without any shift in the C 1s binding energy. The CO$_2$ was completely desorbed between 600 K and 725 K.

Figure 5.5 C 1s photoelectron spectra of the clean OMS-2 surface before and after exposure to carbon dioxide.
Figure 5.6  C 1s/K 2p photoelectron spectra identifying a single species resulting from the adsorption of CO\textsubscript{2} onto OMS-2 framework surfaces.

Figure 5.7  Desorption profile of CO\textsubscript{2} as observed by C 1s spectra at 180 K after exposure to the indicated elevated temperatures.
The O 1s spectrum from the clean surface in Figure 5.8 identifies two species. There is a peak at 529.5 eV and a smaller peak at 531.8 eV. The adsorption of the carbon dioxide resulted in the formation of oxygen atoms in two new chemical environments. One environment results in an O 1s binding energy of 531.8 eV, the same location as the smaller high binding energy peak from the clean sample. The second species has an O 1s binding energy slightly higher than the original 529.5 eV peak which shifted to 530.0 eV, clearly narrowing the separation between the two peaks. Unlike the O 1s spectra, the Mn 2p spectrum in Figure 5.9 was not modified by adsorption of CO₂.

![Figure 5.8 O 1s photoelectron spectrum of the clean OMS-2 surface before and after exposure to carbon dioxide.](image)
5.5 DISCUSSION

5.5.1 The C 1s spectrum

The C 1s peak position, the lack of additional adsorption after the first $\frac{1}{2}$ L exposure of CO$_2$, up to 50 L at 180 K [Figure 5.5] and the persistence of the adsorbate to temperatures in excess of 500 K [Figure 5.7] indicates chemisorption of the carbon dioxide. Physisorption would result in the accumulation of CO$_2$ multilayers and a subsequent increase in the intensity of the C 1s peak relative to the K 2p peaks after exposures beyond 1 L up to 50 L. This did not occur.

The 288.6 eV binding energy of the C 1s electrons is clearly a result of charge transfer from basic OMS-2 sites to a chemisorbed carbon dioxide. The C 1s binding energy falls between what is widely reported for adsorbed carbonate species and carbon monoxide,
and is within the range reported for the bent anionic \( \text{CO}_2^{\delta^-} \) moieties as tabulated in Table 5.1. Based on the C 1s binding energy, the occurrence of the dissociated species, CO, C\(^0\) and carbide can be ruled out. Structures 1-3 in Figure 5.4 (conjugate acids of \( \text{CO}_2 \)) and other potential structures which involve a net basic character of the carbon dioxide towards the surface can be ruled out.

Two questions remain to be answered. The first regards determining which of the surface species, the Mn cations or the structural oxygens, can be identified as Lewis base sites that donate electrons into the \( \text{CO}_2 \) complex. The second involves confirming a result based on the expectation of a discrete \( \text{CO}_2^{\delta^-} \) anion. If the discrete anion exists, then simultaneous, basic, electron donating character towards Mn cations will not be observed. Such electron donating character towards Mn cations would be expected in the bidentate coordination of the Mn cations by carbonate, but would be absent by definition in the case of a discrete \( \text{CO}_2^{\delta^-} \) anion.

### 5.5.2 The O 1s Spectrum

The acidic character of the \( \text{CO}_2 \) towards the OMS-2 is supported by the O 1s spectra which shifts as a result of charge donation from structural oxygens to the \( \text{CO}_2 \) adsorbate. The low binding energy peak at 529.5 eV in the spectrum of the clean surface is due to structural oxygen. The high binding energy peak at 531.8 eV on the clean surface is not readily identified but is probably due to water which is known to reside in the OMS-2 tunnels. Adsorption of \( \text{CO}_2 \) onto the surface resulted in two new surface oxygen species. The first is a new species that has a binding energy at 531.8 eV, the same position as the
unidentified species already present within the sample. This new species at 531.8 eV results from oxygen atoms bonded solely to carbon and not involved in bonding to the surface. The second new species involves structural O$^{2-}$ anions already present within the OMS-2 which have experienced a 0.5 eV increase in their O 1s binding energy as a result of charge transfer towards the CO$_2$ adsorbate. This shift to the binding energy of O 1s electrons from structural oxygen is consistent with either the coordination of structural oxygen anions to open orbitals on the CO$_2$ (according to their VB or MO constructions) or with their transfer of discrete charge to the CO$_2$ resulting in a CO$_2^{5-}$ moiety.

5.5.3 The Mn 2p Spectrum

It seems unlikely that Mn cations would coordinate or donate electrons to a CO$_2$ adsorbate given that most Mn cations in OMS-2 are already in a 4+ oxidation state. In fact, if oxidation of cations were evident in the Mn 2p spectrum, this might suggest a preponderance of Mn$^{3+}$ or Mn$^{2+}$ cations at the surface. However, semi-stable Mn$^{7+}$ oxidation states do exist in the permanganate ion and in manganese heptoxide (Mn$_2$O$_7$). Additionally, charge transfer from oxide cations to a CO$_2$ adsorbate is not without precedent. Molecularly adsorbed (non-dissociated) CO$_2$ has been observed to oxidize Ce$^{3+}$ to C$^{4+}$ in partially reduced CeO$_2$.\textsuperscript{152} In any case, there is no evidence in the Mn 2p spectra of charge transfer to the adsorbed CO$_2$ from the population of Mn$^{3+}$/Mn$^{4+}$ cations which comprise the OMS-2 framework surfaces. A 0.5 eV to 1 eV shift towards higher energy features in the Mn 2p spectrum is expected for 2+ to 3+ and 3+ to 4+ transitions.\textsuperscript{153} No such higher energy features in the Mn 2p spectrum were observed after adsorption of
carbon dioxide. Whatever the actual distribution of charge to surface Mn cations, they were not oxidized by CO$_2$ adsorption.

