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Department of Chemistry

NANOPOROUS CARBON MEDIATED CATALYSIS AND HYDROGEN ADSORPTION

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ABSTRACT

Polyfurfuryl alcohol forms a microporous, glassy carbon upon heating to >600°C under inert conditions. Polyfurfuryl alcohol (PFA)-derived carbons fall under the category of porous, non-graphitizing carbons and have a tunable porosity and surface area. These carbons have received significant attention due to their potential application in capacitors, fuel cell anodes and cathodes, as adsorbents and molecular sieves. Their narrow pore size distribution provides adsorptive selectivity which is based on size and shape. This limits the extent which those molecules can enter and diffuse through their porous network. By incorporating metal nanoparticles into PFA prior to the pyrolysis, catalytically active metal sites can be made that are sheathed by a layer of microporous carbon. The formation of active sites embedded within the porous surface can lead to selective catalysis with reactants that are able to diffuse through the pores. Gas phase reactions had been conducted on such catalysts and a high selectivity was observed for planar, linear molecules. Yet the use of these catalysts had not been expanded into liquid phase reactions due to pore size restrictions. In order to explore the use of such shape selective catalysts for liquid phase hydrogenation reactions, a newly synthesized PFA-derived carbon was examined for use in liquid phase. This forms the crux of this thesis.

A literature survey is provided in Chapter 1. It details the synthesis and formation of PFA-derived carbons, their use as molecular sieves, and applications for these carbons. There is also a review of the synthesis of boron-doped carbon to be used as a support for dispersing metal for enhancing hydrogen exchange processes including adsorption and desorption.

The formation and characterization of selective PFA-derived carbon catalysts is presented in Chapter 2. To form such catalysts, platinum nanoparticles were synthesized using the monomer, furfuryl alcohol, as the reducing agent. Then the nanoparticle and monomer mixture
was polymerized and cured to immobilize the nanoparticles within the polymeric solid prior to pyrolysis. By altering the solvent used in polymerization, mesoporosity was created, or not, while microporosity was retained.

Furthermore, the catalytic activity and selectivity of these catalysts were extensively studied and analyzed in Chapter 3 and Chapter 4. Chapter 3 describes catalytic activity and selectivity of the experimental catalysts compared to a conventional catalyst for liquid phase hydrogenations. Wholly microporous catalysts were not active, but those which were both microporous and mesoporous catalysts were. The active catalysts were shown to be highly selective toward linear, planar molecules. Chapter 4 applies mathematical models to describe the rate limitations of the catalysts as well as the effect of porosity on activity and selectivity.

In Chapter 5 and Chapter 6, a boron substituted carbon, $\text{BC}_x$, is described which was formed by chemical vapor deposition. This could be made either as a non-porous solid or as a thin layer on a high surface area silica aerogel. Chapter 5 outlines the effects of synthesis parameters on the as-synthesized bulk material. The chemical environment of boron in the material was thoroughly characterized and was found to be trigonal planar. Chapter 6 explores the use of high area silica aerogel as a support onto which $\text{BC}_x$ may be deposited. Synthesis and characterization of this material was followed by experiments aimed at measuring its adsorptive properties for hydrogen.

Chapter 7 concludes the work with suggestions on how to increase the activity of PFA-derived carbon catalysts while retaining selectivity. Some of the suggestions, provided with preliminary data, display how mesoporosity and concentration of available active sites are the major factor in activity, while microporosity is the contributing factor in selectivity. These three parameters are intertwined, and altering one correlates to changes in the others.
TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... viii
LIST OF TABLES ........................................................................................................... xiv
ACKNOWLEDGEMENTS ............................................................................................... xvi

Chapter 1 Carbon Materials: Synthesis, Functionalization and Applications .......... 1
  1.1 Introduction to Polymer-Derived Carbon ............................................................. 1
  1.2 Polyfurfuryl Alcohol-Derived Carbons ............................................................... 2
  1.3 Carbons as Catalyst Supports ............................................................................... 12
      1.3.1 Polyfurfuryl Alcohol-Derived Carbon as Catalyst Supports ...................... 13
  1.4 Boron-Carbon Materials ..................................................................................... 21
  1.5 Carbon Applications .......................................................................................... 27
      1.5.1 Catalyst Support.......................................................................................... 27
      1.5.2 Gas Adsorbent ......................................................................................... 28
  1.6 Organization of Thesis and Objective ................................................................. 29
  1.7 References ......................................................................................................... 30

Chapter 2 Controlled Synthesis and Characterization of Platinum Nanoparticles
Sequestered in Nanoporous Carbon ........................................................................... 40
  2.1 Introduction ........................................................................................................... 40
  2.2 Experimental ....................................................................................................... 44
      2.2.1 Reagents ..................................................................................................... 44
      2.2.2. Synthesis ................................................................................................... 45
      2.2.3 Characterization ......................................................................................... 47
  2.3 Results ................................................................................................................ 50
      2.3.1 Pore Volumes and Distributions for Pt₀/NPC .............................................. 50
      2.3.2 Pt₀ Size and Dispersion In the Carbon Matrix .......................................... 53
      2.3.3. Pyrolysis of Pt₀/PFA .............................................................................. 63
  2.4 Discussion .......................................................................................................... 72
      2.4.1 Solvent Effect on Pt₀ Formation ................................................................ 72
      2.4.2 Solvent Effect on the Porosity of NPC ...................................................... 73
      2.4.3 Influence of Platinum on the Pyrolysis of Polyfurfuryl Alcohol ............... 74
      2.4.4 High Temperature Treatment (HTT) Induced Pt₀ Sintering ....................... 78
  2.5 Conclusions ........................................................................................................ 83
  2.6 References ......................................................................................................... 83

Chapter 3 Sequestered Ptᵢ in the Matrix of Nanoporous Carbon: Shape Selectivity in
Liquid Phase Hydrogenations ................................................................................... 88
  3.1 Introduction ........................................................................................................... 88
LIST OF FIGURES

Figure 1-1: Structural representation of amorphous carbon [4] ...................................................... 2

Figure 1-2: The stages of furfuryl alcohol polymerization and the cross linking formation ... 6

Figure 1-3: The simulation of polyfurfuryl alcohol-derived carbon at a maximum temperature of 800°C and a density of 1.72 g/cm³ containing 1450 carbon atoms. (a) A fragment of the final structure displaying the presence of 5- and 7-member rings (noted in bold) and (b) a fragment of the model carbon showing a “hole” in the structure [27] .................................................................................................................................................. 9

Figure 1-4: Model structures found in PFA: (A) methylene bridge, (B) backbone conjugation, (C) 2, 5 carbons, (D) 3, 4 carbons, (E) terminal methyl group, (F) cross-links, (G) polyaromatic domain, (H) carbonyl group [3] ........................................................................................................................................ 10

Figure 1-5: Cumulative pore volume of PFA heated to 200, 300, 400, 500, and 600°C, calculated by the methyl chloride adsorption isotherm [3] ........................................................................................................................................ 11

Figure 1-6: Intrinsic hydrogenation rate constants vs. temperature from model regression [45] ................................................................................................................................................................. 18

Figure 1-7: Conversion of alkenes to alkanes as a function of reaction temperature using a 6.4wt.% platinum loaded nanoporous carbon catalyst [46]. ................................................. 19

Figure 1-8: Relationship between boron concentration and d_{002} layer spacing in BC₅ films [70] .......................................................................................................................................................... 24

Figure 1-9: Proposed formation and structure for BC₅ in which carbon rings are joined by boron atoms ................................................................................................................................................. 25

Figure 2-1: Pore volume of 20 wt.% platinum loaded nanoporous carbon made with Triton X-100, THF or no solvent (neat) ........................................................................................................ 51

Figure 2-2: Pore size distribution of 20 wt.% platinum loaded nanoporous carbon made with Triton X-100, THF or no solvent (neat) ........................................................................................................ 52

Figure 2-3: X-ray diffraction patterns of same platinum weight % (11 wt.%) Pt/NPC made with THF (NPC-THF) and Triton X-100 (NPC-TX) ...................................................................................... 53

Figure 2-4: X-ray diffraction patterns of Pt/NPC_TX after high temperature treatments (800°C and 900°C) under flowing Ar(g) ........................................................................................................... 54

Figure 2-5: Overlapped X-ray diffraction patterns of Pt[111] and [200] peaks for Pt/NPC_Triton X-100 post-high temperature treatment (800°C and 900°C) ........................................ 55
Figure 2-6: X-ray diffraction patterns of Pt/aC (platinum deposited on top of carbon) before and after high temperature treatments (800°C and 900°C) under flowing Ar(g)....

Figure 2-7: Overlapped X-ray diffraction patterns of Pt[111] and [200] peaks for Pt/aC post-high temperature treatments (800°C and 900°C) ..................................................

Figure 2-8(a): Transmission electron microscopy image of 11wt.% Pt loading in NPC_TX ........................................................................................................58

Figure 2-8(b): Transmission electron microscopy image of 11wt.% Pt loading in NPC_THF ........................................................................................................59

Figure 2-8(c): Enlarged TEM image of Pt nanoparticles for 11wt.% Pt loading in NPC_TX ........................................................................................................60

Figure 2-8(d): Enlarged TEM image of Pt nanoparticles for 11wt.% Pt loading in NPC_THF ........................................................................................................61

Figure 2-9(a): Weight loss curves as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX) ........................................63

Figure 2-9(b): Weight loss derivatives as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX) ........................................64

Figure 2-9(c): Mass-spectrometry detection of methane as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX) ........................................65

Figure 2-9(d): Mass-spectrometry detection of carbon monoxide as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX) ........................................66

Figure 2-9(e): Mass-spectrometry detection of carbon dioxide as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX) ........................................67

Figure 2-9(f): Mass-spectrometry detection of hydrogen as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX) ........................................68

Figure 2-9(g): Mass-spectrometry detection of oxygen as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-
PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX). ................................................................. 69

Figure 2-10: Model structures found in PFA: (A) methylene bridge, (B) backbone conjugation, (C) 2, 5 carbons, (D) 3, 4 carbons, (E) terminal methyl group, (F) cross-links, (G) polyaromatic domain, (H) carbonyl group. Where the temperature, T, is dependent on polymerization conditions (for uncured polymer ~300°C, for cured polymer ~350°C) of the polymer ................................................................. 74

Figure 2-11: Model structure of the complete breakdown of the polymer, PFA, thus creating the graphene-like sheet. Where the temperature, T, is dependent on polymerization conditions (for uncured polymer ~500°C, for cured polymer ~550°C) of the polymer ................................................................. 75

Figure 3-1: HRTEM of platinum that is embedded in the carbon matrix ........................................... 90

Figure 3-2: Plot of reactant conversion as a function of time for the hydrogenations of 1-hexene, 1-octene, 1-nonene, and 1-decene using 11 wt.% Pt loaded nanoporous carbon made with Triton X-100 as a function of chain length of the reacting alkene. ....... 96

Figure 3-3: Plot of reactant conversion as a function of time for the hydrogenations of 1-hexene, 1-octene, 1-nonene, and 1-decene using 10 wt.% Pt loaded activated carbon as a function of chain length of the reacting alkene ................................................. 97

Figure 3-4: 2D molecular structures of reactant used to probe effect on activity when an alkyl group is present ........................................................................................................ 98

Figure 3-5: Plot of reactant concentration as a function of time for hydrogenation of 2-methyl-1-pentene, 3-methyl-1-pentene, and 4-methyl-1-pentene using 11 wt.% Pt/NPC_TX, the synthesized catalyst. ................................................................. 99

Figure 3-6: Plot of reactant concentration as a function of time for hydrogenation of 2-methyl-1-pentene, 3-methyl-1-pentene, and 4-methyl-1-pentene using 10 wt.% Pt/aC. ... 100

Figure 3-7: 3D molecular structure of 1-hexene .................................................................................. 101

Figure 3-8: 3D molecular structure of 2-methyl-1-pentene ............................................................... 101

Figure 3-9: 3D molecular structure of 3-methyl-1-pentene ................................................................ 102

Figure 3-10: 3D molecular of 4-methyl-1-pentene .......................................................................... 102

Figure 3-11: Plot of reactant concentration versus time for the hydrogenation of 1-hexene, trans-2-hexene, and trans-3-hexene catalyzed by 11 wt.% Pt/NPC_TX. ............ 104

Figure 3-12: Plot of reactant concentration versus time for the hydrogenation of 1-hexene, trans-2-hexene, and trans-3-hexene catalyzed by 10 wt.% Pt/aC. ....................... 105
Figure 3-13: Schematic for the conformation of trans-2-hexene molecule inside the carbon nanopore. The carbon walls restrict the molecule to its pore mouth configuration, preventing \( \pi-\pi \) bond interactions with the active site..........................106

Figure 3-14: Plot of reactant concentration as a function of time for the hydrogenation of trans- and cis-hexenes using 11wt.% Pt/NPC_TX .................................................................108

Figure 3-15: Plot of reactant concentration as a function of time for the hydrogenation of trans- and cis-hexenes using 10wt.% Pt/aC .................................................................109

Figure 3-16(a): Plot of the concentration as a function time for the hydrogenation of 1,5-hexadiene for the synthesized 11wt.% Pt/NPC_TX catalyst .................................................110

Figure 3-16(b): Plot of the concentration as a function time for the hydrogenation of 1,5-hexadiene for the conventional catalyst, 10wt.% Pt/aC ..........................................................111

Figure 3-17: Plot of selectivity of products as a function of conversion in the hydrogenation of 1,5-hexadiene .........................................................................................112

Figure 3-18: Plot between molecule length and observed reaction rate using 11wt.% Pt/NPC_TX catalyst in the hydrogenation of straight, terminal alkenes .........................113

Figure 3-19: Possible reactions between C\(_6\) compounds during hydrogenation[18] ..........117

Figure 4-1: Plot of the observed rate of reaction as a function of total porosity for 1-hexene hydrogenation catalyzed by a) 11wt.% Pt/NPC_THF, b) 11wt.% Pt/NPC_TX, and c) 11wt.% Pt/NPC_PEG ........................................................................130

Figure 4-2: Plot of observed rate of reaction as a function of total porosity for 1-hexene hydrogenation catalyzed by a) 11wt.% Pt/NPC_THF, b) 11wt.% Pt/NPC_TX, c) 6wt.% Pt/NPC_PEG, and d) 10wt.% Pt/aC (conventional catalyst) ..........131

Figure 4-3: Relationship of observed reaction rate for 1-hexene hydrogenation and mesoporosity of the a) 11wt.% Pt/NPC_THF, b) 11wt.% Pt/NPC_TX, and c) 6wt.% Pt/NPC_PEG .........................................................132

Figure 4-4: The observed rate for 1-hexene hydrogenation as a function of microporosity of a) 11wt.% Pt/NPC_THF, b) 11wt.% Pt/NPC_TX, and c) 6wt.% Pt/NPC_PEG ........133

Figure 4-5: Pore size distributions calculated from methyl chloride adsorption data of three synthesized catalysts ........................................................................................................135

Figure 4-6: Plot of effectiveness factor vs. Thiele modulus for the conventional catalyst (red triangle) and the NPC catalyst (blue squares) in the hydrogenation of 1-hexene using catalyst particles with diameters of 125 and 30 microns, and 215 and 60 microns respectively .....................................................................................................141

Figure 5-1: Approximate span and location of lowest and highest signals in \(^{11}\)B NMR spectra of individual borane classes.[23] ........................................................................157
Figure 5-2: Proposed structure for BC\textsubscript{x} in which carbon rings are joined by B atoms which are in a trigonal configuration ..............................................................158

Figure 5-3: Schematic of the CVD reactor furnace used for the synthesis of BC\textsubscript{x}. (note: The UHP He\textsubscript{(g)} passes through an oxygen and moisture trap prior to being introduced to the benzene.) ..............................................................159

Figure 5-4: X-ray diffraction pattern of BC\textsubscript{x} .........................................................................................164

Figure 5-5: Raman spectra of BC\textsubscript{x} material .................................................................165

Figure 5-6(a): TEM image of BC\textsubscript{x} material displaying turbostratic regions .........................166

Figure 5-6(b): TEM image of highly graphitic regions of the BC\textsubscript{x} material .......................167

Figure 5-6(c): TEM micrograph of the BC\textsubscript{x} material illustrating highly graphitic regions in the material as well as turbostratic regions .............................................................................168

Figure 5-7: Ring diffraction pattern of the BC\textsubscript{x} sample. The inner ring correlates to an interlayer spacing of 0.338 nm..............................................................169

Figure 5-8: The solid state \textsuperscript{11}B HR-NMR spectrum displaying one chemical site for \textsuperscript{11}B, centered at 32 ppm. (Note: the asterisks signify the spinning sidebands observed for solid state NMR) ..................................................................................171

Figure 5-9: The XPS spectra with the curve fit for BC\textsubscript{x} film..............................................................172

Figure 6-1: The correlation between time duration of heat treatment at 900°C and yielding BET .............................................................................................................................................188

Figure 6-2: High resolution \textsuperscript{11}B Solid State NMR Spectra of aerogel coated with BC\textsubscript{x} material ...............................................................................................................................190

Figure 6-3: Comparison of the two normalized spectra; the bulk BC\textsubscript{x} material and the aerogel coated with BC\textsubscript{x}. Both samples were run consecutively at the same settings on the same spectrometer .............................................................................191

Figure 6-4: The hydrogen adsorption isotherms at 77K and 87K for an aerogel coated for 15 minutes .............................................................................................................................................193

Figure 6-5: The hydrogen adsorption isotherms at 77K and 87K for an aerogel coated for 30 minutes .............................................................................................................................................194

Figure 6-6: The hydrogen adsorption isotherms at 77K and 87K for an aerogel coated for 60 minutes .............................................................................................................................................195

Figure 6-7: The plot of concentration of hydrogen per unit area as measured by nitrogen adsorption versus the absolute pressure of hydrogen ..................................................................................196
Figure 6-8: The calculated heats of adsorption from the 77K and 87K isotherms for 15 minute BC$_x$/aerogel adsorbent, 30 minute BC$_x$/aerogel adsorbent, 60 minute BC$_x$/aerogel adsorbent, and the uncoated aerogel .......................................................... 198

Figure 7-1: Reaction scheme for dehydrogenation of higher alkanes (UOP Palcol Process)[6] ........................................................................................................................................ 211

Figure 7-2: Modified reaction scheme for dehydrogenation of higher alkanes using the Pt/NPC catalyst ....................................................................................................................................... 213

Figure 7-3: Step-by-step process of how to create NPC catalyst using BC$_x$ as a metal support to enhance the number of active sites ........................................................................................................................................ 215
LIST OF TABLES

Table 1-1: Propylene and isobutylene hydrogenation conversion using different catalysts. (Note: CMS denotes carbon molecular sieve, C is activated carbon. Data is gathered from Lafyatis et. al.[42] .................................................................16

Table 2-1: Structure and physical characteristics of solvents used in the polymerization of furfuryl alcohol. (Note: For Triton X-100, on average n = 9.5). ........................................46

Table 2-2: Relative porosity in terms of the % of the total volume as well as the average pore size, determined by methyl chloride adsorption ..................................................73

Table 2-3: Crystallite size and dispersion of Pt loaded carbon catalysts before and after high temperature treatments. (Note: 1Indicates same conditions: 5 hours at each specified temperature under flowing Ar, 2Determined by XRD, 3Calculated from the XRD data using Equation 2.4, 4Calculated from moles of H2 chemisorbed. n = 9.5 on average)........................................79

Table 3-1: Probe molecules with corresponding length and width calculated after minimized energies with MM2 simulations.................................................................95

Table 3-2: Molecular dimensions of reactants in probe study of alkyl group addition effect on hydrogenation activity.................................................................101

Table 3-3: Molecular dimensions and non-planarity of probe reactants in examining hydrogenation activity based on internal versus external double bonds .........................105

Table 3-4: Physical constants of the two stereo isomers, t-2-hexene and c-2-hexene ..........109

Table 3-5: Calculated reaction rates of internal/external alkenes hydrogenated by the experimental catalyst and the purchased catalyst..................................................114

Table 3-6: Ratio of observed reaction rates of the hydrogenation between internal and external alkenes........................................................................................................115

Table 3-7: The observed reaction rates using 11wt.% Pt/NPC_TX as the catalyst in the respective hydrogenation ......................................................................................116

Table 3-8: The selectivity of 1-hexene during the hydrogenation of 1,5-hexadiene ..........118

Table 3-9: Initial rates of reaction for the specified product along with the global rate for the hydrogenation of 1,5-hexadiene.................................................................119

Table 3-10: Calculated reaction rates of internal/external alkenes hydrogenated by the experimental catalyst and the conventional catalyst .............................................120

Table 3-11: Initial observed rates of reaction for the specified product along with the global rate for the hydrogenation of 1,5-hexadiene ..................................................121
Table 4-1: Specific porosity of catalysts calculated from methyl chloride adsorption.[1] ..............129

Table 4-2: Table comparing porosity with selectivity (note: selectivity calculated by taking the ratio of observed rates of the respective alkenes). .................................................133

Table 4-3: Weiss-Prater calculations were conducted for the hydrogenation of 1-hexene. Effective diffusivities were taken from previously published data (Note: The calculations were determined at reactant concentrations, \( C_s > 80\% \) of the initial concentration).[4-6] ...........................................................................................................137

Table 4-4: Effective diffusivities calculated from the kinetic data of 1-hexene hydrogenation. (Note: *assumed bulk diffusion) .....................................................................................144

Table 4-5: The calculated rates of adsorption based on liquid-phase uptake experiments ......146

Table 4-6: The diffusion coefficients calculated from liquid adsorption experimental data ...149

Table 4-7: The observed reaction rates for 1-hexene hydrogenation (note: the NPC catalysts contain the same amount of platinum, 11wt.%) .........................................................150

Table 5-1: Reaction parameters for a typical BC\(_x\) run ..........................................................................................160

Table 5-2: Chemical characteristics based on XPS, NMR, XRD and TEM. (note: 1 XPS concentration correlates to atomic %, 2 NMR concentration correlates to weight %, 3 NMR ratios are not just the ratio of B:C, but with B to all other elements in the material, i.e. O. Thus, it is considered to be the lower concentration boundary.) ........173

Table 6-1: Different time lengths at 900°C for Si aerogel and their corresponding surface areas .......................................................................................................................................125

Table 6-2: The initial hydrogen \( \Delta \text{H}_{\text{ads}} \) for each aerogel sample tested ..............................................126

Table 7-1: The effect of solvent molecular weight on the resultant catalyst pore volume (Note: Pore volumes measured by methyl chloride adsorption) .........................................127

Table 7-2: Summary of the effect of activation on a 10wt.% Pt/NPC-THF catalyst. (Note: 1 The metal dispersion calculated by CO chemisorption. 2 The percent conversion of 1-hexene is at the end of two hours.) .................................................................................................129
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Chapter 1

Carbon Materials: Synthesis, Functionalization and Applications

1.1 Introduction to Polymer-Derived Carbon

Carbon material can be derived from a wide variety of precursors including gases (ethane, light hydrocarbons), liquids (resins, pitch) or solids (coal, polymeric solids, wood). Both graphitizing and non-graphitizing carbon materials can be produced from polymeric precursors of which can either be natural or synthetic. Franklin showed that whereas polyvinyl chloride (PVC) when pyrolyzed produced a carbon that would graphitize at temperatures as low as 1000°C, when polyvinylidene chloride (PVDC) was blended with PVC, as in saran, the carbon resulting from pyrolysis of the blend resisted graphitization even at temperatures above 2000°C.[1] She and subsequent workers went on to classify many different polymers as either leading to graphitizing or non-graphitizing carbons upon pyrolysis.

The research described in this thesis is focused upon the use of carbons derived from polyfurfuryl alcohol (PFA). PFA is classified as a precursor that leads to non-graphitizing carbon with carbon residues of ~50% after pyrolysis. Recent work in our group has shown that crosslinking takes place during the acid-catalyzed polymerization of furfuryl alcohol (FA).[2, 3] The crosslinks in the polymer lead to the resistance of graphitization in the solid carbon. On the basis of accumulated data from multiple analytical techniques we have proposed that the structure of PFA-derived carbon is one that is highly reticulated with significant internal curvature and contains molecularly sized pores. The curvature arises from the formation of five- and seven-membered rings in addition to the predominant six-membered rings. Crosslinkages between
these structures lead to inherent stability against graphitization. Figure 1.1 is a graphical representation on the simulation of PFA-derived carbon structure.

![Figure 1-1 Structural representation of amorphous carbon. [4]](image)

1.2 Polyfurfuryl Alcohol-Derived Carbons

PFA-derived carbons are unique materials with variable surface areas and pore structures but narrow pore size distributions. PFA derived carbons were first reported in the early 1960’s. Early work by Lamond and Marsh characterized the physical properties of carbons derived from organic polymers, in particular, if they had similar characteristics as zeolites such as high surface areas.[5] They examined the apparent surface areas of the polymer derived carbon by carbon dioxide adsorption at 195 K and nitrogen at 77 K. They found that the adsorption of carbon dioxide was always higher than nitrogen and that an adsorption maximum occurred between 600
and 800°C. Their work determined that neat PFA-derived carbon had a maximum surface area of ~500 m²/g. However, their follow up work examined the use of CO₂ as an activation agent at 840°C; they reported that when activated the BET surface area of PFA-derived carbon can be pushed beyond 3000 m²/g.[6] They concluded that PFA-derived carbons adsorb in the micropores by capillary condensation, that is, say that at extremely low relative pressures the vapor condenses to a liquid inside of the pore due to an increased number of van der Waals interactions between the gas phase adsorbate inside the confined pore.

Lamond and Marsh’s work was followed up by the paramount works of Walker. Walker was the first to report that PFA-derived carbon could potentially be used as a molecular sieve.[7] Up to that point only Saran carbons (carbons derived from polyvinylidene chloride and polyvinyl chloride) had been demonstrated as carbon molecular sieves.[8-10]

Walker synthesized what he coined as “Composite Carbon Molecular Sieves” or “CCMS”. He used activated carbon as a support for PFA which was thermoset and then pyrolyzed to form a layer of molecular sieve material around a high surface area carbon. The adsorptive properties for the CCMS were measured by examining the uptake of several different adsorbates such as butane, isobutane, neopentane, benzene and cyclohexane. He concluded that the CCMS had slit-shaped pores, evidenced by the large difference between the adsorption of butane/isobutane. Butane is a planar molecule compared to isobutane which is branched and non-planar. Furthermore, a large difference was noted in the adsorption of benzene and cyclohexane, with a much higher uptake for the former. The larger uptake of benzene (planar) compared to cyclohexane (non-planar) provided more support that the pores were slit-shaped. The thesis of Schmitt, under Walker’s tutelage, detailed the findings of CCMS and their derivatives.[11] His work included the effect on increasing the ratio of PFA to support. As the concentration of PFA is increased the yielding surface area of the CCMS decreased abruptly based on isobutane and butane adsorption isotherms. It was noted that the surface area detected by isobutane adsorption dropped at
a much faster rate compared to the surface area determined by butane adsorption. Here, again, the synthesized material displayed preference for planar molecules compared to branched molecules. It was found that as the amount of PFA increased the adsorption properties of the composite became the adsorption properties of the carbonized PFA and not as the modified substrate.

Simultaneously, during Walkers findings, Fitzer and Schafer were reporting the first in-depth analysis of the formation of carbon from pyrolysis of polyfurfuryl alcohol.[12, 13] Their work studied the effects of heating rate, thermosetting, pressure, and temperature during the pyrolysis. By using differential thermal analysis, DTA, it was determined that PFA undergoes two significant weight loss periods during pyrolysis. The first happens at ~340°C and corresponds to water and carbon dioxide, based on gas analysis. The second maximum, at 440°C, corresponds to the formation of carbon monoxide and water. The release of decomposed byproducts resulted in small channels within the carbon, that resulted in it’s inherit micropore structure. The effect of crosslinking the polymer prior to the formation of carbon was also explored. Water and methanol adsorption isotherms were used to determine the respective pore volume. In their concluding remarks they noted that small modification of thermosetting resins do not affect the density, the shrinkage behavior and the pore structure.

The Hucke patent was granted in 1975. In it, Hucke outlined how to produce cohesive bodies of carbon with controlled porosity by blending a carbon yielding binder, a pore forming liquid, and a dispersant. The mixture could be poured into a casting material to form a self-supporting and physically handle able body. In the patented procedure Hucke noted that Triton X-100 acted as an excellent dispersant material. Triton X-100 allowed for the carbon yielding binder (furfuryl alcohol) and the pore forming agent (ethylene glycol) to form a homogenous mixture with uniform porosity upon pyrolysis. He stated, “As Triton X-100 was added in successively larger amounts with all other factors held constant, the pore size decreased steadily...”. In the work presented in this thesis it will be shown that this statement is not accurate and that Triton X-100,
itself alone, can act as a pore former. The patent also described the curing procedure used to produce carbon that has a minimum amount of shrinkage due to pyrolysis. The cured, or thermoset, procedure included subsequent warm water baths at temperatures in the range of 40°C to 100°C for periods of 1 to 24 hours.

The use of carbon molecular sieves for gas separation was demonstrated by Nandi and Walker.[14] They demonstrated that CMS preferred the adsorption of oxygen over nitrogen yet the conventional membrane displayed superior performance. However when the separation was conducted in the presence of water, the CMS displayed no change in performance where as the conventional adsorbent selectivity significantly dropped. To reverse the detrimental effect of water on the separation ability of the conventional membrane temperatures of 300°C were needed.

Chihara et. al. examined published data on micropore diffusivity of gases in carbon molecular sieves by applying physical interpretations.[15] They assumed a narrow pore size centered at 5Å with slit-shaped pores. Their calculations contributed a higher diffusivity for benzene through the CMS compared to other gaseous molecules, including much smaller molecules such at methane. Their work included the examination of potential barriers for diffusing into a 0.5 nm pore. The slit-shaped pores of CMS act as a physical barrier preventing pore adsorption for branched and other non-planar molecules.

In 1994 Mariwala et. al. examined the use of methyl chloride to determine the micropore size distribution of microporous carbon.[16] The conventional standard adsorbate, nitrogen, requires ultra low relative pressures which translate into absolute pressures in the range of $10^{-7} – 10^{-3}$ Torr; these ultra low pressures can be difficult to maintain in a standard porosimetry instrument. Another problem is that at the required temperature to overcome thermal motion of the N$_2$ molecule, 77K, the rates of adsorption in microporous carbons are incredibly slow because of activated diffusion. As a result of slow diffusion the diffusion coefficients are on the order of $10^{-11} – 10^{-16}$ cm$^2$/sec which equates to extremely long adsorption equilibration times.[17] Methyl
chloride does not require liquid nitrogen temperatures for adsorption, thus reducing the transport limited uptake difficulty of nitrogen. Furthermore, methyl chloride has a high vapor pressure at 273K which allows adsorption isotherms at absolute pressures in the range of 0.45 – 700 Torr. Mariwala applied the Horvath-Kawazoe model to the isotherms to predict the micropore pore size distribution.[18] He examined the micropore structure of several commercial carbons using conventional $N_2$ adsorption and compared that to methyl chloride adsorption. The results concluded that using methyl chloride as the adsorbate provided a much simpler method (less stringent temperatures: 273-293K, and shorter equilibration times) for elucidating the micropore pore size distribution. Expanded work on methyl chloride adsorption was able to measure the entire pore distribution of materials from nano- to macroscale.[19]

A mechanism for the polymerization and cross-linking of polyfurfuryl alcohol was postulated by Choura et. al.[20] Figure 1.2 displays the accepted polymerization and cross-linking mechanism for polyfurfuryl alcohol. The reaction proceeds via cationic polymerization where a proton attacks the hydroxyl group off the furfuryl ring to yield water and a carbocation which proceeds to attack other furfuryl alcohol molecules. The cross-linking proceeds when a linear chain attacks another linear chain to form an ethyl bridge or the chain backbone combines with the backbone of another linear chain by a Diels-Alder reaction.

![Figure 1.2 The stages of furfuryl alcohol polymerization and the cross linking formation.](image-url)
To obtain a physical representation of PFA-derived carbon Acharya et. al. conducted computerized simulations based on the following chemical and physical constraints:[4]

1. The nanopore size has mean size of 0.5 nm
2. The carbon hybridization is all sp²; hydrogen-to-carbon ratios are 0.5 – 0.0001
3. The H/C ratio decreases exponentially with increasing density
4. The enthalpies of formation of NPC are 5-10 kcal/mol above graphite
5. The densities lie in the range from 50 to 80% of that of graphite
6. The structural coherence falls off rapidly beyond 1.0-1.2 nm.

These criteria allowed for the computer modeling program SIGNATURE to generate a physical representation from random combinations of fragments. Figure 1.1 depicts the structure determined by Acharya et. al.

At the same time, Petkov, et. al. used pair distribution functions obtained from neutron scattering experiments on nanoporous carbon to examine the constrained physical structure.[21] Their work concluded that crystalline carbon or structural correlations are observed up to around 2 nm but are globally amorphous. That is to say that PFA-derived carbon does contain crystallinity but only on the short order (< 2nm).

Using High Resolution Transmission Electron Microscopy Kane et. al. observed that a significant physical and chemical reorganization occurs as a function of synthesis temperature for carbon molecular sieves derived from polyfurfuryl alcohol.[22] As the pyrolysis temperature is increased, the structure of the CMS transforms from one that is disordered and therefore highly symmetric to one that is more ordered on a length scale of 1.5 nm and hence less symmetric. The work also distinguished that the separation of N₂ and O₂ was strictly from the rate of internal transport within the CMS and not from a difference in surface interaction potential at equilibrium, commonly seen for commercial molecular sieves (i.e. zeolites). The maximum separation factor for
the two gases (N\textsubscript{2} and O\textsubscript{2}) occurred for a CMS that had been pyrolyzed at a maximum temperature of 600°C, which produces a mixture of both locally ordered and globally disordered carbon at the nanoscale.

An adsorption kinetic model for the adsorption processes of CMS was conducted by Nguyen and Do. [23] The model defined two consecutive processes: nonselective adsorption of molecules in meso-micropores followed by the movement of such adsorbed molecules into small micropores through the pore mouth barriers.[23] They used a commercial carbon molecular sieve to model adsorption processes. They argued that adsorption in CMS should be divided into selective and nonselective adsorption where selective adsorption was defined as adsorption in micropores, which imposes some exclusion effect against some adsorbates and nonselective adsorption is defined as all other adsorption. The activation energy at the pore entrance was calculated and observed to always be higher than the activation energy for surface diffusion inside the micropores. Hence, the entrance into the pore mouth is the limiting process for adsorption in micropores.

As noted in the Hucke patent, poly(ethylene glycol) (PEG) provided the pyrolyzed polymer with a higher volume of porosity. To explicitly understand this effect several synthesized mixtures that contained varied ratios of PEG and PFA were analyzed.[24] Furthermore, the effect of PEG molecular weight on the yielding polymer-derived carbon was explored as well. For pore analysis of the synthesized template carbons, Dextran with varied molecular weights was adsorbed from aqueous solutions. It was observed that as the ratio of PEG to PFA was increased the carbon yield after pyrolysis decreased, or inverse relationship was noted. This was not surprising since PEG is known to not be a carbon precursor.[25] Polyfurfuryl alcohol-derived carbons with PEG of molecular weight <2000 g/mol resulted in unconnected pores as no adsorption of the adsorbate medium was noted. However, it is observed that the Dextran adsorbates used in the analysis were of very high molecular weights, with the smallest at 9,900 g/mol. My interpretation is that the
adsorbate molecules are exclusive to meso- and macropores and are inhibited from entering micropores. Thus the effect of PEG additive on the pores in the micro-range was not determined.

A more recent structural model of PFA-derived carbon was conducted by Monte Carlo simulations (MC) in the canonical ensemble.[26] The developed algorithm examined an initial polyfurfuryl alcohol structure to nanoporous carbon. The pair distribution functions of the model structures generated using this method were found to match the experimental PDF of NPCs that show exceptional O₂/N₂ gas selectivity. Figure 1.3 is a reprint of the MC simulated amorphous carbons.[26]

![Figure 1.3](image_url)

**Figure 1.3** The simulation of PFA-derived carbon at a maximum temperature of 800°C and a density of 1.72 g/cm³ containing 1450 carbon atoms. (a) A fragment of the final structure displaying the presence of 5- and 7-membered rings (noted in bold) and (b) a fragment of the model carbon showing a “hole” in the structure.[26]
The genesis in the inherent porosity of carbon from PFA was investigated by Burket et. al. [2, 3] Their published experimental work revealed the underlying properties of polyfurfuryl alcohol that contribute to the porosity in polyfurfuryl alcohol derived carbon. To distinguish the contributing factors in pore formation several samples of polyfurfuryl alcohol polymer were pyrolyzed at different maximum temperatures. The maximum temperatures of interest were 200, 300, 400, 500, and 600°C. Each sample was analyzed using IR and $^{13}$C NMR as well as TGA-MS after the pyrolysis. The formation of carbon during PFA pyrolysis predicated is shown in Figure 1.4. The generation of porosity was observed to occur spontaneously at 300°C, in the micro- and mesopore range. Characterization of the char at this temperature revealed a loss of oxygen which confirmed the rupture of the furan ring ether linkages. The created porosity remained constant at 400°C however, at the onset of 500°C the amount of mesoporosity dropped considerably. The cumulative pore volumes can be seen in Figure 1.4.

Figure 1.4 Models of structures found in PFA: (A) methylene bridge, (B) backbone conjugation, (C) 2, 5 carbons, (D) 3, 4 carbons, (E) terminal methyl group, (F) cross-links, (G) polyaromatic domain, (H) carbonyl group.[3]
At 400°C the hydrogen content was reduced however, no significant changes resulted in the pore structure. When the maximum temperature is increased to 500°C a significant change is observed in the porosity of the char. Thermogravimetric analysis with an online MS detected the evolution of CO, CO$_2$, CH$_4$, and H$_2$O. The drop in mesoporosity is due to the loss of carbonyl groups (seen in Figure 1.4) and leftover heteroatoms. The microporosity is observed to increase at this temperature. Further heating the polymer to 600°C annealed the char by eliminating further oxygen and hydrogen moieties which decreased the mesoporosity. The inherent microporosity was conclusively attributed to crosslinks in the polymer that form odd membered rings upon being pyrolyzed, while the mesoporosity was largely contributed to oxygen moieties in the structure.
After examining the work on synthesis of polyfurfuryl alcohol-derived carbon, it is relevant to present the work that has been done on utilizing these unique carbons as catalyst supports.

1.3 Carbons as Catalyst Supports

The use of conventional catalyst supports such as alumina and silica in certain chemical reactions is problematic because at a high pH they dissolve at high enough rates to cause instability. Even in solutions at low pH, silica had been shown to dissolve.[27] One way to avoid dissolution when doing catalytic chemistry under conditions of high and low pH is to use carbon as the catalyst support. Simply put carbons do not dissolve or otherwise break down at extremes of pH. Other notable qualities of carbon supports include their mechanical strength and high surface area; they are chemically benign, easily and often cheaply produced, and the dispersed precious metal can be recovered by simply burning away the carbon support in air. Another advantage of carbon as a catalyst support is that its surface chemistry can be varied and controlled. This allows for the carbon support to be manufactured with various functional groups, depending on activation, which can be used as anchors for depositing precious metals. The benefits of controlling the surface chemistry include: increased metal dispersion, increased wettability, or, even use of a functional group as a catalyst or co-catalyst.[28-33] The surface modification can be achieved by two methods dry or wet activation.
1.3.1 Polyfurfuryl Alcohol-Derived Carbon as Catalyst Supports

Shape-selective carbon molecular sieves, CMS, (or more commonly referred to as Nanoporous Carbons, NPC) catalysts had been prepared as early as the 1970s, when Trimm and Cooper first reported the preparation of CMS-platinum catalysts.[34] Their work introduced a crude way of making selective carbon molecular catalysts. Mixing furfuryl alcohol, platinum oxide, formaldehyde and phosphoric acid together followed by carbonization. They examined the hydrogenation of linear and branched alkenes in the gas phase over the synthesized PFA-derived carbon support as well as platinum dispersed on a charcoal support for comparison. The CMS support displayed a much higher selectivity for linear alkenes compared to the charcoal support. However, the CMS support had a much lower activity than the charcoal support and deactivation was rapid.

This work was followed up by Schmitt and Walker, Jr.[11, 35] They published two papers that used polyfurfuryl alcohol as a carbon precursor for preparing carbon molecular sieve supports for metal catalysts. The first work was on the preparation of the system. Schmitt incorporated an active carbon as a substrate for platinum containing polyfurfuryl alcohol. When the polymer was carbonized it shrunk, due to loss of volatile decomposition products. When an activated carbon was incorporated as the substrate the shrinkage by the polymer was offset by the expansion of the activated carbon which resulted in macrocracks. The formation of macrocracks enhanced the concentration of diffusing molecules however, the inherent micropores from the carbonized polymer still displayed molecular selectivity in the adsorption of alkenes. Several competitive hydrogenation reactions were conducted to determine shape selectivity capability of the catalyst. For comparison a commercial catalyst was purchased which was platinum on activated carbon. The carbon-carbon molecular sieve (CCMS) catalyst displayed similar reactivities for the competitive hydrogenation of 1-butene and isobutene as the commercial
catalyst; however when 3-methyl-1-butene was substituted for isobutene a definite difference in catalytic reactivity was noted. The CCMS catalyst displayed little activity for the hydrogenation of 3-methyl-1-pentene (<2% at the end of two hours) while the hydrogenation of 1-butene was at 70% at the end of two hours. An equally interesting find was that the CCMS catalyst had an inverse effect on the hydrogenation of cyclopentene and 3-methyl-1-pentene compared to the activity of the commercial catalyst for the same reactants. The commercial catalyst displayed a higher conversion of 3-methyl-1-pentene while the CCMS had a higher activity for cyclopentene. Walker contributed this to the slit shaped pores of CCMS. The more planar molecules were preferentially adsorbed over non-planar molecules. Yet, the activity of CCMS catalyst was much lower than that of the commercial catalyst. The difference in activity was rationalized to be due to several factors including mass transport limitations for reactants and products and lower concentration of active metal sites.[36] The activated carbon filler in the CCMS increased the efficiency of the catalyst by the production of macrocracks in the solid, which lessen the diffusion path length in the micropores.

Similar gas phase hydrogenation work on CMS explored propylene as the reactant.[37] Evidence was provided that the rate determining step in gas phase propylene hydrogenation was activated diffusion. The hydrogenation itself was quick compared to the diffusion process. It was not certain whether the diffusion involved migration within a given pore system to a metal site or migration from a pore that does not contain metal to one that does.

A second and later series of CMS papers conducted by Walker in collaboration with Vannice explored PFA-derived carbon, absent the carbon filler, as a support for dispersing iron catalysts. [38-40] The study examined the effect on carbon pore structure by synthesizing the polymer under different parameters such as (1) altering concentration and type of pore forming agent, (2) altering concentration and type of acid used in catalyzing the monomer and (3) the addition of potassium and boron into the carbon. Their results revealed that carbons produced
with PFA and poly ethylene glycol (molecular weight = 300) resulted in an increased average pore size, \( D_m \), compared to the carbon prepared without PEG. Addition of PEG also displayed a decrease in the degree of molecular sieving. Incorporation of glycerol as the pore forming agent proved to lead to an increased \( D_m \), yet no appreciable decrease in the degree of molecular sieving. It was concluded that regardless of the pore former incorporated during synthesis (Triton X-100, glycerol, or poly ethylene glycol) the difference in the yielding carbon was the average pore size, \( D_m \); the total pore volume remained the same. Additionally, it was determined that HCl and p-toluensulphonic acid (PTSA) catalyzed the polymerization of furfuryl alcohol violently at room temperature, whereas oxalic acid required the monomer to be heated. The acid catalysts also displayed an effect on the porosity of the resultant carbon. The stronger acids, PTSA and HCl, resulted ultimately in a more porous carbon support than that derived from oxalic acid. Furthermore, the lower total pore volume of the oxalic acid-derived polymer resulted in an increase in molecular sieving. Finally they noted that the addition of boron or potassium resulted in an increase in total pore volume and a decrease in \( D_m \).

The next pertinent work on the synthesis of carbon molecular sieves catalyst supports was by Lafyatis et. al. The influences of several parameters on the adsorptive properties of polyfurfuryl alcohol-derived carbon molecular sieves was examined.[41] The monitored parameters included carbonization temperature, time, and the addition of polyethylene glycol additives. Their work postulated that for PFA-derived CMS materials, carbonization at higher temperatures decreased the micropore size. Also, CMS materials that are left for longer periods of time at their final carbonization temperature exhibit a decrease in micropore size.

An extensive exploration of the shape selectivity behavior of these CMS catalysts was conducted by Lafyatis et. al where several catalysts were prepared and used to compare the competitive hydrogenation of propylene and isobutylene in a continuous flow reactor.[42] Some catalysts were prepared by coating a catalyst (Pt on activated carbon or Fe/SiO\(_2\)) with PFA followed
by carbonization to yield an ordered porous carbon layer, producing a catalyst similar to Walker’s CCMS catalyst. Another catalyst was prepared by simply mixing a platinum precursor with PFA then carbonizing the mixture and a third catalyst was prepared by impregnating an activated carbon with a platinum precursor via incipient wetness. The results for all three catalysts are summarized in Table 1.1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Propylene Conversion</th>
<th>Isobutylene Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CMS</td>
<td>0.20</td>
<td>0.025</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.25</td>
<td>0.13</td>
</tr>
<tr>
<td>Pt/C/CMS</td>
<td>0.17</td>
<td>0.037</td>
</tr>
<tr>
<td>Fe/SiO₂</td>
<td>0.17</td>
<td>0.051</td>
</tr>
<tr>
<td>Fe/SiO₂/CMS</td>
<td>0.12</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Table 1.1 Propylene and isobutylene hydrogenation conversion using different catalysts. (Note: CMS denotes carbon molecular sieve, C is activated carbon. Data is gathered from Lafyatis et. al.)[42]

The hydrogenation results demonstrated that Pt/CMS had the largest selectivity ratio, with the conversion of propylene an order of magnitude higher than that of isobutylene. When the neat catalysts (Pt/C and Fe/SiO₂) were covered with PFA and carbonized the addition of a CMS layer increased the catalyst selectivity for the two alkenes. However, the activity of each catalyst decreased for the reactants, propylene and isobutylene, when a CMS layer was present. Selectivity for gas phase hydrogenations was obtained for each catalyst at the expense of a lower global activity. This collection of work also looked into the adsorption uptake of each catalyst to obtain effective diffusion constants, $D_{eff}$. The Pt/CMS catalyst had $D_{eff}$ values of $10^{-8}$ cm$^2$/sec for
propylene and $10^{11}$ cm$^2$/sec for isobutylene. The values for $D_{\text{eff}}$ of the non-sieving catalysts displayed a sharp drop when coating of CMS was added. Values dropped from orders of $10^{-2}$ to $10^{-11}$ cm$^2$/sec while each catalyst had $D_{\text{eff}}$ values for isobutylene < propylene. The effectiveness factor, $\eta$, and Thiele modulus, $\Phi$, were used to further examine the transport limitations of the catalyst. For catalysts with severe intraparticle diffusion limitations the following is true: $\Phi \rightarrow \infty$ and $\eta \rightarrow 1/\Phi$. Kinetic analysis of the CMS catalyst and catalysts coated with CMS revealed strong internal-transport limitations. This was qualitatively shown when the catalyst particle size used in the hydrogenations for the CMS catalyst was varied. As the catalyst particle size decreased, the activity increased. This inverse correlation is due to a smaller particle size that resulted in a reduction of the active diffusion length to the metal active site. Simply, the diffusion length that must be traversed by the molecule is shorter for smaller particles.

Carbon molecular sieves were examined in catalyzing the synthesis of methylamines.[43] The production of methylamines at equilibrium result in a product distribution of trimethylamine (TMA) > dimethylamine (DMA) > monomethylamine (MMA). However, the market demand distribution is dimethylamine > monomethylamine > trimethylamine. The CMS catalysts were formed much like the Walker CCMS catalyst, in that a substrate was coated with a layer of CMS; in this case the substrate incorporated was SiO$_2$-Al$_2$O$_3$. The catalysts, referred to as inorganic oxide modified carbon molecular sieve (IOM-CMS), examined were developed with different ratios of carbon to inorganic oxide. To produce such a catalyst the adsorption properties of TMA, DMA, and MMA on different IOM-CMS catalysts was determined. The adsorption experiments led to the synthesis of an IOM-CMS catalyst that was tailored to have shorter retention times for MMA and DMA than for TMA. In collaboration with Dupont, the IOM-CMS catalysts were examined in the methylamines reactor. The IOM-CMS catalyst had a much higher selectivity of MMA and DMA than the standard catalyst with a ratio of (MMA + DMA)/TMA of 2.3 compared to 1.0. The carbon molecular sieve catalyst proved to be commercially applicable.
A novel method to examine the catalytic selectivity and activity of CMS was conducted by Strano and Foley.[44] They applied a Pt/PFA film on a stainless steel porous support that was then pyrolyzed to form a Pt/CMS catalytic membrane. This served as a catalytic nanoporous carbon membrane. The average Pt particle size was measured to be 7.1 nm. Selective gas phase hydrogenations of alkenes were used to characterize the shape-selective catalytic behavior of metal on NPC catalysis (Figure 1.6).

![Figure 1.6 Intrinsic hydrogenation rate constants vs. temperature from model regression][1]  

The synthesized catalytic nanoporous carbon membrane had a strong preference for terminal, straight chained alkenes compared to when the double bond was internal or branched alkenes. The significant difference was accorded to the rate constants, with a difference by an order of magnitude going from propylene to 1-butene. However, it was distinguished that the observed rate constants were not intrinsic but were heavily influenced by diffusion limitations.

The most recent work has expanded on the synthesis of the active sites in the nanoporous carbon molecular sieve. Rajagopalan et. al. pre-formed Pt nanoparticles in the monomer, furfuryl
alcohol, with a surfactant, Triton X-100, then polymerized to form polyfurfuryl alcohol.[45] The Pt/polymer mixture was cured to form a thermoset polymer rendering the Pt nanoparticles immobile. The thermoset polymer was pyrolyzed at a maximum temperature of 800°C. The robust Pt/nanoporous carbon catalyst (NPC) was heat treated to 800°C under hydrogen flow multiple times in an attempt to induce sintering, however, the Pt nanoparticles never aggregated. Based on HRTEM and STEM images the Pt nanoparticles were characterized of having mean diameters between 2-4 nm. Gas phase alkene hydrogenations were carried out over the Pt/NPC to characterize their catalytic selectivity ability (seen in Figure 1.7)

Figure 1.7 Conversion of alkenes to alkanes as a function of reaction temperature using a 6.4 wt.% platinum loaded nanoporous carbon catalyst.[45]

The smaller molecules displayed a higher reactivity, particularly when the temperature was increased to 100°C and beyond. Another attribute of the catalyst was its preference to linear alkenes compared to branched alkenes which was previously observed on Strano’s Pt/CMS
catalytic membrane.[44] The conversion for isobutylene hydrogenation stayed consistently lower than the conversion of 1-butene. This selective property was exaggerated when heated beyond 150°C, with an increased difference in conversions of the two alkenes as the temperature increased. They concluded that the formation of nanoporous carbon around the preformed platinum nanoparticles takes place via the synthesis of a thermosetting polymer such as polyfurfuryl alcohol that arrests the free transport and agglomeration of the particles. As the polymer starts to crosslink (during thermosetting), it solidifies and all the particle motions are hindered. The series of synthesis steps form platinum nanoparticles that are kinetically “frozen” in the carbon matrix.