The remaining question is whether or not the CO$_2$ behaves with basic character towards Mn cations at the same time as it behaves with an acid towards oxygen anions as it does in the bindentate configuration of a CO$_2$ adsorbate. If the Mn cation sites were behaving with acidic character, accepting electrons associated with oxygen atoms in the carbon dioxide, this would be expected to result in the appearance of lower binding energy features in the Mn 2p spectrum after CO$_2$ adsorption. This is not observed.

5.6 Conclusions

Since charge transfer from structural oxygen to CO$_2$ results in a discrete CO$_2^{δ-}$ anion, and no charge transfer to or from the Mn cations is observed, the acid/base character of CO$_2$ towards framework sites on OMS-2 is concluded to be dominated by Lewis acidity towards basic structural oxygen anions. The most likely bonding configuration based on these data is a discrete bent CO$_2^{δ-}$ anion, probably located over a cation site, which has accepted electrons from structural oxygens into an open orbital. A discrete CO$_2^{δ-}$ anion over a cation site has previously been identified on (0001) α-Cr$_2$O$_3$ surfaces by infrared spectroscopy.$^{92}$ The sXPS data here cannot be used to definitively make a determination of adsorption site, but the source of electrons donated to the adsorbate is identified, an assertion difficult to make through IR spectroscopy.
CHAPTER 6
Conclusions and Future Work

6.1 SUMMARY OF RESULTS AND FUTURE WORK

The stated goals of making more effective use of existing energy vectors, diversifying the sourcing of existing energy vectors, and developing new energy vectors have been advanced through the development of an oxidation protection mechanism for carbon fiber reinforced CMC’s, the characterization of a potential hydrogen storage material, an evaluation of the efficacy of a Co/Al₂O₃ catalyst towards synthetic hydrocarbon fuels, and a determination of acidic character of CO₂ towards specific OMS-2 surfaces.

The mechanism by which heat treating carbon fibers prior to BN deposition results in a compliant interface has been isolated to changes induced to the fiber surface which prevent a strong bond from forming between the fiber and the BN. The precise nature of this change has not been directly observed but is likely due to the removal of reactive oxygen and nitrogen species or a reduction to the amount of surface “edge” carbon. Fiber heated to the CVD-BN deposition temperature and fiber heated to elevated temperatures up to 1600°C should be compared by techniques capable of quantifying the presence of these factors at the fiber surface. Oxygen and nitrogen might be measurable by XPS or AES, but a SIMS technique might be required to detect these species at the level they occur. Since the specimens are fibers, SAM and FIB-SIMS might be required for adequate sampling. TPD-MS experiments might be sensitive enough to detect a difference in the
quantity of nitrogen and oxygen species which evolve from C_{800} and C_{1600} with heat-treatment, but this is a bulk analysis and this study suggests that composites are more sensitive to the surface condition. HRTEM of microtomed fiber cross-sections at the edge of the fiber might reveal rearrangements to the surface that occur during heat treatment. Active surface area measurements from O_{2(g)} adsorption would provide evidence of surface rearrangement. Oxidation resistance across a wider range of temperatures and the behavior of 2-D composites should be investigated. Given the dramatic flexure behavior qualitatively observed for the 1-D composites examined here, the flexure behavior of a 2-D composite in a 4-point bending mechanical analysis might also be unique. SEM images from cut and polished cross sections from a 2-D composite that has been oxidation tested might directly reveal oxidative protection conferred by the interface coating at matrix cracks. The C/BN/SiC composite examined here demonstrated the efficacy of a BN fiber coating but is probably not the optimal configuration of a CMC. The optimal configuration probably consists of a multilayer interface coating and/or multi-component matrix. These systems can be developed using 1-D composites, then extended to 2-D composites.

There are some challenges associated with using ammonia borane as a fuel cell hydrogen storage system. Molecular aminoborane and borazine are unacceptable impurities in a fuel cell hydrogen stream. The evolution of aminoborane also represents a loss to the amount of hydrogen that can be generated from AB. Modified AB structures that might not evolve impurities should be investigated, including the complex of ethylenediamine with BH$_3$ as in the structure BH$_3$-NH$_2$-CH$_2$-CH$_2$-NH$_2$-BH$_3$. Importantly, the means of releasing hydrogen under development in this study requires that that
hydrogen release be net exothermic in character in order to initiate a self-propagating decomposition reaction in a fuel compact. DSC characterization will therefore be important.

The Co/Al₂O₃ catalyst demonstrated promising activity towards C2+ hydrocarbons. Carrying out reactions at a specified temperature, constant partial pressure of CO₂ and variable partial pressure of H₂ will test the validity of the hypothesized mechanism. The mechanism can be invalidated if increasing H* levels do not result in greater specificity towards C2+ hydrocarbons. The close association of the cobalt oxides with the alumina support during preparation of the catalyst affected the degree to which the cobalt oxide was reduced to the metal.

The manner of adsorption of carbon dioxide to OMS-2 framework surfaces has been observed to be a discrete bent, CO₂δ⁻ anion. This validates previous analyses which use CO₂ as a Lewis acid probe for surface basicity. This activated form of CO₂ could be an intermediate species on OMS-2 supported iron in the conversion of CO₂/H₂ feeds to C2+ hydrocarbons.⁴ CO₂ might be hydrogenated on the OMS-2 from spillover of H* which forms on the iron surface. Espinal has prepared other oriented OMS-2 thin films on different single crystal STO substrate surfaces. Some of these films contain surfaces in which the tunnel sites are accessible by XPS analysis. Differences in CO₂ adsorption to these films from the case investigated here can be attributed specifically to adsorption on tunnel sites.


[168]