Continued work on PFA-derived carbons for catalyst supports has expanded their use for catalyzing a myriad of reactions beyond hydrogenations; these include, but are not limited to, Fischer-Tropsch, formation of methylamines, hydrocarbon rearrangements, and dehydrogenation.[43, 46-50] The application of CMS in catalysis for a wide variety of reactions has been reviewed.[51, 52]

The amount of work that has been done on CMS has been well reviewed; however several questions still linger in the CMS research community. One question is whether CMS catalysts can be extended into liquid phase reactions. All of the hydrogenations, as well as the other noted reactions, have been conducted in the gas phase; is it possible to observe shape selectivity in the liquid phase using CMS catalysts? Another area that remains unclear is the exact role of Triton X-100 in the synthesis. It has been used in the synthesis of PFA-derived carbon for various purposes including as a dispersant and surfactant.[53, 54] It has been reported to reduce the overall porosity of PFA-derived carbon.[46, 53] Yet, as I will go in-depth about in Chapter 2, this is not what was observed during the research reported here. The last question that will be addressed is the real usage of the metal in the catalyst, or in other words the effectiveness of the metal. In Strano and Foley’s gas phase hydrogenation reactions, it was concluded that the
low rate constants for examined reactions could not be strictly due to diffusion limitations but could also be due to the limited number of active sites and, if true, how can the number of active sites be increased. These questions will be answered in the presented work of this thesis.

1.4 Boron-Carbon Materials

Boron-carbon structures are of considerable interest owing to their inherent properties such as increased resistance to oxidation, mechanical strength, and electro-chemical properties.[55-59] Boron can be substituted for a carbon atom within the graphene lattice.[60, 61] In the late 1960’s Lowell demonstrated that boron substitution in ash could be done by heating graphite flakes and B₄C together at 2350°C.[60] This simple procedure produced carbons containing 2.35 atomic % of boron. More recent processes for the development of boron-doped carbons by researchers have used chemical vapor deposition (CVD) to incorporate higher concentrations of boron in the carbon lattice. [55, 56, 58, 61-67] While this method has proven to work, there remains considerable discrepancy between the reported boron concentration incorporated into these carbons (7-25 at. %).[62, 65, 67-69]

In the late 1980’s, work in Bartlett’s lab produced several papers that laid the ground work for future studies.[55, 70, 71] Their work concluded that BC₃ is formed as a film with a metallic-like lustrous appearance by the chemical interaction of boron trichloride gas with benzene gas at 800°C (Equation 1.1).

\[
2 \text{BCl}_3 + \text{C}_6\text{H}_6 \rightarrow 2 \text{BC}_3 + 6\text{HCl} \quad (1.1)
\]

The ratio of B:C was established by combusting the BC₃ solid in fluorine to give BF₃ and CF₄ whose yields were determined by IR spectrometry.[55] It was reported that no \( hkl \) reflections
were displayed by the BC$_3$ in its electron-diffraction patterns. Thus, it was concluded that there is no sheet-to-sheet registry within the material and that it does not have a true unit cell. In this way BC$_3$ is quite unlike graphite, which is well known to have an $ABAB$ registry of planes. The lack of orderly layer plane stacking results in the material having only a pseudo-hexagonal structure.

On hot pressing the material at 1200°C it was observed that the BC$_3$ formed boron carbide and graphite (Equation 1.2)[71].

$$12 \text{BC}_3 \rightarrow 33\text{C} + \text{B}_{12}\text{C}_3$$  \hspace{1cm} (1.2)

Bartlett proposed that by conducting the reaction at lower temperatures (800°C compared to Lowell’s 2350°C), the formation of BC$_3$ was favored over that of graphite or boron carbide. He considered BC$_3$ to be being kinetically stable even though it was thermodynamically less stable than the other products. Bartlett’s synthesis exploited the high exothermicity and favorable entropy change associated with HCl formation.[71]

In the 1990’s boron-doped carbon research attempted to find the maximum concentration (atomic %) of boron that can be substituted into the carbon network. In 1993 Fecko, et. al. reported the synthesis of BC$_3$ materials with boron concentrations of 10 at. % by doing the reaction with extremely slow flow rates during a CVD process.[68] The reactants, BCl$_3$ and benzene were flowed at rates of 0.12 and 0.06 ml min$^{-1}$ respectively. These slow flow rates required much longer total CVD times to generate measurable amounts of product. In 1995, Cermignani claimed to increase the total boron concentration to 15 wt. % in the BC$_3$ material by using higher flow rates than Fecko and increased temperature.[62] This method had the advantage of reducing the total process time from days to one hour. Cermignani correlated the concentration of BCl$_3$ in the flow to that of the atomic % of boron in the material. When the concentration of BCl$_3$ was 80% of the flow (in terms of moles), the atomic % of boron was 16.
The work also demonstrated that upon heating the material to its decomposition temperature, the boron present enhanced crystallinity of the graphitic carbon produced compared to that typically produced at such low temperatures.

By the late 1990’s several studies described relationships between temperature, flow rates, and carbon precursors in the production of BC$_3$.[65, 67, 69] Ottaviani evaluated the relationship of BCl$_3$ flow rate with concentration of boron in the product material using acetylene in place of benzene as the carbon precursor. His results were similar to Cermignani, and he claimed to push the maximum boron concentration to 23 at.%, with a BCl$_3$ flow rate of 47%. However, there was also a more surprising find. The examined d$_{002}$ interlayer spacing which is used to deduce the degree of crystallinity of the carbon material displayed an experimental minimum at a boron concentration of 17 atomic %. Ottaviani noted that when the boron-carbon material contained higher boron concentrations than 17 at.% the d$_{002}$ interlayer spacing increased but when the concentration of boron was less than 17 at.% the boron led to decreased d$_{002}$ spacing. It was concluded that at concentrations lower then 17 at.%, B is substituted into the framework, however concentrations higher than 17 at.% boron is intercalated between graphitic planes thus pushing the d$_{002}$ up to larger values. Koh et. al. correlated reaction temperature and boron concentration.[65] He found that as the reaction temperature increased the amount of boron decreased, with the C:B ratios dropping from 7 to 4. The large variation in carbon to boron ratio implied that a BC$_x$ formulation maybe a more accurate description of the material than that of the fixed BC$_3$ formulation. Koh also reported that boron was bonded at the edges of layers of the graphitic lattice rather than within the internal sites of the basal plane.[65]

In agreement with Ottaviani’s work, Hach reported that with increasing boron content up to 17 at.%, a smaller d layer spacing was observed, yet beyond 17 at.% resulted in a larger d layer spacing displaying a similar local minimum for d layer spacing at B concentrations of 17 at.%. [69] The relationship of d$_{002}$ layer spacing and boron concentration is seen in Figure 1.8. To
make their plot Hach also included data from Dahn’s papers.[69, 72] Starting from a basis of boron-rich carbon structures, Hach proposed that a better description of the structure of their material was C₆B rather than BC₃. His argument is that BCₓ develops in the vapor phase via an attack on the benzene ring by a boron electrophile. The boron atoms bridge the adjoining rings together. This bridging results in a solid being formed in which one boron atom on average is associated with one ring of six carbons as shown in Figure 1.9.

![Graph showing the relationship between boron concentration and d₀₀₂ layer spacing in BCₓ films.][69]

Figure 1.8 Relationship between boron concentration and d₀₀₂ layer spacing in BCₓ films.[69]
Figure 1.9 Proposed structure for BC₃ in which carbon rings are joined by B atoms.

More recent work on BC₃ has focused on using theoretical calculations to predict the properties of the solid and on examining alternate synthesis reactions which avoid the use of
Researchers have attempted to incorporate boron into the carbon framework of already synthesized carbon by physical mixing and heating at high temperatures. This approach significantly simplifies the synthesis of BC₇, however the characterization data published has been indefinite at best. For example in Kim’s work, the calculation of B concentration was based upon XPS results but an extremely noisy baseline and weak signal for B 1s in the spectra make it hard to accept the claim that BC₇ had been produced. Another example is seen in Wu’s work, again using XPS to calculated B concentration, the B 1s spectrum of the solid displayed many peaks in addition to those that are associated with the B–C bond in BC₃. If BC₃ is in fact forming via physical mixing and heating, then the chemistry of the reaction must be quite different from that which is produced of BCl₃ and benzene. Given that solid graphite is the carbon precursor, if boron is substituted into the structure this process must take place by a very different pathway than the gas phase synthesis and it may lead to quite a different product even if it has the same stoichiometry.

Theoretical calculations provide insight into the probable characteristics of the BC₇ material. One of the more fascinating characteristics, and one that is highly relevant, is that B in the BC₇ should provide higher affinities for hydrogen adsorption than on an all-carbon basal plane. Other properties of the material after substituting B into the carbon network are a suppressed tendency toward oxidation, as well as, an improved ability to disperse metals atomically. All together these properties make BC₇ a promising new material for catalysis and adsorption.
1.5 Carbon Applications

Carbons are used commercially as heterogeneous catalyst supports due to favorable support characteristics such as high mechanical strength, chemical inertness, and high surface areas.[52] The active metal phase is most commonly added to the carbon by adsorption from a precursor followed by reduction to form the near-zero valent metal.[83]

Support materials affect catalytic performance in a wide range of ways including acting as co-catalysts that alter activity, selectivity, stability and the life of the catalyst. Boudart and Djéga-Mariadassou delineated several of the possible effects of a metal-support interaction including: influencing the ease and extent of reduction of the metal precursor, affecting particle size and shape, inducing shape selectivity and inducing adsorption and diffusion of reactants and products across the surface (e.g. hydrogen spillover).[84] Metal dispersion on carbon supports is dependent on pore structure, pore size distribution, internal surface area, the presence or absence of heteroatoms (sulfur, nitrogen, e.g.), and the presence of acid or base groups at the surface.[37, 43, 85-87]

1.5.1 Catalyst Support

PFA-derived and other carbons have been explored as a shape-selective catalysts and supports because they have pores in the size range of small molecules.[10, 11, 35, 36, 42, 88, 89] The shape selectivity of a catalyst can be divided up into three different types: reactant shape-selectivity, product shape-selectivity and transition state shape-selectivity.[89] Reactant shape-selectivity is defined as the selective conversion of certain reactant molecules when there are other molecules also present.[90] This is based upon differences in the size or shape of different
reactant molecules which results in different rates of diffusion into the pore opening. In product shape selectivity, the reactant has the ability to diffuse to the active site where it forms more than one product in parallel and series. Depending on relative size and shape of the products formed, one may have stronger resistance to diffusion from the active site. Thus, product shape-selectivity is attributed to the catalyst having diffusive selectivity for the least sterically hindered product in the reaction. Transition state selectivity takes place when there are two or more pathways of reaction with two differently sized transition states. Due to steric hindrance imposed by the pore environment in the vicinity of the active site on the transition state, the pathway involving the smaller transition state is favored.

PFA-derived carbon can be produced with good to excellent reactant or product shape-selectivity, for gas phase reactions.[45] However, shape-selectivity in liquid phase reactions has yet to be fully explored.

1.5.2 Gas Adsorbent

Carbon that is derived from PFA has a unique pore size and structure that make it a valuable adsorbent.[87] A simplified picture for the pore structure of carbon is that the pores are slit shaped. This geometry differs greatly from that of other adsorbents whose pores are circular or polygonal in shape. For example, the slit-shaped pores of molecular sieving carbon were shown to adsorb benzene while a zeolite with the same average pore size (0.4 nm) but a more circular pore shape did not.[52] Slit-shaped pores allow carbon materials to adsorb benzene selectively from cyclohexane or isobutane because the diffusion of linear, planar molecules is more favorable than that of non-planar, branched molecules in such pores.[91] The pore structure of the synthesized carbon may also include mesopores (2-100 nm) and micropores (>2nm)
depending upon how it is produced. We will investigate the effects of pore structure, average pore size and boron substitution on the adsorptive behavior of PFA-derived carbons.

1.6 Organization of Thesis and Objective

The overarching goal of this work was to examine the use of polyfurfuryl alcohol-derived carbon as a support for platinum in liquid phase alkene hydrogenations and as an adsorbent for hydrogen adsorption with and without boron incorporation. The results of this research demonstrate a simple technique for producing shape-selective catalyst supports with tuned porosity and chemistry and adsorbents with high heats of adsorption for hydrogen.

- Chapter 2 describes the synthesis procedure and characterization techniques for the formation of platinum nanoparticles sequestered within polyfurfuryl alcohol-derived carbon.
- Chapter 3 examines the effects of sequestering platinum particles in the carbon support on their activity for hydrogenating liquid phase alkenes.
- Chapter 4 explores the relationship of pore structure and hydrogenation activity; mathematical models are used in determining the rate limitation.
- Chapter 5 details the synthesis and characterization of boron doped carbon, BC_x.
- Chapter 6 describes the coating of BC_x on silica aerogel for use as a hydrogen adsorbent.
- Chapter 7 summarizes the results of the research and highlights areas for future work.
The objective of this work is to extend the use of nanoporous carbons catalysts into liquid phase reactions. Thus far, nanoporous carbons have only been shown to display shape selective behavior in gas phase reactions; it would be beneficial to enhance their usability.

1.7 References


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Chapter 2

Controlled Synthesis and Characterization of Platinum Nanoparticles Sequestered in Nanoporous Carbon

2.1 Introduction

Catalysis based chemical synthesis accounts for 60% of today’s chemical products and 90% of current chemical processes.[1] Catalysis is essential to the majority of all chemical syntheses. Carbon is used as a catalyst support in commercial applications worldwide.[2-5] Carbon’s inherit properties, including its chemical inertness, thermal stability, high surface area and low cost give it a special niche as a heterogeneous catalyst support. However, its commercial use as a shape-selective catalyst or support is so far limited.[5, 6] In this chapter we address pore
size engineering and the placement of sequestered metal nanoparticles in PFA-derived carbon for liquid phase hydrogenation reactions.

For practical shape-selectivity in liquid phase reactions pores must be present in two size ranges, mesopores and micropores. Mesopores are required for fast mass transfer of reactants into and out of the support while micropores are essential to providing the steric constraints that are the basis for shape selectivity. To engineer such a carbon support, furfuryl alcohol containing dispersed metal nanoparticles was polymerized and pyrolyzed. The polymer-derived catalyst support had porosity that was dependent upon how the furfuryl alcohol was polymerized, the acid used in the polymerization stage, and whether or not the polymer was cured. To increase the porosity within the PFA-derived carbon, one can add pore formers during the polymerization process, and prior to the pyrolysis of the polymer.[7] Pore forming agents result in pores formed in the mesopore range. There is a relationship between the amount of porosity and the molecular weight of the pore forming agent.[8]

In a recent report, it was shown that furfuryl alcohol (FA) can act as a reducing agent for platinum salts and resulted in the formation of Pt metal at refluxing temperatures. This process leads to a mixture of platinum nanoparticles suspended in the monomer.[6] The monomer and Pt nanoparticles (Ptₙ) suspension can be polymerized by acid, which leads to a viscous dispersion of Ptₙ in poly furfuryl alcohol (PFA). When the dispersion is placed in an oven to cure (at 40°C, 60°C, and 100°C successively), the viscous suspension is converted into a solid. This polymer solid, when heated under flowing nitrogen at 800°C for 6 hours forms a nanoporous carbon (NPC) containing Ptₙ. The platinum in this state is hindered from sintering, even under forced conditions (>800°C). This method of curing the polymer forms a solid before pyrolysis, and the platinum nanoparticles are physically immobilized or “frozen” within the polymer matrix. Upon heating to 800°C, the polymer forms carbon, which surrounds the Ptₙ nanoparticles, thus sequestering them and separating them from other Ptₙ nanoparticles. The sequestering and
isolation of individual nanoparticles by the solid carbon restricts their aggregation, and prevents sintering, which is a problem that plagues Pt\textsubscript{x} on carbon and other support media. Hence, Pt\textsubscript{x} nanoparticles sequestered in NPC rather than supported on activated carbon may be used at temperatures well beyond those normally used with a standard catalyst.

When gas-phase hydrogenation reactions were conducted with the synthesized Pt\textsubscript{x}/NPC catalysts to determine their activity, they displayed molecular sieving properties. The catalysts were active and did display a higher selectivity for smaller, linear alkenes over the larger and/or branched alkenes. This phenomenon was attributed to the narrowness of the pore structure, specifically to the small average pore size in the NPC, which is similar in size to that of the reactants examined (~5Å).

The NPC catalysts that were active for hydrogenation of gaseous alkenes, were however at least two orders of magnitude less active than a standard Pt\textsubscript{x} on carbon catalyst when compared on a per mole of platinum basis. Hydrogen chemisorption combined with particle size characterization by XRD and HRTEM indicated that only a few percent (~1%) of the platinum in the NPC was accessible even to hydrogen let alone to larger organic molecules. This was not surprising since the NPC was fairly dense and much of the platinum was sequestered in carbon that was either non-porous or which had porosity disconnected from the other regions of the solid. Thus although the “dispersion” of the platinum was fixed by the preformation of the Pt\textsubscript{x} nanoparticles, and although these particles did not sinter or grow, and even though the catalysts were active at room temperature, only a fraction of the platinum was in a region of the carbon with requisite porosity to allow for effective ingress and egress of reactants and products. To be useful for important hydrogenation, dehydrogenation and hydrogenolysis reactions of the kind used in organic synthesis and by the pharmaceutical industry, or for reactions useful for fuel cells, the platinum in these carbon materials would need to be made much more accessible and utilizable.
Thus the goal of the work described herein was to examine the process used to produce the sequestered platinum catalysts beginning with nanoparticle formation and ending with the pretreatment. During Ptₙ nanoparticle formation two different catalyzing agents were used for metal reduction: heating (170°C) or UV light (400-320nm). The reasoning for two different methods of forming Ptₙ nanoparticles is that metal nanoparticles upon heating aggregate in solution. This is due to an increase in the number of particle to particle collisions. Hence, if the nanoparticle formation is conducted at room temperature compared to 170°C and if UV light is used to drive the reduction, then less aggregation is likely to occur. Thus two different methods were explored, one using UV light to reduce the platinum salt at room temperature and the other using thermal energy at ~170°C.

Another parameter of catalyst formation that was examined was the solvent used in dissolving the polymerization catalyst, paratoluene sulfonic acid monohydrate. The two solvents examined were tetrahydrofuran (THF) and Triton X-100, a nonionic surfactant. In past work Triton X-100 had been used for two reasons: to dissolve the polymerization catalyst and to prevent Ptₙ particle aggregation. However, the use of Triton X-100 was not systematically studied in the formation of Ptₙ nanoparticles. Thus, it was unknown whether the presence of Triton X-100 was necessary for small Ptₙ nanoparticle formation. To better define the role of Triton X-100, rather than using it as an additive it was used as a solvent for the organic acid that catalyzes the polymerization. For comparison THF also was used as a solvent. THF was used because it is known to not be a nanoparticle stabilizer. If the resulting Ptₙ nanoparticle sizes display no difference with either solvent then it can be concluded that Triton X-100 has no role in stabilizing the Ptₙ nanoparticles. As a reference, a solution was synthesized using no solvent. If Triton X-100 does stabilize Ptₙ nanoparticles when we would expect the use of THF, as the solvent to lead to larger sized particles.
Another critical difference between the two solvents is their effect on the porosity of the carbon formed. Previous reports have correlated the higher molecular weight of the additive (in this case solvent) in poly(furfuryl alcohol) with more porosity formed in the carbon.[7, 9] The two solvents used have very different molecular weights. THF is 72 g/mol and Triton X-100 is ~625 g/mol. Triton X-100 has not been definitively shown to create porosity in PFA derived carbon. However, it does have a higher molecular weight than THF and thus, it is hypothesized that a polymer produced with Triton X-100 will yield a carbon that has more porosity than a carbon derived from PFA produced with THF. The carbon derived from PFA that was polymerized with no solvent is predicted to have the lowest total porosity of the differently synthesized carbons.

Examining liquid phase reactions with these catalysts containing different pore structures will shed light on how the ratio of micropores to mesopores ultimately affects their catalytic activity.

2.2 Experimental

2.2.1 Reagents

Platinum II (acetyl acetonate) or Pt(acac)$_2$, furfuryl alcohol (FA), Triton X-100 (TX), p-toluene sulfonic acid monohydrate (p-TSA), and tetrahydrofuran (THF) were purchased from Sigma Aldrich Co. and used without any further purification.
2.2.2. Synthesis

2.2.2.1. Platinum Nanoparticles From Pt(acac)$_2$

The platinum nanoparticles were synthesized by two different methods. (1) A known amount of platinum (II) acetyl acetonate was added to 5 mL of furfuryl alcohol in a 115 mL round bottom flask. The mixture was refluxed (~170°C) for 16 hrs, which resulted in a black colloidal solution of platinum nanoparticles in furfuryl alcohol. (2) Alternatively, a beaker with 5 mL of furfuryl alcohol and containing a known amount of platinum (II) acetyl acetonate was placed in a cooling bath set at 10°C. Directly overhead was placed a Blak-Ray Longwave Ultra-Violet Lamp (Model B 100 Ap). The lamp and cooling bath were sheathed with aluminum foil and then the system was enclosed by a cardboard box. The UV light catalyzed reduction continued for 48 hours.

2.2.2.2 Polymerization of FA Containing Pt$_x$ with Triton X-100

To a colloidal solution of Pt$_x$ in FA at room temperature was added an additional 5mL of furfuryl alcohol along with 5mL of Triton X-100 surfactant. This was stirred and placed in an ice bath. Next, 0.4g of p-TSA dissolved in 5mL of Triton X-100 was added gradually to the colloidal solution using a syringe pump at a rate of 2.5 ml/hr. The polymerization was allowed to continue for 24 hours. The resultant viscous solution was cured by pouring into a glass vial and heating in stages at 40°C, 60°C and 90°C for 72 hours, respectively.
2.2.2.3 Polymerization of FA Containing Ptₙ with THF

The Ptₙ and PFA also were synthesized with tetrahydrofuran substituted for the Triton X-100. All other procedures remained the same. To a colloidal solution of Ptₙ in FA, 5 ml of FA and 5 ml of THF were added followed by placement in an ice bath. 0.4g of p-TSA dissolved in 5 ml of THF was added via syringe pump at a rate of 2.5 ml/hr. The polymerization was allowed to proceed for 24 hours. The resultant viscous polymer was cured as described in Section 2.2.2.2. Table 2.1 displays the chemical structures as well as physical properties of the two different solvents, Triton X-100 and THF.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Molecular Weight (g/mol)</th>
<th>Boiling Point (°C)</th>
<th>Density (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrofuran</td>
<td><img src="image" alt="Structure" /></td>
<td>72.1</td>
<td>66</td>
<td>0.88</td>
</tr>
<tr>
<td>Triton X-100</td>
<td><img src="image" alt="Structure" /></td>
<td>625</td>
<td>&gt;200</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 2.1  Structure and physical characteristics of solvents used in the polymerization of furfuryl alcohol.  (Note: For Triton X-100, on average n = 9.5)
2.2.2.4 Pyrolysis of Pt/PFA

The solidified resins made with either Triton X-100 or THF were then pyrolyzed in a tube furnace under a slow flow of Ar(g). The sample was heated to 200°C over the course of one hour, maintained at that temperature for two hours and then the temperature was raised to 800°C at 2.5°C/min, at which point the temperature was held fixed at 800°C for 8 hours. The sample was cooled to room temperature in the furnace under flowing argon for 8 hours. The amount of platinum loaded into the carbon was calculated from the final total mass of the sample and the initial mass of platinum (II) acetylacetonate that was added. The catalyst was crushed into particles and sieved; we retained the particles ranging in size (diameter) from 90 to 180μm.

2.2.3 Characterization

2.2.3.1 Methyl Chloride and Nitrogen Adsorption (Pore Volume)

A methyl chloride adsorption isotherm was used to calculate the total pore volume and the average pore size of the carbons according to the Horvath-Kawazoe and the Kelvin models in the micro- and mesopore regions, respectively. A slit pore shape was assumed for pores less than 0.7nm. The diameter of the methyl chloride probe molecule was taken to be 0.418 nm. The apparatus and models have been extensively detailed by Mariwala. [10] Nanoporous is a synonym for having micropores and mesopores, which is the IUPAC term for pores with widths less than 2 nm and between 2 nm and 50 nm for the latter.
The apparent surface area of the carbons was calculated utilizing a nitrogen isotherm measured on a Micromeritics Gemini 2370 (Micromeritics, Norcross, GA) and the BET equation.[11] Samples were out gassed at 100°C overnight before analysis.

2.2.3.2 X-Ray Diffraction (XRD)

XRD patterns were collected on a Scintag PAD V powder x-ray diffractometer using Cu Kα radiation source with a step size of 0.01° 20 and a count time of 0.5 seconds. Acquisition conditions were 35 kV and 30 mA. A NIST SRM 640c silicon standard was used to correct the line positions and broadening of the carbon patterns. Carbons were finely ground and packed into the cavity of a quartz zero-background holder (The Gem Dugout, State College, PA). The average metal crystallite size was calculated by the Scherrer equation (Eq. 2.3).[12] $k$ is taken to be 0.9, $B$ is the full width at half max of the Pt [111] peak, $\theta$ is the position of the peak, and the x-ray wavelength was 1.5412 Å.

$$L = \frac{k \cdot \lambda}{B \cos(\theta)}$$ (2.2)

2.2.3.3 Transmission Electron Microscopy (TEM)

The images of platinum loaded nanoporous carbon were examined using a Hitachi HF2000 High Resolution Transmission Electron Microscope. In addition to the high-resolution
images, the average size of the platinum nanoparticles was calculated using images taken on a HD2000 Scanning Transmission Electron Microscopy.

2.2.3.4 Thermogravimetric Analysis-Mass Spectrometry (TGA-MS)

The pyrolysis of platinum nanoparticles dispersed in polyfurfuryl alcohol was carried out in a TGA-MS at a heating rate of 10°C/min to 800°C under a flowing argon atmosphere. The main gaseous products were carbon dioxide, hydrogen, methane, carbon monoxide and water. The gaseous products were monitored as a function of pyrolysis temperature using an on-line mass spectrometer.

2.2.3.5 Carbon Monoxide Chemisorption

The concentration of active metal sites was determined by CO pulse chemisorption. A Micrometrics AutoChem II 2920 was used to quantify the active sites. The catalysts were reduced under flowing hydrogen at 350°C for 4 hours prior to the experiment. The samples were dosed with a stream containing a known concentration of carbon monoxide. The amount of carbon monoxide left in the stream after passing through the sample was quantified by an online thermal conductivity detector (TCD). The stoichiometry of adsorption on each platinum site was taken to be one to one. [13] The relationship between dispersion and crystallite size is:

\[
D_m = 0.6(V_m / A_m) d \text{ (nm)}
\] (2.1)
where:

\[ V_m = \frac{m}{\rho N_{Av}} \]  

(2.2)

is for a spherical particle, \[14\] Note that

\( A_m \) is the area per metal atom and \( m \) is the atomic mass, \( \rho \) is the bulk density, and \( N_{Av} \) is Avogadro’s number. Platinum, which is an fcc metal, has a site density of \( 1.2 \times 10^{15} \) Pt cm\(^{-2}\).\[15\] Here \( A_m \) is one over the site density, which equals \( 8.06 \times 10^{-16} \) cm\(^2\).\[15\]

2.3 Results

2.3.1 Pore Volumes and Distributions for Pt\(/\)NPC

The synthesis of well-dispersed platinum nanoparticles entrapped within a matrix of nanoporous carbon had been reported.\[6\] In short, Pt(acac)\(_2\) was mixed with FA under refluxing conditions yielding Pt\(_x\) nanoparticles in FA solution. To this colloidal solution Triton X-100 was added followed by the placing the vessel containing the mixture in an ice bath and adding the polymerization catalyst, which dissolved in Triton X-100. The total amount of Triton X-100 added was determined by keeping a ratio of Triton X-100 to FA at 1:1. Triton X-100 was added to the solution to disperse the nanoparticles and to reduce bubble formation in the resin. Triton X-100 has been well established to be a nonionic surfactant that under mild conditions can retard the rate of aggregation of metal nanoparticles, by forming micelles around them.\[16-18\] However, upon further investigation, the formation of Pt\(_x\) nanoparticles was determined not to be affected by the presence of Triton X-100 in the FA solution. This was determined by
synthesizing three different Pt,FA solutions, the first with Triton X-100, the second with THF and lastly, with neither, i.e. a neat Pt,FA solution. No change was noted in the Pt size, however, a major difference was observed in the cumulative pore volumes and pore size distributions of the carbons produced from these three suspensions after pyrolysis (see Figure 2.1 and 2.2). Figure 2.1 illustrates that the three differently synthesized polymers yield a very similar maximum cumulative pore volume in the micropore range (<2 nm) of ~0.12cc/g. Yet, for the polymer synthesized with Triton X-100 (Pt-PFA-TX) a much larger volume is observed in the mesopore range. By contrast the THF and neat polymers yield very little porosity in the mesopore range.

Only once before has Triton X-100 been reported to act as a pore forming agent during the pyrolysis of PFA.[19] The porosity incorporated in the carbon by the Triton X-100 arises from its decomposition during heating. The gases produced by pyrolytic decomposition escape the solid polymer-carbon material slowly and leave behind voids which result in mesopore volume. The pure polymer after pyrolysis displays almost no mesoporosity, because it has none of the byproducts of Triton X-100 decomposition; hence there is little mesopore formation. In the case of THF, which has an extremely low boiling point, it escapes even before pyrolysis during the curing process. Thus, this approach leads to the same results, in terms of porosity, as neat furfuryl alcohol.

Figure 2.2 displays the pore size distribution of the three samples. All three differently synthesized polymers display an average pore size of 6-7Å. The polymer synthesized with Triton X-100 had the broadest pore size distribution while the two other polymers, THF and neat, have a very narrow pore size distribution.
Figure 2.1: Pore volume of 20% wt. platinum loaded nanoporous carbon made with Triton X-100, THF or no solvent (neat).
Figure 2.2: Pore size distribution of 20% wt. platinum loaded nanoporous carbon made with Triton X-100, THF or no solvent (neat).

In going from THF to Triton X-100, the micropore volume increased slightly (0.13 cc/g to 0.15 cc/g) but the mesopore volume increased more than 5 fold, from less than 0.01 cc/g to 0.05 cc/g, respectively.

2.3.2 Pt\textsubscript{x} Size and Dispersion In the Carbon Matrix

X-ray diffraction studies showed that for 11wt.% Pt\textsubscript{x}/NPC_TX the average particle size of the platinum nanoparticles was in the range of 3-4 nm as can be seen in Figure 2.3. The
nanoparticle size was calculated using the full width half max (FWHM) of the Pt [111] peak (seen at ~37°) based on the Scherrer equation (Equation 2.2).

Figure 2.3: X-ray diffraction patterns of same platinum weight % (11 wt.%) Pt/NPC made with THF (NPC_THF) and Triton X-100 (NPC_TX).
Figure 2.4: X-ray diffraction patterns of Pt/NPC_TX after high temperature treatments (800°C and 900°C) under flowing Ar\textsubscript{(g)}.\textsuperscript{2}
Figure 2.5: Overlapped X-ray diffraction patterns of Pt [111] and [200] peaks for Pt/NPC_Triton X-100 post-high temperature treatment (800°C and 900°C)
Figure 2.6: X-ray diffraction patterns for Pt/aC (platinum deposited on top of carbon) before and after high temperature treatments under flowing Ar\(_{\text{g}}\).
Figure 2.7: Overlapped X-ray diffraction patterns of Pt [111] and [200] peaks for Pt/aC post-high temperature treatment (800°C and 900°C)

Figure 2.4 compares the diffraction patterns after heat treatments of the synthesized Ptₓ/NPC_TX catalyst. The Pt [111] and [200] peaks display no changes. Figure 2.5 is an enlarged view of the Ptₓ [111] and [200] peaks overlaid on top of each other from Figure 2.4. These peaks are almost identical in broadness and no change is observed after heating up to 900°C and holding the temperature there for 5 hours.

For comparison a commercial catalyst was purchased containing a similar Pt concentration (10 wt. %) on activated carbon. The exact same heat treatments were conducted with the commercial catalyst. The diffraction pattern observed in Figure 2.6 displays that the Ptₓ nanoparticles for the commercial catalyst have undergone a dramatic change. Examining the peaks overlaid on top of each other, (Figure 2.7) it is observed that the Ptₓ nanoparticles have
severely sintered during the heat treatments. Based on Equation 2.2, an increased in the narrowness of the peak translates to larger particles. Using the Pt [111] peak to calculate the particle size, the original Pt nanoparticle size was about 3 nm, but upon heating the nanoparticles increased to 37 nm at 800°C and 41 nm at 900°C. This is an increase by over a factor of ten and a loss of dispersion by an order of magnitude, from ~20% to ~2% too.

Transmission electron microscopy was used to verify the particle sizes as well as to indicate how well dispersed the platinum is throughout the carbon network.

![Transmission electron microscopy image of 11% wt. Pt loading in NPC_TX.](image)

Figure 2.8 (a): Transmission electron microscopy image of 11% wt. Pt loading in NPC_TX.
Figure 2.8 (b): TEM image of 11wt.% Pt loading in NPC_THF
Figure 2.8 (c): Enlarged TEM image of Pt nanoparticles for 11wt.% Pt loading in NPC_TX.
Figure 2.8 (d): Enlarged TEM image of Pt nanoparticles from 11wt.% Pt loading in NPC_THF.

Figure 2.8 (a) and (c) are of images from the catalyst synthesized with Triton X-100 while Figures 2.8 (b) and (d) are images from the catalyst synthesized with THF. The TEM images revealed that Pt is surrounded by carbon resulting in the Pt nanoparticle surface being largely covered by carbon. This is clearly observed in Figure 2.8(d), where a Pt nanoparticle at the very edge still has a clear layer of carbon completely around it. The same picture also depicts
the lattice fringes for Pt, yet carbon is still seen atop of the observed lattices. Both catalysts have the same average particle sizes. The nanoparticle size determined from TEM is in good agreement with that which was calculated from the x-ray diffraction pattern; each has average particle diameters of between 3 and 4 nm.

2.3.3. Pyrolysis of Pt/PFA

Platinum is considered an excellent catalyst for C-C bond breaking as well as C-C bond formation.[20-22] During pyrolysis, both kinds of reactions take place during the transformation of polymer to carbon. With platinum present in the resin prior to pyrolysis it could have a catalytic effect on the decomposition reactions. With this in mind, the course of pyrolysis for several differently synthesized PFA polymers was monitored by TGA-MS to determine if the presence of platinum influenced the decomposition of the polymer and the subsequent formation of the carbon. The samples investigated were 20 wt.% Pt/PFA_THF, 20 wt.% Pt/PFA_TX, PFA_THF and TX where TX is Triton X-100. The gases that were monitored included CO, CO₂, H₂, CH₄, and O₂.
Figure 2.9 (a): Weight loss curves as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX)
Figure 2.9 (b): Weight loss derivatives as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX)
Figure 2.9 (c): Mass-spectrometry detection of methane as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX).
Figure 2.9 (d): Mass-spectrometry detection of carbon monoxide as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX).
Figure 2.9 (e): Mass-spectrometry detection of carbon dioxide as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX).
Figure 2.9 (f): Mass-spectrometry detection of hydrogen as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX).
Figure 2.9 (g): Mass-spectrometry detection of oxygen as a function of pyrolysis temperature for Pt/PFA synthesized with THF (Pt-PFA-THF) and Triton X-100 (Pt-PFA-TX) and for PFA synthesized with THF (PFA-THF) and for pure Triton X-100 (TX).

TGA-MS analysis of the pyrolysis of polyfurfuryl alcohol with THF present as a solvent indicated that weight loss, corresponding to the release of gaseous by-products, occurred mainly between 300°C and 500°C (Figure 2.9(b)). The onset in the formation of carbon dioxide occurs at 300°C (Figure 2.9(e)), while that of carbon monoxide, methane and hydrogen took place at temperatures beyond 450°C (Figures 2.9(d), (e), (f)). When platinum nanoparticles were present in the mixture (to make the 20% wt. Pt/PFA nanocomposite) with THF as a solvent, their presence resulted in small, but noticeable changes in the weight loss curve. The weight loss for
the Pt\textsubscript{x} containing material, seen in Figure 2.9(a) and (b), began at lower temperatures (>100°C) resulting from the formation of carbon dioxide Figure 2.9(e). This could be produced from the decomposition of the acetylacetonate ligand left in the mixture after the platinum precursor was reduced during nanoparticle formation. Carbon monoxide, methane and hydrogen again were released at temperatures greater than 450°C as in the case of pure polyfurfuryl alcohol. The same pyrolysis was repeated with the aim of making 20 wt.% Pt in NPC from platinum acetylacetonate and polyfurfuryl alcohol, but now with Triton X-100 in place of THF as the diluent. The weight loss curve shows the evolution of gases such as hydrogen and methane at much lower temperatures (300°C-400°C) in addition to formation of carbon monoxide, and carbon dioxide (Figure 2.9(e)). A decomposition study of Triton X-100 alone showed that the surfactant completely breaks down between 300°C - 400°C releasing decomposition products of hydrogen, carbon monoxide, carbon dioxide and methane. This indicates that the decomposition of Triton X-100 molecules is responsible for the evolution of methane and hydrogen at lower temperatures. The reason that this observation is important is that the complete decomposition of the Triton X-100 during pyrolysis also leads to the noticeable formation of mesoporosity in these carbons as shown by Figure 2.1 and 2.2.

The formation of methane, Figure 2.9(c), when Pt\textsubscript{x} is in the composite made from Triton X-100, occurs at a lower temperature than from the polymer not containing Pt\textsubscript{x}. This shift results in the evolution of methane at 320°C, when Pt is present versus 380°C when it is not. A similar correlation is noted in the THF-synthesized composite for methane production in that the presence of Pt resulted in a lowered temperature for CH\textsubscript{4} evolution. A large methane peak at 510°C is noted when Pt is absent, but on the addition of Pt the methane peak is shifted to 490°C with a smaller peak noted at 320°C. Though measurable, these are not major shifts in the temperatures for the onset of evolution of these gases.
One decomposition gas product whose temperature of formation is significantly affected by the presence of Pt is carbon dioxide. When examining the TGA (Figure 2.9(e)) for carbon dioxide release, there is a shift of the peak toward much lower temperatures when Pt is present then when it is not. In both of the Pt-containing polymer composites, with either Triton X-100 or THF as solvent, a shift of ~60°C is observed. With the Triton X-100 sample, the shift is from 380°C to 320°C, while for the THF-prepared composite the shift is from 320°C to 260°C.

2.4 Discussion

2.4.1 Solvent Effect on Pt$_x$ Formation

The Pt$_x$ nanoparticles were prepared by reduction of the precursor, platinum acetylacetonate, in the presence of furfuryl alcohol under refluxing conditions (170°C) or at 25°C with UV radiation. It is known that alcohols can act as reducing agents in the synthesis of platinum nanoparticles.[23-26] The metal salt is reduced to yield zero-valent metal atoms, which collide in solution with metal ions, metal atoms or metal clusters to form irreversible “seeds” of stable metal nuclei. The metal seeds grow as a result of aggregation and clustering. The diameters of particles in the colloids vary based on reduction temperature, and to a lesser degree, the alcohol used, and to the ratio of alcohol to metal precursor.[23, 27] However, refluxing Pt(acac) and FA at 170°C or irradiating it at 25°C in FA led to the same average particle size and distribution.

Furfuryl alcohol is a reducing alcohol, resulting in particles being formed with average diameters of 3-4 nm as determined by TEM images and the XRD pattern in Figure 2.3. The use of Triton X-100 during the synthesis slightly increased the average diameter by approximately 0.5
nm when compared to the particle diameter of Pt\(_x\) formed using THF as the solvent. The small difference in Pt\(_x\) nanoparticle diameter is noted by the TEM images, seen in Figure 2.8.

This difference in average particle sizes for the THF versus Triton X-100 catalysts can be rationalized as follows. For one, the use of Triton X-100 during the synthesis created more porosity during the pyrolysis, as shown in Figure 2.1. The increase in porosity is due to an overall increase in the number of pores – especially mesopores. The mesopores are large enough to allow for efficient platinum transport. With more platinum mobility there will also be more sintering upon heating during pyrolysis, thus forming larger particles. A more subtle, but equally important difference between the THF derived and Triton X-100-derived materials is in curing time. Since THF is a highly volatile liquid with a very high vapor pressure (≈ 129 mmHg at 20°C), when the polymer is cured at 60°C it takes a few hours to form a solid composite than when Triton X-100 makes up the mixture. Triton X-100 has a relatively low vapor pressure (< 1 mmHg at 20°C) and it requires days to fully solidify. The longer time required for solidification (at 60°C) allows for more Pt\(_x\) aggregation to take place prior to the platinum particles being immobilized within the highly cross-linked solid polymer. However, in either case, with THF or Triton X-100, the average size of the Pt\(_x\) is still small and comparable to Pt nanoparticles observed on commercially available catalysts.

2.4.2 Solvent Effect on the Porosity of NPC

The carbon catalyst support synthesized with Triton X-100 (\(M_w >600\) g/mol) had more porosity than the THF-synthesized catalyst support (\(M_w = 72.11\) g/mol). The porosity in the mesopore range (2 nm < \(x\) < 50nm) of the Triton X-100 catalyst tripled going from 10% of the
total volume for the THF catalyst to 30% of the total volume, seen in Table 2.4. By contrast the amount of microporosity is only slightly increased when Triton X-100 was used. In addition, the average pore size remained constant for both samples, even though the mesoporosity had increased significantly in the material prepared with Triton X-100.

Furthermore, it was concluded from the porosity results that when Triton X-100 was incorporated as the solvent during synthesis more porosity, particularly in the mesopore range, was formed. This is due to the difference in molecular weights of the solvents examined. The THF solvent has a much lower molecular weight than that of Triton X-100; by close to a factor of 10 seen in Table 2.1. The much larger solvent molecule, Triton X-100 (MW > 600 g/mol), will leave behind larger voids when decomposed compared to the void left behind when THF (MW = 72 g/mol) has decomposed. The analysis from the methyl chloride adsorption data is shown in Table 2.2.

<table>
<thead>
<tr>
<th>Carbon Material</th>
<th>Microporosity (%)</th>
<th>Mesoporosity (%)</th>
<th>Average Pore Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/NPC_THF</td>
<td>90</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Pt/NPC_TX</td>
<td>70</td>
<td>30</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 2.2 Relative porosity in terms of the % of the total volume as well as the average pore size, determined by methyl chloride adsorption.

2.4.3 Influence of Platinum on the Pyrolysis of Polyfurfuryl Alcohol

The genesis of porosity in cured polyfurfuryl alcohol has been studied.[8, 28-30] Most recently Burket et. al. monitored the pyrolysis by TGA-MS, XPS, and ^1^H NMR to provide a
mechanism for the carbon formation. Figure 2.10 depicts the first onset of polymer breakdown based on Burket’s work.\[30\]

![Diagram of polymer structures](image)

Figure 2.10: Model structures found in PFA: (A) methylene bridge, (B) backbone conjugation, (C) 2, 5 carbons, (D) 3, 4 carbons, (E) terminal methyl group, (F) cross-links, (G) polyaromatic domain, (H) carbonyl group. Where the temperature, $T_1$, is dependent on polymerization conditions (for uncured polymer $\sim 300^\circ C$, for cured polymer $\sim 350^\circ C$) of the polymer.
Figure 2.11: Model structure of the complete breakdown of the polymer, thus creating the graphene-like sheet. The temperature, $T_2$, is dependent on polymerization conditions (for uncured polymer ~500°C, for cured polymer ~550°C).

At 25°C, polyfurfuryl alcohol is composed of mainly methylene (-CH$_2$-) and methylyne (=CH-) bridges seen in Figure 2.10 A and B. When heated during the curing process cross-linking begins as noted in Figure 2.10 F. The cross-linking proceeds by two different methods, either via methylene bridge or Diels-Alder condensation. Heating to 300°C (Figure 2.10) begins the generation of micropores, as well as a significant amount of mesoporosity. The microporosity is created by coalescence of furan rings to form highly disordered aromatic domains. The mesoporosity is inferred to result from partially fractured ether linkages, which form carbonyl
groups amidst the aromatic domains (noted in Figure 2.10 as H). The oxygen hetero atoms left over from the furfuryl ring, as well as the residual carbonyl groups provide a buffer between aromatic domains. These oxygenated buffer groups prevent aromatic sheets from coming into close contact and their increased curvature resulted in larger sheet to sheet distances than observed in graphite. Heating to >500°C results in the elimination of oxygen moieties as well as to the complete decomposition of the polymers as noted in Figure 2.11. The loss of the residual groups correlates to the evolution of the following gases: CO, CO₂, CH₄ and H₂. It was observed that upon the release of these gases there is a collapse in the mesoporosity present. It was concluded that the formation and evolution of these gases resulted from the decomposition of the oxygenated buffers. This series of steps result in the microstructure of nanoporous carbon.

When platinum is present in the polymer, the decomposition of the polymer occurs at lower temperatures. Platinum metal is known to catalyze the cleavage of –C-O- bonds in oxygenated hydrocarbons, particularly in oxygen-rich systems at temperatures as low as 200°C.[22, 31] This explains the early formation and evolution of oxygenated species such as CO and CO₂ during the pyrolysis. The Ptₓ nanoparticles become reactive during the decomposition of the polymer, regardless of solvent used in the synthesis. In pyrolysis of PFA made with either THF or Triton X-100, a similar shift is noted in the onset evolution of CO₂; in both cases the change in temperature is 60°C lower. A higher concentration of carbon monoxide is observed in the synthesized PFA using Triton X-100 as the solvent versus the PFA synthesized with THF. This is due to Triton X-100 having a relatively higher O:C ratio (1:3). However production of oxygenated species is not the only reaction affected by the presence of platinum; production of methane is also affected.

The scission of the ether bridges generates methane during pyrolysis. It was observed that when platinum was present in the polymer, methane evolved at a lower temperature than
when platinum was absent from the polymer. Platinum is presumed to lower the activation energy for the formation of methane during the pyrolysis. Another attribute due to the presence of platinum is that beyond 400°C the H/C ratio significantly decreased for platinum-containing polymers. The decreased ratio is a result of the evolution of CH₄ and H₂. Formation of H₂ is due to dehydrogenation reactions that occur during aromatic sheet formation. Platinum is well established as a catalyst for dehydrogenation reactions.[32-34] Thus, the aromatic sheet formation was inferred to be catalyzed by the presence of platinum due to a lowering of the activation energies for hydrogen formation. In short, hydrogen molecules in close proximity to Ptₓ form weak bonds on the metal surface that then migrate and desorb as H₂ gas. By catalyzing the decomposition of the polymer, Ptₓ leads to the early onset of aromatic domain formation.

### 2.4.4 High Temperature Treatment (HTT) Induced Ptₓ Sintering

The Ptₓ crystallite size was characterized by XRD before and after the HTT to establish the thermal stability of the materials (Figure 2.4 and 2.5). It was interesting that heating at 900°C for 5 hours did not induce any sintering for the experimental catalyst. Figure 2.5 displays the XRD spectra of the material before and after high temperature treatment; the two overlaid spectra cannot be differentiated from one another. These nearly identical patterns indicate that the platinum nanoparticles in Pt/NPC material are highly resistant to sintering.

For comparisons, a commercial catalyst (Pt/aC) containing Pt supported on top of activated carbon was subjected to the same high temperature treatment. The diffraction patterns of the commercial catalyst revealed that the Ptₓ species undergoes extensive sintering at 800°C and at 900°C noted in Figures 2.6 and 2.7. The Ptₓ metal was originally 3 nm in diameter,
however, upon heating the diameter increased to 36 nm and 41 nm respectively. Extreme sintering into such large particles yields fewer Pt on their surfaces, and proportionally increases the number of atoms forming the bulk. The surface atoms of a catalyst, are the active locales for catalysis. When the concentration of surface atoms decreases the activity decreases. For the commercial catalyst the original dispersion is ~30 % (for \( d = 3 \) nm) upon heating the dispersion falls to ~3% (for \( d = 41 \) nm); calculated by Equation 2.5. Thus, it is best to have a very high dispersion in order to maximize the amount of metal that is used in catalysis. For spherical Pt, the relationship is:[35]

\[
D_m = 1.1 / d
\] (2.4)

In Equation 2.4 \( d \) has units in nm and \( D_m \) is the fraction of atoms present at the surface. The \( D_m \) values for the catalyst were calculated from the respective Pt crystallite size, which was obtained from their XRD diffraction patterns and are given in Table 2.3. The calculated or theoretical dispersions assume that the entire surface of the metal particle is active.

It is evident that heating causes a detrimental impact on crystallite size for the commercial catalyst. The “free” platinum, or platinum on top of the carbon, sinters to a much larger diameter lowering the metal dispersion. The commercial catalyst has a theoretical dispersion of 36.6%, but when heated to 800°C this number drops by a factor of ten to less than 3%.
<table>
<thead>
<tr>
<th>Pt-Carbon Material</th>
<th>HTT(^1) (°C)</th>
<th>Crystallite Size, (d), (nm)(^2)</th>
<th>Theoretical Dispersion, (D_m)(^3)</th>
<th>Measured Dispersion, (D_m)(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt embedded in Carbon (Pt/NPC_TX)</td>
<td>None</td>
<td>4</td>
<td>27.5%</td>
<td>1.5%</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>4</td>
<td>27.5%</td>
<td>1.5%</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>4</td>
<td>27.5%</td>
<td>1.5%</td>
</tr>
<tr>
<td>Pt on Carbon (Pt/aC)</td>
<td>None</td>
<td>3</td>
<td>36.6%</td>
<td>28.4%</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>36</td>
<td>3.0%</td>
<td>2.2%</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>41</td>
<td>2.6%</td>
<td>1.7%</td>
</tr>
</tbody>
</table>

Table 2.3: Crystallite size and dispersion of Pt loaded carbon catalysts before and after high temperature treatments. (Note: \(^1\)Indicates same conditions: 5 hours at each specified temperature under flowing Ar, \(^2\)Determined by XRD, \(^3\)Calculated from the XRD data using Equation 2.4, \(^4\)Calculated from moles of CO chemisorbed.)

The Pt/NPC_TX theoretical dispersion remained unchanged when heated to high temperatures. Sequestering the platinum generates a platinum particle that is “kinetically frozen” and resists sintering. An adverse effect of sequestering the platinum is that the apparent dispersion is much lower than expected. When platinum is sequestered, it may be “land locked” by carbon, translating to less accessible surface sites and hence, the much lower measured dispersions than theoretical dispersions. In simple terms, much of the platinum in the catalyst is embedded in regions of the carbon particle which are disconnected from the outer regions of the carbon particles; as such they do not participate in carbon monoxide chemisorption or in catalytic reaction but they are counted in the dispersion calculation.

We can calculate the amount by which the apparent dispersion is diminished by this effect by accounting for platinum that is inaccessible. This is done by considering the density and
total porosity of the nanoporous carbon. The average Pt nanoparticle is 4 nm, so the volume of
the particle can be calculated from Equation 2.5.

\[
\text{Volume of 4 nm particle} = \frac{4}{3} \pi (2.0 \times 10^{-9} m)^2 \tag{2.5}
\]

Now the dispersion measured by carbon monoxide chemisorption is very low compared
to the theoretical dispersion. However the theoretical dispersion is based on two assumptions – a
one to one CO to platinum stoichiometry and complete access of CO to all platinum – that is to
say all the platinum particles no matter, how large or small, are accessible and can chemisorb CO
on their surfaces. To account for a value of just 1.5% measured by CO chemisorption, we would
either have to have very large particles (~ 73 nm) or we must be in violation of one of the other
assumptions.

The first assumption is that of atomic dispersion. If instead of one atom we consider one
unit cell of platinum metal as the minimum sized metal particle, then it would have four platinum
atoms in it. Accounting for geometry and using the same stoichiometry for chemisorption, this
four atom cluster would have a surface area of 9.2 \times 10^{-19} \text{ m}^2. For a sample of 0.1g of Pt in this
state, there would be a maximum theoretical surface area of 71.6 \text{ m}^2; thus, dividing the measured
by the theoretical surface area, the new maximum dispersion is 9.9\% or about a factor of 3 lower
than that computed for atomic dispersion. Next we need to correct for the inaccessibility of some
of the platinum particles. Inaccessible platinum adsorbs no CO, so we must find a way to account
for this. The total pore volume, \( V_p \), per gram and the density, \( \rho \), are known, thus the void fraction,
\( \varepsilon \), can be determined as shown in Equation 2.6.
If we assume that the total pore volume accounts for pores accessible to CO and the density accounts for porosity that is inaccessible as well as accessible, then the $\varepsilon$ should give the fraction of pores which are accessible. Since the platinum is known to be well distributed throughout the material, it is just as probable to be found in the inaccessible pores as the accessible pores. Thus $\varepsilon$ should give the fraction of platinum which is available or accessible. We find that the total pore volume is 0.21 cc/g and the density is 1.6 cc/g, thus $\varepsilon = 0.13$. Thus only about 13% of the platinum particles embedded in the carbon is accessible. When we multiply this through we compute a prediction for the measured “dispersion” of only 1.3%. This is in good agreement with the measured value of 1.5%. Hence, we can see that about 85-90% of the surface of platinum is buried in the carbon and are not accessible.

For those platinum particles that are accessible the question arises as to what kinds of catalytic chemistry they can produce. The HRTEM images of Pt$_x$ particles near the carbon particle edges indicate that the platinum particles are still embedded in porous carbon. To what extent can these platinum particles participate in shape selective catalysis? Gas phase reactions of alkenes indicated a strong preference for reactivity of shorter molecules than for longer ones in the hydrogenation reaction. Would such an effect carry over for liquid phase reactions of a similar kind? How would these steric effects come into play with longer chain alkanes and their isomers? So it is with questions such as these in mind that we proceeded to examine the catalytic activity of that portion of the platinum which was accessible for reaction.
2.5 Conclusions

The use of Triton X-100 in the polymerization process created a mesoporous carbon. THF or FA alone have lower molecular weights than Triton X-100 and yield less porous carbons. The generation of mesoporosity in the carbon is directly related to the presence of a high molecular weight solvent used to dissolve the acid for the polymerization reaction. By contrast the presence of platinum during the pyrolysis has little effect on the production of porosity. The placement of Pt\(_x\) within the cured polymer does induce the formation of carbon at lower temperatures by catalyzing the degradation of the polymer. This was determined by observing the evolution of pyrolysis degradation products (CH\(_4\), CO\(_2\), etc.) at a lower temperature than when Pt\(_x\) are not present. By using a strong acid to catalyze the polymerization of FA at low temperature, the Pt\(_x\) nanoparticles are entrapped and embedded in the polymer matrix. The carbon surrounding Pt\(_x\) prohibits transport movement of the particle even at higher temperatures, creating a “kinetically frozen” or frustrated state for the platinum particles. The dispersion, \(D_m\), of the Pt for Pt/NPC remains unaffected by thermal stress when compared to a commercial catalyst which undergoes considerable undesirable sintering under the same conditions. However, the sequestered Pt\(_x\) has a lower \(D_m\) because such a high fraction of the nanoparticles are embedded within nanoporous and disconnected regions of the carbon.

2.6 References


Chapter 3

Sequestered Ptx in the Matrix of Nanoporous Carbon: Shape Selectivity in Liquid Phase Hydrogenations

3.1 Introduction

Shape-selective catalysts are an ever growing interest in the catalysis community. In a recently published review on selective catalysis Somarjai states, “…we emphasize the need to focus on reaction selectivity, instead of activity, as the next great challenge of catalysis.”.[1] A major goal for catalysis science is the development of new and useful heterogeneous catalysts for carrying out multipath reactions with high selectivity and which lead to major gains in energy efficiency, as undesirable by-products are eliminated.[2] Recent research in the selective catalysis field is spurred by the concern that we are currently at the end of cheap energy. It is desirable to have highly active and selective catalysts to increase the energy efficiency of commercial processes.

Current shape-selective catalysts, zeolites, are a technology that originated in the 1960’s with pioneering work at Mobil industries.[3] Zeolitic catalysts are alumino silicates with crystalline and porous structure. These catalysts are acidic in nature.[4] However, in some very important reactions, such as dehydrogenation, an acidic surface on the catalyst support is so undesirable that it excludes the exploration of shape-selectivity. Thus, an alternative to a zeolite is a carbon molecular sieve, which has a chemically benign surface and shape-selective properties.
Shape-selective carbon molecular sieves CMS, (now referred to as Nanoporous Carbons, NPC) catalysts had been prepared as early as the 1970s, when Walker first reported the preparation of CMS-platinum catalysts. He and his coworkers formed a carbon composite catalyst by pyrolyzing a mixture of polyfurfuryl alcohol (PFA) and platinum salts, which created a catalytic molecular sieve layer over particles of activated carbon.[5, 6] The authors noted that during the carbonization of the polymer, as it shrunk in volume, the activated carbon particles actually expanded. This resulted in the formation of macro-cracks in the top layer of the NPC, which served to reduce the average diffusion length between the micropores within the layer and therefore enhanced mass transfer and diffusion between platinum active sites present in the carbon. These effects in combination thereby increased overall catalytic effectiveness of the composite compared to what it would have been had the ad-layer of carbon been completely microporous.

Reactant shape-selectivity, whereby the global rate of reaction is dominated by the rate of reactant ingress, was noted with catalysts prepared by similar methods.[7, 8] Product shape-selectivity induced by molecular sieving carbon over amorphous silica-alumina was evident in the conversion of methanol and ammonia into a non-equilibrium distribution of methylamine products which favored the formation of mono and dimethylamine.[9] This reaction was catalyzed by a composite reminiscent of the Walker catalyst in that it consisted of a layer of polyfurfuryl alcohol derived carbon covering the underlying particles of silica-alumina, the actual solid acid catalyst. Molecular egress of trimethylamine from the porous oxide was limited by the resistance of its transport through the micropores of the carbon overlayer and this formed the basis for the observed product shape-selectivity.

Recently, catalysts consisting of nanoporous carbon and nickel were reported and it was argued on the basis of selectivity patterns in the decomposition of methanol, that this catalyst
showed evidence for transition-state shape-selectivity. Transition-state selectivity was implicated because the methanol was decomposed cleanly into CO and H₂ with negligible amounts of other products produced.[10] The high selectivity to synthesis gas was the basis for the authors’ supposition that transition-state selectivity was induced by steric constraints imposed within the carbon micropores in the vicinity of active surface of the nickel particles. Transition-state selectivity is actually difficult to distinguish from product shape-selectivity and to support a hypothesis invoking it, diffusion effects must be rigorously accounted for first.

More recently, catalysis utilizing the shape-selective effects imposed by the nanoporous carbon pore structure has been extended by creating supported membranes that work in concert with a catalytically active component to produce both reaction and separation, simultaneously.[9, 11] In particular, very low defect platinum-loaded NPC membranes act as a permselective reactor. The platinum-containing catalytic membranes showed good size selectivity in the hydrogenation of different simple alkenes. After analysis of the reaction and diffusion phenomena, the ratios of the intrinsic rate constants for the alkene hydrogenations within these membranes were determined to be much more sensitive to the alkene chain length (propylene/isobutylene and 1-butene/isobutylene) than were the ratios of the intrinsic rate constants for the same alkene hydrogenations reported for platinum supported on activated carbon catalysts.[11] Since the analysis of the membrane reaction data explicitly took into account diffusion as a function of size for the alkenes, the increased differences in the magnitudes of the intrinsic rate constants as a function of alkene chain length versus those of the standard catalysts were inferred to result from the imposition of steric constraints by the carbon micropores in going from reactants to products. In other words, there was evidence in support of the hypothesis that transition-state selectivity was involved in accounting for the differences in the intrinsic kinetics of hydrogenation. This hypothesis was bolstered by HRTEM images, which showed that the micropores of the carbon acted as channels for reactant and products by extending all the way to
the surface of platinum particles (Figure 3.1). Hence, interesting new chemical effects due to steric hindrance may arise and may be usefully exploited as an important effect of embedding the active metal particles within the carbon.

![Figure 3.1 HRTEM of platinum that is embedded in the carbon matrix.](image)

Recently, we reported a new synthetic procedure to control the state of the platinum embedded within the molecular sieve carbon.[12] In this method we now sequester *preformed* platinum nanoparticles within the matrix of nanoporous carbon, whereas in our earlier approach, and that of previous workers, the platinum nanoparticles were formed spontaneously from salt precursors during pyrolysis of polyfurfuryl alcohol. Sequestration by this method effectively “freezes” the platinum particles in place, eliminating their mobility and this in turn prevents these particles from sintering even at temperatures as high as 800°C in flowing hydrogen.[12] At the same time, these catalysts exhibit shape and size selectivity effects expected for a molecular
sieving carbon and as reflected in their reactivity patterns for the gas phase hydrogenation of small chain alkenes. In such reactions the global rates of reaction decreased as a function of increasing chain length and branching. The catalysts were active for ethylene hydrogenation even at room temperature, but as the carbon chain length increased and or branched, the activity at room temperature fell off sharply. This was thought to be due primarily to activated transport and the resultant diffusive resistance induced by the micropores as the sizes of the reactant and product increased. However, it could also be that there are other steric effects also at play which arise from the nanopores of the carbon extending to the very surface of the platinum nanoparticles. In terms of the Thiele Modulus, the former effect would be manifested in a drop in $D_e$ with larger reactant size, whereas the latter would be due to a change in $k_i$ (the intrinsic rate constant) due to steric effects. In either case, the magnitude of the loss in catalytic effectiveness, even for light alkenes, needs to be overcome in order for catalysts of this kind to be useful for practical applications such as higher alkene and arene hydrogenation or dehydrogenation in the liquid phase. Herein, we examine the activities of catalysts which include micropores, along with embedded nanoparticles of platinum, but we have also explored the effects of incorporating mesopores for more effective transport of liquid phase alkenes within the carbon. By examining such simple hydrogenation reactions, we can come to understand better and to define more accurately their behavior in terms of changes in activity and selectivity patterns based on changes in synthesis variables.
3.2 Experimental

3.2.1 Reagents

Both a 10wt.% Pt/NPC_TX and 10wt.% Pt/NPC_THF catalysts were synthesized (see Chapter 2). n-Undecane, 1-hexene, trans-2-hexene, cis-2-hexene, trans-3-hexene, 1-octene, 2-methyl-1-pentene, 3-methyl-1-pentene and 4-methyl-1-pentene and their respective hydrogenated forms: n-hexane, n-octene, 2-methylpentane, 3-methylpentane, 4-methylpentane were purchased from Sigma Aldrich Co. 1-nonene, n-nonane, 1-decene, and n-decane were purchased from TCI America Inc. The alkenes used were deoxygenated by purging with Ar for 1 hour prior to use. A conventional catalyst characterized as activated carbon with 10wt.% Pt deposited on the surface was purchased from Alfa Aesar and is denoted as “Pt/aC”.

3.2.2 Reaction and Setup

3.2.2.1 Batch Reactor Setup and Reaction Conditions

A stainless steel 100 mL low-pressure, low temperature batch reactor (PARR 5100) was used for the hydrogenation reactions. 0.5g of catalyst was reduced in the batch reactor prior to the reaction. The reaction was started by introducing a 50 ml solution, containing 40 ml solvent and 10 ml reactant into the reactor followed by pressurizing to 4 bar with UHP hydrogen. The reaction temperature was kept constant at 30°C. The reaction time was started when the internal stirrer was started.
3.2.2.2 Pretreatment and Reduction of Catalyst

Pretreatment of the synthesized catalyst was done in a quartz tube by heating to 800°C under flowing UHP argon. At 800°C, a mixture of UHP argon and hydrogen (70:30) was introduced into the reactor at a flow rate of 100 cm³/min and the catalyst was maintained under these conditions for 3 hours. The reactor was slowly brought down to room temperature while an argon flow was maintained through the reactor to protect the reduced catalyst. The vessel was heated to 125°C under flowing argon, upon reaching 125°C the gas was switched to UHP hydrogen and held there for 1.5 hours. Once the vessel began to cool it was pressurized with UHP hydrogen to two bars and left overnight. The following day the vessel was checked for leaks as would be noted by a drop in pressure. The vessel was then depressurized to introduce the reactant and solvent after which it was repressurized to reaction pressure.

3.2.2.3 Reaction Product Characterization

Before the start of the reaction, a sample of reactant solution was collected and denoted as the time zero, which signified zero concentration of product. During the reaction, samples were collected at different intervals over a 2 hour time period, unless otherwise noted. Premixed standard solutions containing the respective reactant and its product were used for calibration of the GC.

Models of the reactant and product molecules were produced using ChemDraw 3D. Molecular lengths and angular deviations were calculated by standard molecular mechanics methods.
3.2.3 Characterization

3.2.3.1 Carbon Monoxide Chemisorption

The concentration of active metal sites was determined by chemisorbing CO. A Micrometrics AutoChem II was used in dosing the sample with hydrogen. The exact setup is described in Section 2.2.3.5

3.2.3.2 Pore and Surface Area Measurements (N$_2$ and Methyl Chloride Adsorption)

The total pore volume and the average pore size were calculated from methyl chloride adsorption isotherms using the Horvath-Kawazoe slit-shape pore model.[13] The catalyst was heated to 350°C and held there for 4 hours under vacuum prior to adsorbing either methyl chloride or nitrogen. The apparent surface area (m$^2$/g) was measured by using a Micrometrics ASAP 2000 multi-point BET analyzer and nitrogen adsorption isotherms. The catalyst was pretreated by storing in an oven at 100°C over night.

3.2.3.3 Gas Chromatography – Flame Ionization Detector

The product collected during the hydrogenation reaction was analyzed using a Varian CP 3800 GC equipped with a flame ionization detector and an xTi-5 column from Restek.
3.3 Results and Discussion

3.3.1 Reactant Structural Effect on Reactivity

3.3.1.1 Size of Molecule

In order to probe the effect of the reactant size on selectivity, hydrogenations of differently sized and shaped alkenes were done under the same conditions using an 11wt.% Pt/NPC catalyst. The molecules used as reactants in examining size/length effects are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Length (Å)</th>
<th>Width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexene</td>
<td>6.3</td>
<td>1.5</td>
</tr>
<tr>
<td>1-octene</td>
<td>8.8</td>
<td>1.5</td>
</tr>
<tr>
<td>1-nonene</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>1-decene</td>
<td>11</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 3.1: Probe molecules with corresponding length and width calculated after minimized energies with MM2 simulations.

The cross sectional sizes of this group of reactant molecules are nearly the same, but their lengths vary systematically. The largest molecule examined was 1-decene with a corresponding length of ~11 Å while the smallest probe molecule, 1-hexene, is half of that length. Each of these reactants is a simple straight-chained alkene with a terminal double bond placed at the first carbon. Hence, differences in activity can be attributed to differences in chain length. The
catalytic reactivity displayed the expected decrease with an increase in the length of the reactant molecules (1-hexene > 1-octene > 1-nonene > 1-decene) as shown in Figure 3.2.

Figure 3.2 Plot of reactant conversion as a function of time for the hydrogenations of 1-hexene, 1-octene, 1-nonene, and 1-decene using 11wt.% Pt loaded nanoporous carbon made with Triton X-100 as a function of chain length of the reacting alkene.

Bulkier molecules have slower diffusion time when entering and diffusing through the carbon nanopores.[11, 12, 14] Sequestering the Pt\textsubscript{x} in the carbon requires the reactant to traverse through the pore to come in contact with the active site. The conventional catalyst does not display such behavior with size (Figure 3.3). Not only does the reactant size affect the observed activity, but the product size will as well. Thus, for longer, straight chain alkenes, the corresponding hydrogenated product will diffuse more slowly than the shorter straight chain alkane.
Figure 3.3 Plot of reactant conversion as a function of time for the hydrogenations of 1-hexene, 1-octene, 1-nonene, and 1-decene using 10wt.% Pt loaded activated carbon as a function of chain length of the reacting alkene.

3.3.1.2 Alkyl Group Location Relative to Double Bond

The effect of steric hindrance on reactivity of the double bond of an alkene was probed by keeping the molecular weight of the reactant nearly constant. To examine the effect of steric constraints induced by alkyl groups, hydrogenation reactions of 1-hexene, 2-methyl-1-pentene, 3-methyl-1-pentene and 4-methyl-1-pentene were completed using two different catalysts. A conventional catalyst (10wt.% Pt on activated carbon) and the synthesized Pt/NPC catalyst (11wt.% Pt) were tested and compared for the hydrogenations of these alkenes. The results are
shown in Figure 3.5 and 3.6. The Pt/NPC catalyst displayed a significant change in activity depending upon the placement of the alkyl group. By contrast, with the conventional catalyst, all the reactants, 2-methyl-1-pentene, 3-methyl-1-pentene and 4-methyl-1-pentene were hydrogenated completely within 60 minutes; which is to say that the reactivity of the different reactants was very similar (Figure 3.5).

Incorporating a methyl group on the 2-carbon (Figure 3.4) greatly reduced the activity of the experimental catalyst, (Pt/NPC) compared to its activity for hydrogenation of the unbranched alkene, 1-hexene. By comparison no such effect is observed with the conventional catalyst.

![Figure 3.4 2D molecular structures of reactants used to probe effect on activity when an alkyl group is present.](image-url)
Figure 3.5 Plot of reactant concentration as a function of time for hydrogenation of 2-methyl-1-pentene, 3-methyl-1-pentene, and 4-methyl-1-pentene using 11wt.% Pt/NPC_TX, the synthesized catalyst.
Figure 3.6 Plot of reactant concentration as a function of time for hydrogenation of 2-methyl-1-pentene, 3-methyl-1-pentene, and 4-methyl-1-pentene using 10wt.% Pt/aC.

With the Pt/NPC catalyst it was noted that 2-methyl-1-pentene was less reactive than 3-methyl-1-pentene. However, the more interesting result was in the comparison of the reactivity toward 3-methyl-1-pentene versus that for 4-methyl-1-pentene. It was observed that 3-methyl-1-pentene reacts faster than 4-methyl-1-pentene.

Intuitively, this was not expected, since there is an expected increase in steric hindrance due to the methyl group being closer to the double bond. Hence, it was important to consider the structural details of these molecules (Figure 3.7, 3.8, 3.9, and 3.10). Molecular planarity, tabulated in Table 3.2, is defined as the RMS deviation from the least squares plane fitted to the selected carbon atoms in the models.
Table 3.2 Molecular dimensions of reactants in probe study of alkyl group addition effect on hydrogenation activity.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecular Dimensions (Å) [length x width x height]</th>
<th>Deviation from Molecular Planarity (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl-1-pentene</td>
<td>4.8 x 2.8 x 1.5</td>
<td>0.308</td>
</tr>
<tr>
<td>3-methyl-1-pentene</td>
<td>4.8 x 3.5 x 1.3</td>
<td>0.310</td>
</tr>
<tr>
<td>4-methyl-1-pentene</td>
<td>4.8 x 2.5 x 1.3</td>
<td>0.315</td>
</tr>
</tbody>
</table>

Figure 3.7 3D molecular structure of 1-hexene

Figure 3.8 3D molecular structure of 2-methyl-1-pentene
The Pt/NPC catalyst displayed a reactivity that decreased in the following order: 1-hexene > 3-methyl-1-pentene > 4-methyl-1-pentene > 2-methyl-1-pentene. There is no simple analytical expression for the diffusivity of molecules transported in this configuration or molecular sieving regime. However, molecular dynamic simulations and experimental evidence of transport in zeolites generally lead to the expectation that similarly sized molecules transport in micropores with diffusivities that are of the same order of magnitude.[15, 16] If this is the case then the differences we observe in global rates among these alkenes do not arise solely due to differences in their diffusivities – the rates are too different for small changes in the diffusivity to account for them. Instead it seems more likely that the differences in the reactivity of the alkenes arise from different degrees of conformational restraint, i.e. steric hindrance in forming the π-
bond between the metal and the double bond and hindrance which is imposed by the walls of the micropores at the surface of the platinum particle surfaces.

It is no surprise that the most sterically hindered double bond of all the isomers, located on 2-methyl-1-pentene, was observed to have the lowest reactivity. Although, the methyl group is closer to the double bond in 3-methyl-1-pentene than for 4-methyl-1-pentene, the former reacts faster than the latter – somewhat counter intuitively. However, when looking at the energy minimized structures (Figure 3.9 and 3.10), the double bond in 3-methyl-1-pentene is more in plane with respect to all other carbon atoms (correlating to the lower value for molecular planarity in Table 3.2). This may render it more streamlined, and less hindered and therefore a higher probability of access to the platinum particle surface with the steric constraints imposed by the carbon nanopores. By contrast the double bond in 4-methyl-1-pentene is more out of plane with the other carbon atoms except the methyl group. Thus, the double bond of the 4-methyl-1-pentene must be less able to chemisorb on the platinum surface when the confines of the carbon nanopore are also imposed.

To better understand the steric hindrance effects of these catalysts a new set of hydrogenations was conducted that explored the effect of double bond placement.

### 3.3.1.3 Internal Placement of Double Bond

Another variable that can illustrate sterical hindrance effects lies in the placement of the unsaturated bond along the carbon chain. To study the effect of double bond placement the following reactants were used to probe activity: 1-hexene, trans-2-hexene, trans-3-hexene. Again, the Pt/NPC-TX and Pt/aC were used as the catalysts for the liquid phase hydrogenation reactions. The probe reactants have almost the same dimensions and quite similar non-
planarities, thus any differences in their rates of hydrogenation should be due mostly to the effect of double placement. The reaction results can be seen in Figure 3.11 and the effect is quite dramatic. By contrast, the results for hydrogenation of the same probe reactants over Pt/aC are shown in Figure 3.12. Over the conventional catalyst there is very little effect of double bond placement.

![Figure 3.11: Plot of reactant concentration versus time for the hydrogenation of 1-hexene, trans-2-hexene, and trans-3-hexene catalyzed by 11wt.% Pt/NPC_TX.](image-url)
Figure 3.12 Plot of reactant concentration versus time for the hydrogenation of 1-hexene, *trans*-2-hexene, and *trans*-3-hexene catalyzed by 10w.t% Pt/aC.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dimensions</th>
<th>Non-Planarity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length (Å)</td>
<td>Width (Å)</td>
</tr>
<tr>
<td>1-hexene</td>
<td>6.32</td>
<td>1.53</td>
</tr>
<tr>
<td><em>trans</em>-2-hexene</td>
<td>6.38</td>
<td>1.53</td>
</tr>
<tr>
<td><em>trans</em>-3-hexene</td>
<td>6.31</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Table 3.3 Molecular dimensions and non-planarity of probe reactants in examining hydrogenation activity based on internal versus external double bonds.
For trans-2-hexene, the methyl and propyl groups on either side of the double bond point out of plane made with the double bond. This makes it difficult for the double bond to align parallel to the catalyst surface due to the constraints imposed by the micropore as shown schematically in Figure 3.13.

Figure 3.13 Schematic for the conformation of trans-2-hexene molecule inside the carbon nanopore. The carbon walls restrict the molecule to its pore mouth configuration, preventing \( \pi-\pi \) bond interactions with the active site.

The propyl and methyl groups occupy much more volume, restricting the twisting and turning contortions that are needed to bring the double bond of the alkene into close proximity with the Pt\(_x\) nanoparticle surface when that surface is accessible only via the narrow pores of the carbon.
When small groups, i.e. hydrogen atoms, are attached to the double bond, they can more readily rotate and allow for adsorption of the unsaturated bond on the active site. Thus, added contortion in the intermediate formed at the surface is exacerbated by the presence of the carbon micropores, since they partially cover the platinum and limit access to its surface.

The effect of stereoregularity was also examined by comparing the conversion of trans-2-hexene versus cis-2-hexene (Figure 3.14). In the case of trans-2-hexene, all the carbon atoms are in the same plane and, hence, it is easier for the molecule to align its double bond with the platinum surface even in the presence of the micropores of the carbon. By contrast, cis-2-hexene has a methyl and a propyl group out of plane with respect to the carbon double bond, which make this less favorable. Table 3.4 lists the physical properties of the two stereo isomers. Cis-2-hexene is smaller than trans-2-hexene, yet trans-2-hexene has a higher activity. This reinforces that planarity of the molecule must be considered when predicting activity using Pt/NPC_TX as the catalyst.

This is very different than what was observed for the conventional catalyst which showed no preference for a specific molecular orientation (Figure 3.15), by displaying the very similar reactivities for trans-2-hexene and cis-2-hexene.
Figure 3.14 Plot of reactant concentration as a function of time for the hydrogenation of *trans-* and *cis-*hexenes using 11wt.% Pt/NPC_TX.
Figure 3.15 Plot of reactant concentration as a function of time for the hydrogenation of trans- and cis-2-hexenes using 10wt.% Pt/aC.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dimensions (Å)</th>
<th>Deviation from Molecular Planarity (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length</td>
<td>Width</td>
</tr>
<tr>
<td>t-2-hexene</td>
<td>6.3</td>
<td>1.5</td>
</tr>
<tr>
<td>c-2-hexene</td>
<td>5.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 3.4 Physical constants of the two stereo isomers, t-2-hexene and c-2-hexene.
3.3.1.4 Two External Double Bonds

The effect of having multiple double bonds in the reactant was probed using 1,5-hexadiene, which has double bonds positioned at the terminal ends of the molecule. Hydrogenation of 1,5-hexadiene was catalyzed by 11wt.% Pt/NPC_TX catalyst (Figure 3.16(a)) and compared with a conventional catalyst with 10wt.% Pt loaded on the surface of the carbon (Figure 3.16(b)). Both catalysts displayed the same two products, namely 1-hexene (intermediate product) and n-hexane (terminal product).

![Graph](image)

Figure 3.16(a) Plot of the concentration as a function time for the hydrogenation of 1,5-hexadiene for the synthesized 11wt.% Pt/NPC_TX catalyst.
The reaction went to 100% conversion within one hour over the conventional catalyst, whereas the NPC catalyst took almost 48 hours for complete conversion. The conventional catalyst displayed a strong and immediate selectivity for n-hexane as the concentration ratio of 1-hexene/n-hexane was always less than one, even at very low conversions and was 0.01 at 95% conversion. However, due to the shape-selective nature of the Pt/NPC-TX catalyst, the selectivity of 1-hexene/n-hexane was greater than one up to 40% conversion and remains as high as 0.3 even at 95% conversion (Figure 3.17).
Figure 3.17 Plot of selectivity of products as a function of conversion in the hydrogenation of 1,5-hexadiene.

The slow hydrogenation rates in the shape-selective catalyst versus the classical catalyst can be attributed to mass transport resistance or to a lower intrinsic rate constant, $k_i$, or to a combination of both. To further understand the reactivity the heterogeneous catalytic kinetics for these probe molecules and both catalysts was determined.
3.3.2 Heterogeneous Catalysis Kinetics

3.3.2.1 Reaction Rate

Observed reaction rates were calculated for a set of hydrogenations catalyzed by 11wt.% Pt/NPC_TX examining the length effect of the reactant. The relationship with reaction rates and reactant length can be seen in Figure 3.18.

![Figure 3.18 Plot between molecule length and observed reaction rate using 11wt.% Pt/NPC_TX catalyst in the hydrogenation of straight, terminal alkenes.](image-url)
The noted trend in Figure 3.18 expresses a decrease in reaction rate as the molecular length is decreased. The observed rate is relatively high for smaller molecules, then drops as the reactant length increases.

Another factor impacting the reaction rate is placement of the double bond. When the double bond is placed internally, the observed rate drops precipitously for the Pt/NPC catalysts as opposed to the conventional catalyst as noted in Table 3.5. The rate of hexane formation from \textit{trans}-3-hexene is almost zero for the NPC catalyst with a rate of 0.00060 mols hr\(^{-1}\) g\(^{-1}\). The selectivity of the catalysts was calculated by taking the ratio of observed rates between external and internal double bonds. The selectivities of Pt/NPC_TX and Pt/aC can be seen in Table 3.6. The catalyst demonstrating larger selectivity values had a higher activity for terminal alkenes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>(r_{\text{obs}}) (mols hr(^{-1}) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>11wt.% Pt/NPC_TX</td>
<td>1-hexene</td>
<td>0.097</td>
</tr>
<tr>
<td></td>
<td>trans-2-hexene</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>trans-3-hexene</td>
<td>0.0006</td>
</tr>
<tr>
<td>10wt.% Pt/aC</td>
<td>1-hexene</td>
<td>0.868</td>
</tr>
<tr>
<td></td>
<td>trans-2-hexene</td>
<td>0.258</td>
</tr>
<tr>
<td></td>
<td>trans-3-hexene</td>
<td>0.282</td>
</tr>
</tbody>
</table>

Table 3.5 Calculated reaction rates of internal/external alkenes hydrogenated by the experimental catalyst and the purchased catalyst.
Table 3.6 Ratio of observed reaction rates of the hydrogenation between internal and external alkenes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactants</th>
<th>$r_{obs\ 1\text{-hexene}}/r_{obs\ 1\text{-hexene}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(external/internal alkene)</td>
<td>(ratio of observed rates (mol hr$^{-1}$ g$^{-1}$))</td>
</tr>
<tr>
<td>11wt.% Pt/NPC_TX</td>
<td>1-hexene/t-2-hexene</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>1-hexene/t-3-hexene</td>
<td>161</td>
</tr>
<tr>
<td>10wt.% Pt/aC</td>
<td>1-hexene/t-2-hexene</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>1-hexene/t-3-hexene</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The selectivity of the synthesized catalyst is much higher when compared to the conventional catalyst. For the conventional catalyst, placing the double bond internally produced only a factor of three drop in the reaction rate, thus indicating that the selectivity between internal and external bonds is small. However, the experimental catalyst displayed a strong dependence of rate on double bond placement with a ratio of activity for 1-hexene to 3-hexene of more than two orders of magnitude. The selectivity difference between the two catalysts originates from sequestering the active sites in the carbon framework instead of placing on top of the carbon framework.

The observed reaction rates for the addition of a methyl group on the alkene can be seen in Table 3.7. When the methyl group is in close proximity (2-methyl-1-pentene) to the double bond, this isomer has the lowest rate of reaction, which is due to the steric hindrance imposed by the methyl group and the carbon nanopore. Moving the methyl group just one carbon away resulted in an increase in the activity by a factor of five. Thus, an alkyl group’s proximity to the
unsaturated bond should be considered when thinking about catalyzing reactions with the NPC catalyst.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>( r_{\text{obs}} ) (mols hr(^{-1}) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexene</td>
<td>0.097</td>
</tr>
<tr>
<td>\textit{trans}-2-hexene</td>
<td>0.016</td>
</tr>
<tr>
<td>\textit{cis}-2-hexene</td>
<td>0.010</td>
</tr>
<tr>
<td>2-methyl-1-pentene</td>
<td>0.010</td>
</tr>
<tr>
<td>3-methyl-1-pentene</td>
<td>0.053</td>
</tr>
<tr>
<td>4-methyl-1-pentene</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Table 3.7 The observed reaction rates using 11wt.% Pt/NPC_TX as the catalyst in the respective hydrogenation.

Table 3.7 displays the difference in activity for \textit{cis}- and \textit{trans}-2-hexenes. \textit{Trans}-2-hexene has a higher activity than \textit{cis}-2-hexene. Based on the physical data in Table 3.4, the \( c \)-2-hexene is slightly smaller, however it is more non-planar. The slit pores of the NPC catalyst display that linear, more planar molecules are more streamlined and thus a higher diffusion coefficient.

Before examining the kinetics of the diene hydrogenation, it is first relevant to examine the probable reaction pathway. The reaction pathway for the hydrogenation of 1,5-hexadiene is shown in Figure 3.19.[18]
Figure 3.19 Possible reactions between C₆ compounds during hydrogenation[18]

The thermodynamic order of stability of the alkene isomers is: \( \tau \)-hex-2-ene > \( c \)-hex-2-ene > \( c \)-hex-3-ene > \( \tau \)-hex-3-ene > 1-hexene.[18] Hexane, the completely saturated product, is the most stable. In both hydrogenation reactions, the only products observed were 1-hexene and \( n \)-hexane, thus isomerization can be excluded in the analysis of the catalytic reactions. The pathway is characterized by adsorption and diffusion in the pore, adsorption on an active site, addition of two hydrogen atoms, desorption from the active site, and diffusion out of the pore. Table 3.8 shows the selectivity to 1-hexene at various levels of 1,5-hexadiene conversion for both of the catalysts.
It was observed that the Pt/NPC catalyst had a higher selectivity for the formation of 1-hexene. At ~50% hexadiene conversion the selectivity to 1-hexene is about 50% for the NPC catalysts versus ~3% over the conventional catalyst.

The initial rates of formation for 1-hexene and n-hexane were calculated along with global rates of reaction and can be seen in Table 3.9. The initial rate of 1-hexene production was twice that of n-hexane formation for the NPC catalyst. For the conventional catalyst, the rate of n-hexane formation is more than double that of 1-hexene formation. On the conventional catalyst there are no steric constraints in the vicinity of the platinum particles. Thus the diene can adsorb and react completely to n-hexane before desorbing from the active site. By contrast many of the platinum sites in the NPC catalysts are constrained by the carbon nanopore. Thus there is not enough room for the hexadiene to be hydrogenated at one end and then rotate so that the other end is hydrogenated before desorbing away from the active site. However, not all of the Pt

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1,5-Hexadiene Conversion (%)</th>
<th>Concentration of 1-hexene formed (% of Product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11wt.% Pt/NPC</td>
<td>10</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>47</td>
</tr>
<tr>
<td>10wt.% Pt/aC</td>
<td>10</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 3.8 The selectivity of 1-hexene during the hydrogenation of 1,5-hexadiene
particles are completely covered by carbon, owing to some higher activity and lower selectivity sites within the NPC catalyst also contributing to the process.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial 1-hexene $r_{obs}$ (mols hr$^{-1}$ g$^{-1}$)</th>
<th>Initial n-hexane $r_{obs}$ (mols hr$^{-1}$ g$^{-1}$)</th>
<th>Global $r_{obs}$ (mols hr$^{-1}$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11wt.% Pt/NPC</td>
<td>0.032</td>
<td>0.018</td>
<td>0.051</td>
</tr>
<tr>
<td>10wt.% Pt/aC</td>
<td>0.181</td>
<td>0.391</td>
<td>0.573</td>
</tr>
</tbody>
</table>

Table 3.9 Initial rates of reaction for the specified product along with the global rate for the hydrogenation of 1,5-hexadiene.

### 3.3.3.2 Reaction Rates Per Active Site

Another method of reporting the reaction rate is to define it in terms of the moles of active sites, in this case platinum. In Chapter 2 carbon monoxide chemisorption was done on both the experimental and conventional catalysts in order to determine the number of active sites per gram that each catalyst had. The moles of hydrogen adsorbed directly correlates to the amount of platinum exposed for reactivity. The 11wt.% Pt/NPC-TX catalyst adsorbed 11 μmoles of H$_2$ per gram, while the 10wt.% Pt/aC catalyst adsorbed 35 μmoles of H$_2$ per gram. Based on these experimental concentrations, the reaction rates were calculated in terms of mols of conversion per sec. per mole of Pt.

The reaction rates calculated this way for the set of internally positioned double bond is reported (Table 3.10)
When the 1-hexene reaction rate is calculated on a per mole of Pt basis, the experimental catalyst was no longer an order of magnitude lower. Comparatively, the experimental catalyst differs greatly, from the conventional catalyst in terms of reaction rate only when the double bond is placed internally. The reaction rates for trans-2-hexene and trans-3-hexene for the experimental catalyst are at least an order of magnitude lower compared to the conventional catalyst; for tran-3-hexene the NPC catalyst is three orders of magnitude lower. The amount of Pt exposed for reaction within the experimental catalyst is low compared to that which is exposed for the conventional catalyst, even though they contain approximately the same concentration of metal in terms of grams. However, the Pt that was exposed was highly active for hydrogenation when the molecule could reach its surface.
The observed reaction rate was recalculated in terms of moles of Pt for Table 3.9 (Table 3.11). The table displays that the initial rate for 1-hexene for the experimental catalyst and the conventional catalyst is relatively close. Yet, for the observed initial rate for n-hexane, there is an order of magnitude difference between the two catalysts, with the conventional catalyst having a higher activity. The global observed rate difference for the two catalysts is about half an order of magnitude. This is much closer than that which was observed when the global rates were calculated in terms of grams of catalyst, wherein the conventional catalyst displayed higher activity by over a full order of magnitude.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial 1-hexene $r_{obs}$ (mols sec$^{-1}$ mol Pt$^{-1}$)</th>
<th>Initial n-hexane $r_{obs}$ (mols sec$^{-1}$ mol Pt$^{-1}$)</th>
<th>Global $r_{obs}$ (mols sec$^{-1}$ mol Pt$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11wt.% Pt/NPC</td>
<td>0.404</td>
<td>0.227</td>
<td>0.643</td>
</tr>
<tr>
<td>10wt.% Pt/aC</td>
<td>0.718</td>
<td>1.55</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Table 3.11 Initial observed rates of reaction for the specified product along with the global rate for the hydrogenation of 1,5-hexadiene.

The heterogeneous kinetics analysis displayed that the experimental catalyst has lower activity than the conventional catalyst. When this is calculated in terms of grams of catalyst, the experimental catalyst is a full order of magnitude lower than the conventional catalyst for the most reactive hydrogenation. However, when the observed rates were calculated in terms of moles of platinum, the experimental catalyst displayed a similar activity for the hydrogenation of 1-hexene. These calculated results reveal that even though most of the platinum in the NPC catalyst is not utilized, what platinum is utilized is highly active, even at room temperatures.
3.4 Conclusions and Future Work

The synthesized Pt/NPC catalyst displayed very different patterns of activity for the liquid-phase hydrogenations when compared to the conventional catalyst. The selectivity of the NPC catalyst synthesized with Triton X-100 catalyst was much higher than that of the conventional catalyst. Exemplifying this, the difference in reactivities for 1-hexene hydrogenation compared to trans-3-hexene for the synthesized catalyst was >160, compared to the conventional catalyst, which displayed a difference in reactivity of only ~3. The NPC catalyst synthesized with THF displayed very low activity for the hydrogenation of 1-hexene. By sequestering Pt within the carbon network, the pores act as a permeable, yet selective membrane. Molecules containing terminal unsaturated bonds were able to traverse into the pore to react and diffuse out. Molecules with lower activity due to steric hindrance were characterized by having internally positioned unsaturated bonds and alkyl groups attached to the unsaturated bond. To a lesser degree, molecules that are non-planar, larger, and branched also reacted more slowly over Pt/NPC. The experimental Pt/NPC catalyst has two main hurdles to attaining both high selectivity and high activity (in comparison to the conventional catalyst) --diffusion and the number of active sites. In the next chapter issues associated with porosity and transport will be examined to better identify the origins of rate limitations for the NPC catalysts.

3.5 References


Chapter 4
Sequestered Pt, in the Matrix of Nanoporous Carbon: Key Parameters and Limiting Factors for Catalyzed Liquid Phase Hydrogenations

4.1 Introduction

The previous chapter examined the catalytic nature of Pt/NPC catalysts in liquid phase hydrogenations. The work displayed how the pore structure affected their activity with the pore size distribution correlating to their hydrogenation activity. It was observed that the confined pore walls restrict the diffusivity and conformations of the reactant molecules. This attributed to the NPC catalyst displaying a high selectivity toward linear, non-branched liquid alkenes. Also, the confined pores appear to contribute to a lower activity than the conventional catalyst, but when a careful analysis is done of reaction rates and kinetics, we find that the active sites in the NPC catalysts are very active. It is the purpose of this chapter to apply rudimentary chemical engineering catalyst analysis and tests to determine the key parameters and limiting factors of the nanoporous carbon catalysts with the aim of developing a deeper understanding of them.

The catalytic activity of Pt/NPC was observed to be dependent on the pore structure of the carbon. However, due to the active sites being located inside the pore, the pore structure influences transport and concentration of active sites. An increase in porosity will increase molecular transport and will increase the amount of active sites available. Yet, it is not obvious which parameter has the strongest influence on the catalyst activity.

In order to elucidate the limiting parameter, porosity effects were examined and mathematical models were adopted to determine the catalyst efficiency and effective diffusivities for the hydrogenation of 1-hexene. Of the numerous hydrogenations conducted in the last
chapter, 1-hexene resulted in the highest activity for all of the explored catalysts. For this reason, the reaction data for the hydrogenation of 1-hexene will be used as a starting point for deeper understanding. The NPC catalysts have remarkable selectivity, now we need to understand its origin and determine from where the limitations on rate may arise. This chapter will address the rate limitation of NPC catalysts.

4.2 Experimental

4.2.1 Reagents

An 11wt.% Pt/NPC_TX, and 11wt.% Pt/NPC_THF catalysts were synthesized (see Chapter 2). The following reagents were obtained from Sigma Aldrich Co. and used as is: 1-hexene, n-hexane, 1-heptene, 1-octene, 3-methylpentane, 2,2-dimethylbutane, isoctane, benzene, cyclohexane, heptane, isoctene, octane, and decane. A conventional catalyst characterized as activated carbon with 10wt.% platinum deposited on the surface was purchased from Alfa Aesar and is denoted as “Pt/aC”. All catalysts were previously characterized in Chapter 3.

4.2.2 Liquid Adsorption Setup

Prior to liquid adsorption, catalysts were pretreated by heating to 350°C for two hours under flowing argon in a quartz tube. First the catalyst material was weighed in a Petri dish to determine its initial mass. The adsorbate was pippeted into the Petri dish until the catalyst material was completely submerged (~2g of adsorbate). The adsorbate was then pippeted out after a certain period of time referred to as the “adsorption time”. The Petri dish was then
replaced on the microbalance and the initial “wet” mass was recorded. When the adsorbent mass was stable the mass was recorded again. For adsorbates with very low vapor pressures, prior to weighing, the wetted sample was placed in fume hood until it was observed to being close to being visibly dry. They were then placed on the microbalance to determine the mass adsorbed. The mass uptake was measured as a function of soak time. The rates of adsorption were calculated along with their respective diffusion coefficients.

4.3 Results and Discussion

4.3.1 Catalyst Pore Structure Effect on Reactivity

4.3.1.1 Total Porosity

To examine the effect of total porosity, three catalysts were synthesized, all containing slightly different amounts of porosity. Two catalysts have already been described, one synthesized with Triton X-100 (TX) as the solvent during polymerization and one using tetrahydrofuran (THF) as the solvent. Here, a third catalyst was synthesized, using polyethylene glycol (PEG) as the solvent. The porosity of catalysts can be seen in Table 4.1. It should be noted that the PEG synthesized catalyst contains a lower amount of platinum due to less platinum being needed within it for it to be active for the liquid phase hydrogenations. Microporosity pertains to pores < 2nm, while mesoporosity are pores between 2nm and 50nm.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( V_{\text{micro}} ) (cc/g)</th>
<th>( V_{\text{meso}} ) (cc/g)</th>
<th>( V_{\text{Total}} ) (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6wt.% Pt/NPC_PEG</td>
<td>0.19</td>
<td>0.13</td>
<td>0.32</td>
</tr>
<tr>
<td>11wt.% Pt/NPC_TX</td>
<td>0.18</td>
<td>0.06</td>
<td>0.24</td>
</tr>
<tr>
<td>11wt.% Pt/NPC_THF</td>
<td>0.15</td>
<td>0.01</td>
<td>0.16</td>
</tr>
<tr>
<td>10wt.% Pt/aC</td>
<td>0.33</td>
<td>0.19</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 4.1 Specific porosity of catalysts calculated from methyl chloride adsorption.\[1\]

When the total porosity for the three synthesized catalysts is plotted against the observed reaction rate a linear relationship is noted, seen in Figure 4.1.
Figure 4.1 Plot of the observed rate of reaction as a function of total porosity for 1-hexene hydrogenation catalyzed by a) 11wt.% Pt/NPC_THF, b) 11wt.% Pt/NPC_TX, and c) 11wt.% Pt/NPC_PEG.

The observed rate varies linearly with the total porosity. Figure 4.2 demonstrates the observed rate as a function of total porosity for the hydrogenation of 1-hexene catalyzed by the NPC catalysts and the conventional catalyst. The linear behavior noted for the Pt/NPC catalysts that were synthesized does not extend to the conventional catalyst. A linear extrapolation of the rate data from the Pt/NPC catalysts would lead to a predicted rate for the conventional catalyst that would be at least three times lower than it actually is. In other words the dependence of rate on porosity predicted from the Pt/NPC catalysts is well below that for the conventional catalyst. The reason is that most of the metal is utilized in the conventional catalyst, whereas for the
Pt/NPC catalysts a good portion of the metal is not used for reaction and is trapped in nonporous sections of the catalysts or in sections of disconnected porosity.

Figure 4.2 Plot of observed rate of reaction as a function of total porosity for 1-hexene hydrogenation catalyzed by a) 11wt.% Pt/NPC_THF, b) 11wt.% Pt/NPC_TX, c) 6wt.% Pt/NPC_PEG, and d) 10wt.% Pt/aC (conventional catalyst).

4.3.1.2 Microporosity versus Mesoporosity

A more in-depth examination of the relationship of porosity and observed rates display some strong trends. The total porosity is broken down between the two ranges of micro and mesoporosity. Figure 4.3 displays observed rate for 1-hexene hydrogenation as a function of
mesoporosity in the synthesized catalysts. Figure 4.4 reveals the relationship of observed rate for 1-hexene hydrogenation as a function of microporosity in the synthesized catalysts.

Figure 4.3 Relationship of observed reaction rate for 1-hexene hydrogenation and mesoporosity of the a) 11wt.% Pt/NPC_THF, b) 11wt.% Pt/NPC_TX, and c) 6wt.% Pt/NPC_PEG.
Figure 4.4 The observed rate for 1-hexene hydrogenation as a function of microporosity of a) 11wt.% Pt/NPC_THF, b) 11wt.% Pt/NPC_TX, and c) 6wt.% Pt/NPC_PEG.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Micropore (% of total volume)</th>
<th>Mesoporosity (% of total volume)</th>
<th>Selectivity (1-hexene/t-2-hexene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/NPC_TX</td>
<td>75</td>
<td>25</td>
<td>5.9</td>
</tr>
<tr>
<td>Pt/NPC_PEG</td>
<td>59</td>
<td>41</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table 4.2 Table comparing porosity with selectivity (note: selectivity calculated by taking the ratio of observed rates of the respective alkenes).
Examining Table 4.2, it was observed that as the percent of total volume in the micropore region increased the selectivity increased while an increase of mesopores resulted in a decrease in selectivity. The two hydrogenation reactants, 1-hexene and t-2-hexene, displayed a significant difference in activities. Thus, if this selectivity was to vary with porosity, it will be easily observed for t-2-hexene versus t-3-hexene.

4.3.1.3 Average Pore Size

The average pore sizes of the synthesized catalysts are all centered relatively closely. The major difference noted was in the breadth of the distributions, especially for the catalyst synthesized using PEG as the solvent. The pore size distribution for three different synthesized catalysts is presented in Figure 4.5.
Figure 4.5 Pore size distributions calculated from methyl chloride adsorption data of three synthesized catalysts.

The catalyst synthesized with PEG revealed the most broad pore size distribution of all experimental catalysts, with the average pore size centered at 1.0 nm, compared to the other two catalysts which are centered between 0.55 and 0.65 nm. The conventional catalyst has a very broad distribution, centered at 0.9 nm. When PEG was used as the solvent, a significant fraction of porosity was distributed at pore sizes above 1.0 nm, which resulted in the decrease in selectivity, and an increase in activity.
4.3.2 Determining Rate Limitation

4.3.2.1 Weiss-Prater Criterion

One method of determining if diffusion limitations are present is to calculate the Weiss-Prater number for the specific reaction. The equation relating to a first order, irreversible reaction is seen as Equation 1.[2, 3]

\[
\Phi = \frac{(-r_A)_{obs}L^2}{D_eCs}
\]  \hspace{1cm} (1)

Where \( r_A \) is the global reaction rate of component A per unit catalyst volume, \( L \), for a spherical shaped pellet is the radius divided by three, \( D_e \) is the effective diffusivity and \( C_s \) is the concentration of the reactant in the bulk. For the conventional catalyst, which contains mesopores and macropores, and for which the active sites lay on the surface, we can assume that \( D_e \) is that for bulk liquid diffusion. When \( \Phi \ll 1 \), internal diffusion can be neglected, and when \( \Phi \gg 1 \), the reaction is controlled by internal diffusion. The values of \( \Phi \) calculated for all the catalysts for the hydrogenation of 1-hexene are listed in Table 4.3.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weiss-Prater Number (Φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11wt.% Pt/NPC-THF</td>
<td>9.7 x 10³</td>
</tr>
<tr>
<td>11wt.% Pt/NPC-TX</td>
<td>17</td>
</tr>
<tr>
<td>6.6wt.% Pt/NPC-PEG</td>
<td>2.3</td>
</tr>
<tr>
<td>Conventional Catalyst</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 4.3 Weiss-Prater calculations were conducted for the hydrogenation of 1-hexene. Effective diffusivities were taken from previously published data (Note: The calculations were determined at reactant concentrations, $C_s$, >80% of the initial concentration).[4-6]

The Weiss-Prater numbers for the given catalysts determine that the NPC catalysts have a rate dependence on the diffusion of the reactant, as opposed to the conventional catalyst, which displays no diffusion limitations. The NPC-THF catalyst value of $Φ$ is much larger than 1, at about $10^4$, indicating a very strong internal diffusion dependence on the rate, while the TX catalyst is about 10 which correlates to internal diffusion dependence, but it is much less the case, and the conventional catalyst is less than one indicating no internal diffusion dependence.

4.3.2.2 Effectiveness Factor and Thiele Modulus

Next, the Thiele Modulus and effectiveness factor for the conventional and NPC catalysts were determined. Because 1-hexene has the highest global rate for the NPC catalyst, if its rates are diffusion limited, then all the other hydrogenations, which are slower, must also be diffusion limited. The effectiveness factor, $η$, is defined as the ratio of the observed reaction rate to that which would occur if all of the active sites inside of the catalyst particle were exposed to reactant at the same concentration and temperature as that at the outside surface of the particle. The Thiele Modulus, $φ$, is a dimensionless number that relates the rate constant, effective diffusivity
and particle size.[7] The effectiveness factor is a function of the Thiele modulus as can be seen in Equation (2) and (3).[4, 8]

\[
\eta = \frac{(r_A)_{\text{obs}}}{r_A(C_A^*)} = \frac{Tanh\varphi}{\varphi}, \quad (2)
\]

\[
\eta \rightarrow 1, \text{ as } \varphi \rightarrow 0
\]

\[
\eta \rightarrow 1/\varphi, \text{ as } \varphi \rightarrow \infty
\]

\[
\varphi = \frac{R}{3} \sqrt{\frac{k\rho_s}{D_{EA}}}, \quad (3)
\]

Here \((r_A)_{\text{obs}}\) is the observed reaction rate for component \(A\) per unit catalyst mass, while \(r_A(C_A^*)\) is the reaction rate for component \(A\) per unit catalyst mass if the concentration of \(A\) were at \(C_A^*\), which is the molar concentration of fluid reactant at surface of catalyst. For Equation (3), \(R\) is the radius of a spherical particle, \(k\) is the first order rate constant for catalytic reaction, \(\rho_s\) is the density of the catalyst and \(D_{EA}\) is the effective diffusivity of component \(A\) through the porous solid. The relation of observed rate to the effectiveness factor and the relation of the particle size to the Thiele Modulus is observed in Equation (4).

\[
\eta_1 \frac{r_{\text{obs},1}}{r_{\text{obs},2}}, \quad \varphi_1 = \frac{R_1}{R_2}, \quad (4)
\]
The effectiveness factor can be calculated experimentally by measuring the reaction rates for several catalyst particle sizes under otherwise identical conditions. The effectiveness factor value approaches unity when no increase in rate per unit quantity of catalyst occurs on subdivision. For instance, for the same catalyst, let two particles have radii \( R_1 \) and \( R_2 \). The ratio of their rates will be \( \eta_1 / \eta_2 \) and the ratio \( R_1 / R_2 \) will be equal to the ratio of \( \varphi_1 / \varphi_2 \) (Equation 4). The relation of the effectiveness factor to the Thiele Modulus for a first-order irreversible reaction in a sphere is noted in Equation 5.

\[
\eta_1 = \frac{3}{\varphi_1} \left[ \frac{1}{\tanh \varphi_1} - \frac{1}{\varphi_1} \right], \quad \eta_2 = \frac{3}{\varphi_2} \left[ \frac{1}{\tanh \varphi_2} - \frac{1}{\varphi_2} \right]
\] (5)

\[
\eta_1 = x \eta_2 \quad \text{, where } x \text{ is the ratio of observed rates and}
\]

\[
\varphi_1 = y \varphi_2 \quad \text{, where } y \text{ is the ratio of particle sizes}
\]

The \( \eta_1 \) in Equation 5 can be substituted for \( x \eta_2 \), and \( \varphi_1 \) can be substituted out for \( y \varphi_2 \). Since the values for \( x \) and \( y \) are known, you can set two equations to equal the same \( \eta \) value and graph to see where they converge.

If the experimental catalyst is operating in a kinetically controlled regime, then \( \eta_1 = \eta_2 \) even if \( R_1 \neq R_2 \); if, however, the experimental catalyst is operating in the fully diffusion controlled regime, then \( \eta \) falls in the \( 3/\varphi \) region and \( \eta_1 / \eta_2 = R_2 / R_1 \). The hyperbolic tangent approaches unity as \( \varphi \) is increased and \( \eta \) approaches \( 3/\varphi \) at large values of \( \varphi \). The magnitude of \( \varphi \) can increase if the particle is large (\( L \rightarrow \infty \)), if the catalyst has low porosity and has high resistance to internal
transport \((D_{rA} \to 0)\), or if the intrinsic rate constant for reaction is large \((k \to \infty)\). Then, if the catalyst operates in the diffusion controlled regime at both particle sizes, the effectiveness factor will be larger for the smaller particle.

In Figure 4.6, the general plot of effectiveness factor versus Thiele modulus is shown along with the data for the conventional catalyst and the NPC-TX catalyst. The differences between the catalysts are distinguished by where the points for the respective particle diameters fall on the plots. The two different particle diameters used in hydrogenating 1-hexene with the conventional catalyst were 125 and 30 μm. However, no noticeable differences in observed rates were seen in the two different particle diameters, thus the catalyst does not display diffusion limitations. This correlates to the one data point on the zero-sloped part of the plot. When examining the plot for the synthesized catalyst a huge discrepancy is noted in effectiveness factor in going from a 60 μm particle to a 215 μm particle. The overall lower activity for the large diameter particle is due to diffusion limitations of the reactant. Surface adsorption of the reactant (required by both catalysts) is fast, while pore diffusion (required of Pt/NPC) is slow.
Figure 4.6 Plot of effectiveness factor vs. Thiele modulus for the conventional catalyst (red triangle) and the NPC catalyst (blue squares) in the hydrogenation of 1-hexene using catalyst particles with diameters of 125 and 30 microns, and 215 and 60 microns respectively.

4.3.2.3 Effective Diffusivity

The effective diffusivity is a measure of how fast a particular compound diffuses into, and through a specific material. It has been well documented that the differences in effective diffusivity between two or more reactants or products can be used to separate and produce a desired product in a catalytic reaction.[9-13] Thus, it was desirable to determine the effective diffusivities of 1-hexene for the synthesized catalysts, Pt/NPC_TX and Pt/NPC_THF.
If it is assumed that the intrinsic rates of reaction are the same for Pt in PFA-derived carbon catalysts, whether they are pyrolyzed with THF, Triton X-100, or polyethylene glycol, their differences in effectiveness at the same conditions and particle size arose from differences in effective diffusion coefficients. When 1-hexene was hydrogenated by 11wt.% Pt/NPC synthesized using THF, the conversion was barely measureable at the end of the two hours. This very small reactivity then equates to a very small effectiveness factor, \( \eta \), lying well down on the \( 1/\varphi \) part of \( \eta \) versus \( \varphi \). We can compare the effectiveness factors for 11 wt.% Pt/NPC_TX catalyst (subscript 1) and the 11 wt.% Pt/NPC_THF catalyst (subscript 2).

\[
\frac{\eta_1}{\eta_2} = \frac{\varphi_1}{\varphi_2} = \frac{1}{\varphi_2} \quad (6)
\]

Thus the ratio of \( \eta \) is equal to that of the ratio between the inverse ratios of \( \varphi \) seen in Equation 6.

\[
\frac{\eta_1}{\eta_2} = \frac{L_2}{L_1} \sqrt{\frac{k_{i2}}{D_{c2}}} \quad (7)
\]

If the catalysts’s particle sizes were held constant \( (L_1 = L_2) \) and if the intrinsic rate constants, \( k_i \), were the same for both Pt/NPC catalysts, then if we make the further assumption - that the intrinsic rate constant for the conventional catalyst is the same as that for the
experimental ones – then we can compute effective diffusivities for the experimental catalysts using a value for diffusion in the bulk to provide an order of magnitude estimate for diffusivity in the conventional catalyst. When we do so we find that the Pt/NPC catalysts with only micropores has a diffusivity for 1-hexene about $10^9$ smaller than the bulk diffusivity. The Pt/NPC catalyst prepared with Triton X-100 has a diffusivity for 1-hexene which is about seven orders of magnitude larger than the all-microporous catalyst.

$$\frac{\eta_1}{\eta_2} = \sqrt{\frac{1}{D_{e2}}} = \sqrt{\frac{D_{e1}}{D_{e2}}}$$ \hspace{1cm} (8)

$$\left(\frac{\eta_1}{\eta_2}\right)^2 = \frac{D_{e1}}{D_{e2}}$$ \hspace{1cm} (9)

From these assumptions the effective diffusivity, $D_e$, was calculated by using the bulk diffusion value as the $D_e$ value for the conventional catalyst.[6] The values for $D_e$ are presented in Table 4.4.
The effective diffusivity for the NPC catalyst prepared with THF is extremely low compared to the other two catalysts. The difference between the two synthesized catalysts for diffusivity of 1-hexene is approximately eight orders of magnitude. This demonstrates the importance of creating mesopores within the catalyst system. The TX synthesized catalyst can be utilized for shape-selective reactions in the liquid phase, while the THF synthesized catalyst cannot be used in shape-selective reactions in the liquid phase. The relatively small amount of mesoporosity is paramount for activity in NPC catalyst.

But the problem with this analysis is that we have made various assumptions about the most subtle parameter -- the intrinsic rate constant and thusly, about the chemistry. In other words with these assumptions, we have loaded all the differences between these catalysts solely into the effective diffusivity and since the observed rate differences are indeed significant the differences in diffusivities for 1-hexene appear to be orders of magnitude different. Furthermore it is not unexpected for the diffusion coefficient for a molecule transporting in a molecular sieve to be below $10^{-10}$ cm$^2$/sec and, therefore, many orders of magnitude lower than that of bulk diffusion. This implies the results are reasonable, but we can only know if the results of the assumptions are indeed reasonable by testing them against experiment. Thus, in the next section

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Effective Diffusivity (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11wt.% Pt/NPC-THF</td>
<td>$5.1 \times 10^{-13}$</td>
</tr>
<tr>
<td>11wt.% Pt/NPC-TX</td>
<td>$1.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>Conventional Catalyst, 10wt.% Pt/aC</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

Table 4.4 Effective diffusivities calculated from the kinetic data of 1-hexene hydrogenation.
(Note: *assumed bulk diffusion).
we conduct adsorption experiments with the aim of determining the real diffusivities in these catalysts.

4.3.2.4 Diffusion Coefficient Calculated from Hydrocarbon Adsorption

Hydrocarbons were adsorbed using the catalyst as adsorbents. This was done to determine the diffusion coefficients for the respective reactants and products. The observed rates of the hydrocarbon liquid phase adsorption experiments can be seen in Table 4.5.
<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Rate of Adsorption (x $10^{-3}$ cm$^3$/g*sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt/NPC_TX</td>
</tr>
<tr>
<td>1-hexene</td>
<td>3.55</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.85</td>
</tr>
<tr>
<td>1-heptene</td>
<td>1.94</td>
</tr>
<tr>
<td>1-octene</td>
<td>1.68</td>
</tr>
<tr>
<td>1-decene</td>
<td>1.35</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>0.99</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>0.62</td>
</tr>
<tr>
<td>Isooctane</td>
<td>0.40</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.19</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.59</td>
</tr>
<tr>
<td>Heptanes</td>
<td>2.41</td>
</tr>
<tr>
<td>Isooctene</td>
<td>2.24</td>
</tr>
<tr>
<td>Octane</td>
<td>1.41</td>
</tr>
<tr>
<td>Decane</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Table 4.5 The calculated rates of adsorption based on liquid-phase uptake experiments.

The overall rates for the adsorbents, fastest to slowest are as follows: Pt/aC > Pt/NPC_TX > Pt/NPC_THF. The respective diffusion coefficients for each adsorbent and adsorbate system can be calculated based on the kinetics of the adsorption using Equation 9. [14]
Where $R_p$ is the adsorption rate (mol/sec*mL), $\rho$ is the density of particle (g/mL), $C_{ads}$ is the concentration of adsorbent per unit weight of adsorbent (mol/g), $t$ is time (sec), $k_{ads}$ is the adsorption rate constant (mL/g*sec), $C_i$ is the concentration of adsorbate in the interparticle space (mol/mL), and $K$ is the adsorption equilibrium constant (mL/g). This equation can be rearranged for a linear fit, noted in Equation 10.

$$\frac{\delta C_{ads}}{\delta t} = C_{ads} \left( \frac{-k_{ads}}{K} \right) + k_{ads} * C_i \quad (10)$$

Plotting the change of adsorbed concentration with respect to time yields the intercept $k_{ads} * C_i$ and the slope $k_{ads}/K$. The diffusion coefficient can be determined from the Sherwood Number, however, first the adsorption rate constant, $k_{ads}$, must be related to the mass transfer coefficient, $k_c$ (cm/sec).[15] This is done by dividing the adsorption rate constant by the surface area per unit mass of the adsorbent determined experimentally. Once $k_c$ is calculated the relationship to $D_c$ is noted in Equation 11.

$$N = \frac{k_c * d_p}{D_c} \quad (11)$$
Here, $N$ is the Sherwood Number, which in this case has a value of 2 for stagnant flow, $k_c$ is the mass transfer coefficient (cm/sec), $d_p$ is the average particle diameter (cm) and $D_c$ is the diffusion coefficient (cm$^2$/sec).[8]

The calculated diffusion coefficients correlating to the respective adsorption rate constants in Table 4.6 can be seen in Table 4.7.
<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Diffusivity (x 10⁻⁸ cm²/g·sec)</th>
<th>Pt/NPC_TX</th>
<th>Pt/NPC_THF</th>
<th>Pt/aC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexene</td>
<td>7.04</td>
<td>6.06</td>
<td>3.26</td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>3.67</td>
<td>1.15</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>1-heptene</td>
<td>3.85</td>
<td>2.83</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>1-octene</td>
<td>3.33</td>
<td>2.51</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>1-decane</td>
<td>2.67</td>
<td>0.60</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>1.97</td>
<td>2.60</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>1.24</td>
<td>2.13</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Isooctane</td>
<td>0.79</td>
<td>1.60</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2.36</td>
<td>4.83</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>3.15</td>
<td>3.70</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>Heptanes</td>
<td>4.78</td>
<td>1.12</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>Isooctene</td>
<td>4.44</td>
<td>1.35</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Octane</td>
<td>2.79</td>
<td>0.83</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>Decane</td>
<td>0.87</td>
<td>1.73</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6 The diffusion coefficients calculated from liquid adsorption experimental data.

The overall diffusion coefficients are all relatively similar with the difference between all catalysts being no more than an order of magnitude. These diffusion coefficients do not correlate to what was observed in catalytic activity for the three catalysts (Table 4.7).
The observed reaction rates for 1-hexene hydrogenation (note: the NPC catalysts contain the same amount of platinum, 11wt.%).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$r_{\text{obs}}$ (mols/cm$^3 \cdot$ hr)</th>
<th>$r_{\text{obs}}$ (mols/g*hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>$1.8 \times 10^{-1}$</td>
<td>$8.6 \times 10^{-1}$</td>
</tr>
<tr>
<td>Pt/NPC_TX</td>
<td>$1.2 \times 10^{-1}$</td>
<td>$9.7 \times 10^{-2}$</td>
</tr>
<tr>
<td>Pt/NPC_THF</td>
<td>$1.2 \times 10^{-4}$</td>
<td>$3.9 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Table 4.7

The difference between the least active catalyst, Pt/NPC_THF, and the most active catalyst, Pt/aC, for 1-hexene, is 4-5 orders of magnitude. However, such a large difference is not observed for the measured diffusivities. It can be extrapolated that for even less active reactants (e.g. 1-octene, 1-decene, etc), the difference in the observed reaction rate would be much larger. The effective diffusion coefficients calculated from 1-hexene hydrogenation were previously calculated (Table 4.4). Comparing the effective diffusion coefficients (determined from catalysis) to the diffusion coefficients (determined from liquid adsorption tests), in Table 4.4, shows large discrepancies.

Although the rates of 1-hexene adsorption do vary across the three catalysts, they do not vary by the orders of magnitude we see in the variation in the catalytic rates of reaction. When we assumed the catalytic chemistry was all about the same with the same rate of reaction to a first approximation – we computed large differences in 1-hexene diffusivities across these catalysts. However, when we made the measurements of rates of adsorption, we observe this cannot be the case. Upon analysis, the diffusion coefficients between these three catalysts differ by only an order of magnitude at most. Adsorption into the mesopores of the conventional catalyst and the
Pt/NPC-Triton X-100 catalyst is fast, but further transport into the micropores is slow. The fact it is just as slow as it is in the Pt/NPC-THF catalyst which is only microporous. Here the difference in the effectiveness factor must come back again to the real difference in the intrinsic rate constants at the Pt sites. These differences are the steric constraints imposed by a pore which extends down to a larger platinum surface. The platinum on the conventional catalyst is in the mesopores and macropores which have no such constraints.

4.4 Conclusions

From the Weiss-Prater number the NPC catalysts are diffusion limited while the conventional catalyst is not. This is more evident for the NPC catalyst synthesized using THF. The Weiss-Prater number is in good agreement with an analysis of the effectiveness factor versus the Thiele modulus, as it also displayed that the NPC catalysts are diffusion limited. The conventional catalyst was found at the zero slope of the plot, while the NPC catalysts fell on the $3/\varphi$, indicating diffusion limitations. The liquid adsorption experiments displayed that the NPC catalyst made with THF had lower rates of adsorption and lower diffusion coefficients compared to the NPC catalyst made with Triton X-100 and the conventional catalyst. However, the lower values cannot be the primary or sole actor in the very low activities observed for the hydrogenation of 1-hexene. Thus, it is concluded that the concentration of active sites has a larger impact on the activity of these catalysts, and that while an increase in pore size increases the diffusivity, the major factor is that it frees up more active sites.

Future work should be exploring how to increase the number of active sites while not increasing porosity to the extent of no longer being selective. This can be done several ways. One is to oxidize the carbon surrounding the Pt particles taking advantage of their catalytic effect.
in that process. The oxidation could be done at temperatures where only a catalyst would activate the carbon. This would allow for selective oxidation of carbon embedding the Pt. The porosity may increase slightly, but the concentration of active sites should increase tremendously. This work could then explore how much of the catalytic activity is influenced by active sites and how much is influenced by the porosity. However, catalyst poisoning would be an issue since oxidation of the carbon would produce carbon monoxide, a known poison to platinum. Another method would be to decrease the size of the platinum nanoparticles.

One way of doing this would be to form platinum particles on a stabilizing support and then coat that support with PFA, followed by pyrolysis to form the NPC catalyst. A material that has been gaining attention as a metal support is BC$_x$. It has been shown experimentally to stabilize atomic sized Ti particles.[16] With this in mind, the next Chapter will examine the synthesis of BC$_x$.

### 4.5 References


Chapter 5

Formation and Characterization of BC\(_x\) by Chemical Vapor Deposition of Benzene and Boron Trichloride

5.1 Introduction

Boron substituted in the carbon lattice, commonly referred to as BC\(_x\), forms a graphite-like crystal structure, with as much as 25 at.% boron incorporated into the carbon framework, according to recent reports.[1] Boron atoms at substitutional sites do not cause a distortion in the carbon crystal structure due to similar atomic size. However, the electrical properties of the doped carbon are altered because boron has one fewer electrons than carbon. Thus, it acts as an electron acceptor which creates a hole-carrier in the valence band, ultimately enhancing the electrical conductivity.[2, 3]

Recently the effect of synthesis conditions on the amount of boron incorporated into the C lattice has been recently explored.[2, 4-7] Early work by Lowell demonstrated boron substitution by heating graphite flakes and B\(_4\)C.[8] This procedure yielded concentrations of 2.35 atomic % of boron at 2350°C. Current procedures use chemical vapor deposition (CVD) from a flowing mixture of a carbon precursor (benzene, CH\(_4\), etc.) and boron trichloride (BCl\(_3\)), into a furnace at >700°C. [2, 4, 6, 9-15] This method has incorporated a higher concentration of boron into the carbon lattice, improving upon previous techniques.[9, 12, 15-17]

However, the exact structure and maximum boron concentration is still largely debated.[9, 12, 15-17] The main reason for this originates in how boron is incorporated into the carbon lattice; is it via substitution or intercalation.[1, 14, 17-19] Furthermore, the accepted hypothesis is that boron can be substituted into the lattice up to concentrations of ~16 atomic %.
Beyond this concentration, incorporated boron is found at both interstitial (steps and edges) and intercalation sites. This conclusion was based on several studies that examined the diffraction patterns of different samples with various boron concentrations, ranging from 0 to 22 atomic \%. As the boron concentration increased from 0 to 16 at.\%, the $d_{002}$ spacing decreased, approaching graphite’s interlayer spacing of 3.35 Å.[19] When the boron concentration was increased above 16 at.\% the interlayer spacing increased. The increased spacing is attributed to boron being intercalated in the framework, ultimately moving the carbon sheets further apart. The currently accepted structure for BC$_x$ depicts boron substituted in a trigonally bonded configuration, yet, very few researchers have published data on the bonding configuration of boron. Thus, in this research we sought to further characterize the incorporation of boron into the carbon lattice in order to verify or to nullify the proposed structure.

To provide more information on the BC$_x$ structure this work integrates results from XPS, XRD, TEM and solid state $^{11}$B MAS High Resolution-NMR studies. The use of solid state NMR has yet to be fully exploited to examine the boron configuration in BC$_x$.

Previous reports were unable to resolve the boron tetrahedral peak from the boron trigonal peak due to low field strength spectrometers.[18, 20-22] The use of a 21 T magnet for solid state $^{11}$B MAS HR-NMR studies provides high enough resolution to resolve the trigonal peak clearly from the tetrahedral peak of B with great accuracy. Figure 5.1 displays the range where $^{11}$B compounds appear on $^{11}$B NMR spectra.[23]
Figure 5.1 Approximate span and location of lowest and highest signals in $^{11}$B NMR spectra of individual borane classes.[23]

The structure for BC$_x$ that has been proposed by several researchers can be seen in Figure 5.2. If the currently proposed structure is correct, then the HR-NMR spectrum will display a strong signal for trigonally configured boron as opposed to the tetrahedral environment of boron in boron carbide (B$_4$C).
Figure 5.2 Proposed structure for BC₃ in which carbon rings are joined by B atoms in a trigonal planar configuration.

5.2 Experimental

5.2.1 Reagents

Benzeneₐ(99%) as obtained from Sigma Aldrich was purged for one hour with UHP Arₐ prior to use. Boron trichlorideₐ(99.9%) was obtained from Sigma Aldrich and used without further purifications. Soda-lime was purchased from Sigma Aldrich. The carrier gas used was UHP Heₐ was purchased from Pennsylvania State University general stores.
5.2.2 Synthesis and Setup

5.2.2.1 CVD Reactor Setup and Preparation

A schematic of the BC$_x$ CVD reactor is given in Figure 5.3. The reactor consists of a Lindberg Model Blue M furnace setup with a temperature controller.

![Diagram of CVD reactor](image)

Figure 5.3. Schematic of the CVD reactor furnace used for the synthesis of BC$_x$. (note: The UHP He$_{(g)}$ passes through an oxygen and moisture trap prior to being introduced to the benzene.)

In a typical experiment the carrier gas, helium, bubbles through a flask containing benzene. The flow of the helium gas is controlled by a mass flow controller. The flow of
benzene is directly controlled by the flow of the carrier gas. The flow of boron trichloride is controlled by a mass flow controller.

Prior to each experiment in order to burn away any physisorbed species, the reaction chamber was preheated to 900°C and held at that temperature for two hours, then it was cooled to room temperature. Each BC$_x$ synthesis began by heating the furnace reactor to 900°C in one hour and holding there for two hours under flowing UHP He$_{g}$. The reactant gases were then introduced and the reaction time was started when the desired flow rates had been achieved. The BC$_x$ film was deposited on a sample container as well as on the chamber walls. The gaseous by-product of the reaction, HCl, was neutralized by bubbling the exit gases through an aqueous solution of soda-lime. The standard conditions used for depositing BC$_x$ with the CVD setup are listed in Table 5.1.

<table>
<thead>
<tr>
<th>Typical Reaction Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Duration (min)</td>
</tr>
<tr>
<td>BCl$_3$ Flow (ml/min)</td>
</tr>
<tr>
<td>Benzene Flow (ml/min)</td>
</tr>
<tr>
<td>Total Flow (ml/min)</td>
</tr>
</tbody>
</table>

Table 5.1 Reaction parameters for a typical BC$_x$ run.
5.2.3 Characterization

5.2.3.1 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed with a monochromatic Al Kα source at instrument (Kratos, Axis Ultra; England) with a pass energy of 80 eV for survey spectra and 40 and 20 eV for high resolution spectra. Data were collected with a photoelectron take-off angle of 90° from the surface. All spectra taken were referenced to the Au 4f\textsubscript{7/2} peak located at 84.0 eV.

5.2.3.2 X-Ray Diffraction (XRD)

X-Ray diffraction patterns were collected using a Scintag PADV theta-2-theta Powder Diffractometer using non-monochromatized Cu Kα radiation source with a step size of 0.02° 2θ and a count time of 0.5 sec. Acquisition conditions were 35 kV and 30mA. A NIST SRm 640c silicon standard was used to correct the line position and broadening of the carbon patterns. The Bragg equation (Equation 5.1) was utilized to calculate the $d$-spacing of the boron-carbon material ($d_{002}$). The x-ray wavelength was 1.5412 Å and $\theta_{002}$ is the angle of the (002) peak. Average crystallite sizes in the $c$-direction ($L_c$), which is perpendicular to the layer planes were calculated by the Scherrer equation (Equation 5.2) where $k$ is taken to be 0.9, and $B$ is the full width at half max of the peak of interest, while $\theta$ is the position of the peak.

\[
\lambda = 2d_{002}\sin \theta_{002} \quad (5.1)
\]

\[
L = \frac{k\lambda}{B \cos \theta} \quad (5.2)
\]
5.2.3.3 Raman Spectroscopy

Raman spectra were recorded using a confocal Raman microscope spectrometer (Renishaw inVia microRaman) set for 1 μm spot sizes, with excitation from a 35mW HeNe laser (514 nm) and optics set for 12 mW at the sample spectra were recorded at 2 cm\(^{-1}\) resolution. The microcrystalline planar size \(L_a\) was calculated from the ratio in intensities of the D-peak to the G-peak \((I_D/I_G)\) (Equation 5.3) where \(R\) is equal to the ratio of intensities.

\[
L_a = 44R^{-1/4} \tag{5.3}
\]

5.2.3.4 \(^{11}\)B Solid-State NMR Spectroscopy

Solid state \(^{11}\)B MAS NMR Bloch decay experiments were conducted on a Varian Inova spectrometer interfaced to a home-built 3.2 mm magic-angle spinning (MAS) probe operating at a magnetic field strength of 21.1 T (observation frequency of 288,960,736.2 MHz for \(^{11}\)B). A short \((\pi/10)\) pulse was used at a radio frequency strength of 100 kHz so that quantitative information could be obtained and a frequency region of 200 kHz was sampled. For processing, an exponential filter of 200 Hz was applied to the time domain data and the data set was zero filled to 4096 complex data points before being Fourier transformed.
5.2.3.5 Transmission Electron Spectroscopy (TEM)

The images were recorded with a Hitachi HF2000 High Resolution Transmission Electron Microscopy instrument.

5.3 Results and Discussion

5.3.1 CVD BC$_x$ Films

The XRD spectrum of the as-deposited material is shown in Figure 5.4. The peak at 2$\theta$ angle of 26.5° is attributed to the $d_{002}$ spacing between planes of the graphitic structure. The full width half max (FWHM) of the peak is inversely proportional to the crystallite size of the graphitic carbon sample in the $L_c$ direction. A decreased FWHM results in an increase in crystallite size. The broadness of the peak is indicative of turbostratic carbon which is characterized by high crystallinity on the short range order.[24, 25] No long range order is present in the carbon sheets. The diffraction pattern observed is similar to what has been reported in previous work. [1, 14]
For the peak observed at 26.5° in Figure 5.4, the $d_{002}$ was calculated to be 0.344 nm and the $L_c$ was determined to be 3.6 nm. An inverse linear dependence of the full width half max (FWHM) of the peak with boron content was recently reported.[14] As the boron concentration increased the FWHM decreased. This was attributed to boron catalyzing the graphitization of the BC$_x$ structure.

Raman spectroscopy is commonly used to elucidate the microstructure of carbonaceous species. There are two specific absorption peaks for carbonized materials. The first peak is located in the range of 1340 – 1360 cm$^{-1}$ and is called the D-peak, referring to “defects” in the carbon structure. The second peak is in the range of 1580 – 1600 cm$^{-1}$ and is referred to as the G-peak which correlates to “graphite” regions in the carbon structure. The Raman spectra of the BC$_x$ sample can be seen in Figure 5.5.
Figure 5.5. Raman spectra of BC$_x$ material.

Highly crystalline graphite displays a single peak in the G-peak range. Amorphous and glassy carbons display the G-peak and the D-peak in their Raman spectra. The BC$_x$ sample displayed two peaks, the first at 1348 cm$^{-1}$ and the second at 1581 cm$^{-1}$. The G-peak represents in-plane bond stretching vibrations of carbon atoms in graphite, while the D-peak correlates to the vibrations of the defect carbon atoms, particularly the ones in a non-graphitic structure.

The microcrystalline width, $L_a$, was calculated to be 4.4 nm based on the ratio of the two peaks intensities (Equation 5.3). The $I_D$ is the intensity of the peak at 1348 cm$^{-1}$ and $I_G$ is the intensity of the peak at 1581 cm$^{-1}$. The $L_a$ value is the degree of crystallinity parallel to the graphene plane.

Transmission electron microscopy (TEM) was conducted on the BC$_x$ material to examine the morphology of the material (Figure 5.6(a-c)). The images display two distinct features of the BC$_x$ material. Discrete regions resembling graphite were observed on the short
order. The graphite-like regions are highly crystalline with distinct spacing and order. Turbostratic regions in the material were also found. Turbostratic components can be described as non-crystalline and appear out of focus in the images. TEM images of BC₃ show that the crystallites have short range order but lack long range order, which correlates to the XRD diffraction pattern and Raman spectra.

The electron diffraction pattern gathered from the TEM can be seen in Figure 5.7. It has two significant rings, with the inner ring correlating to a \( d \)-layer spacing of 0.338 nm. The rings are uniform, and discrete, and are commonly observed for polycrystalline materials.

Figure 5.6(a) TEM image of BC₃ material displaying turbostratic regions.
Figure 5.6(b) TEM image of highly graphitic regions of the BC$_x$ material.
Figure 5.6(c) TEM micrograph of the BC₃ material illustrating highly graphitic regions in the material as well as turbostratic regions.
Solid state $^{11}$B NMR studies were carried to determine the chemical bonding environment of boron in BC$_x$. There are several interactions that play a role in the shape and size of the NMR signal. In liquids, multiple sites are commonly distinguished based solely on chemical shifts (the interaction of the nucleus with the magnetic moment induced by neighboring electrons). However, in solids, other interactions dramatically influence the NMR spectrum. For nuclei that possess a nonzero quadrupole moment (nuclei with $I > \frac{1}{2}$ such as $^{11}$B), the predominate interaction is the quadrupolar interaction, which is the interaction of the nucleus with the surrounding electric field gradient (EFG). Other problematic interactions, such as dipole-dipole coupling can be averaged under MAS conditions.
The non-zero quadrupole moment \((4.06 \times 10^{-30} \text{ m}^2)\) of \(^{11}\text{B}\) causes the nucleus to interact strongly with the surrounding EFG. While the quadrupolar interaction can be averaged by MAS to first order, the second order quadrupolar interaction significantly alters the central transition \((m = -1/2 \rightarrow 1/2)\) and cannot be averaged under MAS nor by spinning at any one fixed angle[26].

The resulting anisotropy then manifests itself in the NMR spectrum causing resonances to appear as broad MAS powder patterns and not as single isotropic peaks. For a nucleus in a symmetric chemical environment (octahedral or tetrahedral coordination), the interaction of the EFG across the nucleus is uniform and the associated broadening is diminished. However, for nuclei in an asymmetric environment (defined as a lack of symmetry either the \(X\) or \(Y\) axis), such as a trigonal planar coordination, resonances can become significantly broadened. This broadening has been observed in the \(^{11}\text{B}\) MAS NMR spectrum of \(\text{BC}_x\) [27].

Several researchers have used NMR to characterize \(\text{BC}_x\) materials, however, due to the second order quadrupolar broadening of resonances in the \(^{11}\text{B}\) NMR spectra, the individual contributions of the B atoms were difficult to resolve[1, 20-22]. To obtain better resolution, spectra were acquired at the highest available field strength (21.1 T) because second order broadening scales inversely with magnetic field strength. The \(^{11}\text{B}\) NMR spectra can be seen in Figure 5.8.

Analysis of the \(^{11}\text{B}\) MAS NMR spectra of a pure \(\text{BC}_x\) indicated a single chemical environment as evidenced by a single resonance centered at 32 ppm corresponding to boron bonded in a trigonal coordination[23, 28-30]. The low intensity peaks (marked with asterisks) on either side of, and slightly overlapping with, the main resonance correspond to spinning sidebands, which occur at integer multiples of the rotor spinning speed.
Figure 5.8. The solid state $^{11}$B HR-NMR spectrum displaying one chemical site for $^{11}$B, centered at 32 ppm. (Note: the asterisks signify the spinning sidebands observed for solid state NMR)

X-ray photoelectron spectroscopy (XPS), another technique that examines the chemical states of B in the framework, was adopted (Figure 5.9). Four deconvolution lines were used to obtain good agreement between the measured and fitted B1s spectra. The different chemical states of boron are centered at 187.5, 189.7, 191.4, and 193.4 eV respectively. The 193.4 peak is conventionally attributed to -B-O- bonds due to their high bond strength, while the lower energy peak, 187.5 eV, is assigned to boron carbide bonds. The two middle peaks at 189.7 and at 191.4 are typically attributed either to substitutional boron or interstitial (steps, edges or intercalated)
boron. The bond strength of substitutional boron should be higher than interstitial boron due to boron having discrete chemical bonds. Based on comparative bond strengths, the 191.4 eV peak was attributed to substitutional boron and the 189.7 eV peak to doped boron not substituted. The carbon to boron atomic ratio was determined to be 3 to 1, which corresponds to what has been proposed in the literature for the CVD synthesis of BC$_x$.[2, 9, 11, 16, 22]

![XPS spectra with curve fit for BC$_x$ film.](image)

**Figure 5.9** The XPS spectra with the curve fit for BC$_x$ film.
5.4 Discussion

5.4.1 BC$_x$ Composition and Structure

The boron concentration in the BC$_x$ films was determined by XPS and by solid state $^{11}$B NMR. The concentration determined by solid state NMR equates to the bulk concentration while XPS is a surface characterization tool, thus it represents only the first few atomic layers. The concentration determined by NMR was calculated using a boric acid standard as the reference. The respective concentrations determined by solid state NMR and XPS are reported as well as the $d_{002}$ lattice spacing determined by XRD and TEM. The B:C ratio that was calculated from XPS and $^{11}$B Solid State NMR (Table 5.2) are also given.

<table>
<thead>
<tr>
<th>B Concentration</th>
<th>B:C Ratio</th>
<th>$d_{002}$ Lattice Spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS$^1$</td>
<td>$^{11}$B NMR$^2$</td>
<td>XPS</td>
</tr>
<tr>
<td>17</td>
<td>15.9</td>
<td>1:3</td>
</tr>
</tbody>
</table>

Table 5.2 Chemical characteristics based on XPS, NMR, XRD and TEM. (note: $^1$ XPS concentration correlates to atomic %, $^2$ NMR concentration correlates to weight %, $^3$ NMR ratios are not just the ratio of B:C, but with B to all other elements in the material, i.e. O. Thus, it is considered to be the lower concentration boundary.)

The presence of substitutional boron has been shown to cause a contraction of the layer spacing compared to graphite, while intercalated boron leads to an expansion of the graphite layer spacing.[8, 17, 19, 31, 32] Theoretical calculations have predicted that the layer spacing decrease is due to two reasons; the decrease in $\pi$ electron density and Poisson contraction along the $c$-axis.
due to expansion along the $a$-axis.[19] The $a$-axis expansion originates from the larger bond length of –B–C– as compared to –C–C–, globally stretching the graphene-like lattice.[32, 33]

The electronic structure of boron is similar to carbon, but with one fewer electron in the outer shell. Thus, substitution of boron, an electron deficient atom, for carbon will globally decrease the number of $\pi$ electrons. This yields weaker interactions between sheets thus lowering the repulsion between them and allowing them to come in closer proximity to one another. The interlayer spacing determined from the XRD diffraction pattern (Figure 5.4) equates to approximately 0.345 nm, which is similar to graphite’s interlayer spacing of 0.335 nm. Transmission electron microscopy provides an alternate means of determining the interlayer spacing.

The diffraction pattern gathered from TEM (Figure 5.7) also revealed an interlayer spacing of 0.338 nm. This $d_{002}$ value is smaller than the value calculated from the XRD pattern. The difference in $d_{002}$ spacing can be attributed to the TEM analysis being on a sample area on the order of square nanometers, while that for XRD over the bulk of the sample. However, the interlayer spacing determined from both methods is similar to what has been published on B doped carbons. The incorporation of B into the carbon lattice reduces the interlayer spacing at a lower temperature than expected due to $c$-contraction from –B–C– bonds being longer than –C–C– bonds, as well as reduced $\pi$-electron cloud repulsion arising from a lack of $\pi$ electrons perpendicular to the layer plane from boron.

The TEM micrographs of the samples display two distinct orientations, graphitic and turbostratic. These phases were also observed by Serin, et. al. who concluded that at low B concentrations (5-10 at.%) onion-like phases were dominant, while at higher B concentrations (25 at.%) a turbostratic phase was dominant.[13] In Figure 5.6(c), the different structural orientations of BC$_x$ can be observed. Some highly graphitic regions were present, as well as amorphous regions. Both phases were clearly seen and neither form is dominant. Based on the literature, the
TEM micrographs in Figure 5.6(a-c), indicate that the boron concentration in the material was between 10 at.% and 25 at.%. [15]

5.4.2 Chemical Nature of B in BC$_x$

X-ray photoelectron spectroscopy data was used to calculate the atomic percent (at.%) of boron in BC$_x$. Boron accounts for ~17 at.% in the BC$_x$ sample. Figure 5.9 shows four peaks in the XPS spectra at 193.4, 191.4, 187.5, and 189.7 eV.

From the integrated peak intensities obtained from spectral fitting of NMR resonances, the boron concentration in the bulk can be calculated and compared to the concentration calculated by XPS. The concentration for boron can be determined in a sample by using a standard as a reference. The concentration of boron is directly proportional to the area under the NMR peak. The bulk concentration was calculated to be ~15.9 wt.% from NMR versus 17 at.% for XPS. The two concentrations are close considering that the two techniques analyze different aspects of the sample; XPS analyzes the surface, while NMR analyzes the bulk. The difference can be due to several possibilities. Firstly, the amount of the sample examined is different. Secondly, the surface of the sample may have a higher concentration of boron than in the bulk. In the XPS data two peaks were denoted as doped boron; one attributed to substitutional and one attributed to interstitial, where interstitial could be step, edge sites or intercalation. Based on the interlayer spacing, it is doubtful that boron is intercalated. This leaves edge and step sites. The boron located at edge sites would result in higher concentrations calculated by XPS. This would account for the higher concentration provided by XRD as compared to NMR. Finally, the chosen spot on the sample on which XPS was conducted could have been boron-rich and would yield
slightly higher boron concentrations. However, it is noted that other areas of interest displayed similar concentrations. Regardless, the concentration of boron in the carbon framework measured by different methods is in good agreement with the literature published under similar operating synthesis conditions.[9, 12, 14]

5.5 Conclusions

BC$_x$ was synthesized by simultaneously flowing BCl$_3$ and benzene vapor into a reaction chamber preheated to 900°C. The amount of boron incorporated into the material was determined by $^{11}$B Solid State MAS-NMR and XPS. Boron was effectively included in the carbon framework based on the graphite-like lattice spacing (~0.344 nm) as determined by XRD and TEM. Additionally, boron is in the trigonal configuration (noted by the high resolution NMR) as opposed to the tetrahedral which is observed for BC$_4$. Had boron been on interstitial sites, the lattice spacing would appear much larger than graphite. By incorporating boron into the framework, the repulsive interactions between the sheets were reduced by a global lowering of π electrons as well as Poisson contraction along the c-axis resulting in smaller lattice spacing. The material can further be considered non-porous for practical purposes due to similar lattice spacing as graphite. For this material to be used as an adsorbent it must be either synthesized with pores, modified to incorporate porosity or be used as a coating on a highly porous support. This will be addressed in the following chapter.
5.5 Acknowledgments

The solid state $^{11}\text{B}$ NMR was setup at Pacific Northwest National Laboratory by Sarah Burton and Joseph Ford. The experiments were conducted by Dr. Michael Davis. The NMR results were analyzed with the help and knowledge of Dr. Michael Davis and Dr. Karl Mueller.

5.6 References


Chapter 6

Coating of Silica Aerogel with BCx as an Hydrogen Exchange Material

6.1 Introduction

Hydrogen has been widely recognized as a potential replacement for the current mass energy source, petroleum. The allure of hydrogen as a fuel source originates from a myriad of benefits including, but not limited to, it’s a clean energy that produces non-pollutant byproducts, it can be obtained through various methods such as dehydrogenation and electrolysis, it is light weight and has an extremely high mass energy density (4x that of gasoline), and it is renewable.[1-3] However, for hydrogen to be implemented into commercial use it is imperative that a suitable adsorbent material be found for its storage and transportation.

The United States Department of Energy (DOE) had proposed hydrogen storage targets for 2005, 2010 and 2015. As of today, not all of the 2005 goals have been met and as of late, the 2010 and 2015 targets have been reduced.[4] It has been problematic in finding a material that meets all of the DOE requirements. Materials that have high binding energies such as metal hydrides have low surface areas and, require high temperatures for desorption while materials that display high weight percent uptakes, such as carbon, have extremely low binding energies that require liquid N$_2$ temperatures for loading. A wide range of novel materials and nanocomposites have been examined as potential hydrogen carriers however none have emerged as viable.[5-10] Theoretically, the target adsorption energy range is 15 - 20 kJ/mol; this range allows for realistic adsorption levels and desorption at ambient conditions during operating processes.[11, 12]
As previously mentioned in Chapter 4, the potential of BC\(_x\) as a material extends over a wide variety of areas such as electronics, adsorbents and thermal-resistant materials.[13-17] At the nanoscale hydrogen storage is a matter of hydrogen adsorption and desorption which can be thought generally as hydrogen exchange between the gas phase and the solid surface. In the exploration of BC\(_x\) as a hydrogen exchange material, its non-porous character must be overcome. The physical structure of BC\(_x\) is very similar to that of graphite with an interlayer spacing, ~0.34 nm, and like graphite it is not porous and has is a low surface area solid. It is important for a material to have a very large surface area, exposing as many adsorption sites as possible leading to higher uptakes. Several avenues may be used to overcome this problem including: post synthesis activation, synthesis using a porous template, or to simply coat a highly porous support. BC\(_x\) is known to have high resistance to oxidation which makes it challenging to activate, particularly in a systematic and controlled way. Furthermore, the high temperature that would be required for activation make this process extremely energy intensive. The template method requires two steps, first the coating of the template with BC\(_x\) material and then dissolving of the template. This solution is simpler and more efficient than activation, but it is very expensive.

A third possibility is to attempt coating a porous support with the BC\(_x\) material. This has the advantage of being inexpensive and it requires only one processing step. Ideally, one can envision forming a thin layer of BC\(_x\) material over a support with high surface area and a large degree of mesoporosity. The support should contain a large fraction of mesopores and macropores to allow for BC\(_x\) precursors to easily enter the structure and to form the layer during the chemical vapor deposition. In other words it would be best to have the deposition process occur in the absence of internal mass transfer within the support. A logical material to begin with is silica. Silica is inexpensive, its surface is chemically a weak acid and its porosity is easily manipulated. Silica aerogel is highly mesoporous with high pore interconnectivity and good overall thermal stability. It also has low density, low dielectric constant, and great heat insulation.
properties.[18-21] The aerogels of silica are formed by low-temperature sol-gel chemistry. The final step is crucial to their properties; when the still wet gels are dried by evaporation they yield so-called xerogels. Aerogels are formed by drying above the critical point of water. This eliminates the gas-liquid interface and the crushing forces induced by surface tension as the liquid meniscus shrinks. The process is called supercritical drying and it provides the material with a highly interconnected pore structure. It is common that pores occupy above 90% of the solid’s total volume and the greater percentage of the volume stems from mesopores.[22-27]

The goal then of this portion of the research is to form a nanocomposite from a thin layer of BC$_x$ film on the surface of a silica aerogel and to examine its properties and its behavior as a hydrogen exchange material. However, the same material may also be used as a support for platinum because theory indicates that BC$_x$ will interact strongly with platinum and thereby maintain it in a highly dispersed state. Thus, not only would a material of this kind have interesting static interactions with hydrogen, with the inclusion of platinum, dynamic interactions with hydrogen, such as hydrogen spillover, could be added to the simple gas-surface interactions. Using XRD, $^{11}$B solid state High Resolution-NMR, XPS, N$_2$ adsorption and hydrogen adsorption (77K, 87K), the properties of a BC$_x$ coating on an aerogel were studied.

The results and discussion in this chapter are organized as follows. The aerogel was subjected to several different reaction times at 900°C to find how much pore structure collapse there would be and these results are considered first. Then the novel BC$_x$/aerogel nanocomposite materials, so produced were carefully examined to determine how B is incorporated in the carbon framework. Lastly, the material was tested as a hydrogen exchange material with particular attention paid to the isosteric heats of adsorption of hydrogen.
6.2 Experimental

6.2.1 Reagents

Granular silica aerogel was purchased from United Nuclear Scientific Equipment & Supplies. The reactants for BC$_x$ synthesis can be found in Chapter 5 in section 5.2.1 Reagents.

6.2.2 Deposition of BC$_x$ on Aerogel

A known mass of aerogel was placed in the quartz boat. The boat was then put in the CVD reactor and UHP He was flowed through the furnace tube overnight. A schematic of the CVD furnace can be seen in Figure 4.3. After He had flowed through the tube for a minimum of 24 hours, the furnace was heated to 900°C during a one hour period. Benzene vapor and BCl$_3$(g) were then passed through the furnace. The overall flow was controlled with a Brooks 5850E Series MFC. After the CVD process had been carried out, the gas was switched back to pure UHP He and the furnace was cooled to room temperature. UHP He was flowed through the furnace for 48 hours directly followed by flowing 5% H$_2$/UHP He gas mixture for 24 hours. This was to insure that all unreacted species had been purged out of the reactor, as BCl$_3$ is dangerously reactive with oxygen.

6.2.3 Characterization

6.2.3.2 Nitrogen Adsorption

The apparent surface area (m$^2$/g) was measured on a Micrometrics ASAP 2000 multipoint BET analyzer. The materials were pretreated by storing in an oven at 100°C over night.
6.2.3.3 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed with a monochromatic Al Kα source at instrument (Kratos, Axis Ultra; England) with a pass energy of 80 eV for survey spectra and 40 and 20 eV for high resolution spectra. Data were collected with photoelectron take-off angle of 90° from the surface. All spectra taken on samples were referenced to the Au 4f\(_{7/2}\) peak located at 84.0 eV.

6.2.3.4 \(^{11}\)B Solid State NMR

Solid state \(^{11}\)B MAS NMR Bloch decay experiments were conducted on a Varian Inova spectrometer interfaced to a home-built 3.2 mm magic-angle spinning (MAS) probe operating at a magnetic field strength of 21.1 T (observation frequency of 288.9607362 MHz for \(^{11}\)B). A short (\(\pi/10\)) pulse was used at a radio frequency strength of 100 kHz so that quantitative information could be obtained and a frequency region of 200 kHz was sampled. For processing, an exponential filter of 200 Hz was applied to the time domain data and the data set was zero filled to 4096 complex data points before being Fourier transformed.

6.2.3.5 Hydrogen Adsorption Isotherms (77K, 87K)

Hydrogen sorption properties of BC₅/aerogel nanocomposites were measured using Micromeritics ASAP 2020. The samples were degassed at 400°C for 12 hours until the pressure
inside the chamber was less than $10^{-6}$ bar. A leak test was then performed and the free space was measured using helium as non-adsorbing gas. Hydrogen gas was introduced into the sample chamber with a low pressure, incremental dose of 1 cm$^3$/g STP and the measurements were done at 77K and 87K, respectively. The isosteric heat of adsorption was measured using Claussius-Clapeyron equation shown as Equation 1.

$$Q_{st} = \left( \frac{R \ln(P_{87}/P_{77})}{1/77 - 1/87} \right)_n$$ (1)

Where $Q_{st}$ is the isosteric heat of adsorption, $R$ is the ideal gas constant and $P_{77}$ and $P_{87}$ are the hydrogen pressures obtained from the adsorption isotherm measured at 77K and 87K, respectively.

5.3 Results and Discussion

5.3.1 Synthesis and Reaction Time Dependence

One of the crucial properties for the support to have is thermal stability. Silica aerogels have been shown to be thermally stable with the pore structure withstanding temperatures as high as >1000°C.[20] However, the temperature at which an aerogel’s pores collapse can vary markedly. The variation correlates with different Si precursors used during the synthesis and with different conditions used for the drying process.[18, 20] The CVD BC$_x$ synthesis was conducted at 900°C. Hence, it was important to determine if, and when, the pores began to collapse in the Si aerogel. To determine the stability of the aerogel pore structure at 900°C,
samples were heat treated for different times, ranging from 0 to 60 minutes. To measure the extent of pore collapse, N\textsubscript{2} adsorption was carried out after each temperature treatment and the data was used to calculate the apparent surface area (using BET method). The apparent surface area of a material is related to the total porosity. A decrease in surface area will directly correlate with a collapse in porosity. The changes in apparent surface area with the duration of the heat treatment at 900°C are summarized in Table 6.1 and Figure 6.1.

It was concluded from this data that the pores begin to collapse quickly at 900°C. After only 15 minutes, the surface area had dropped by almost half. Figure 6.1 displays the relationship between surface area and duration of the heat treatment which is seen to be nearly an exponential decay. At the beginning of the heat treatment, the rate of collapse of porosity is the greatest and then it gradually levels off as the duration of the heat treatment is extended to 60 minutes or beyond.

<table>
<thead>
<tr>
<th>Treated Time (min.)</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>733</td>
</tr>
<tr>
<td>15</td>
<td>465</td>
</tr>
<tr>
<td>30</td>
<td>201</td>
</tr>
<tr>
<td>60</td>
<td>93</td>
</tr>
</tbody>
</table>

Table 6.1 Different time lengths at 900°C for Si aerogel and their corresponding surface areas.
Figure 6.1. The correlation between time duration of heat treatment at 900°C and yielding BET surface area, determined by N₂ adsorption.

6.3.2 Aerogel Coated with BCₓ Chemical Characterization

The previous chapter described the synthesis and detailed characterization of BCₓ material that was deposited on the inside of the quartz reactor tube. In this chapter we deposited the material on a high surface area Si aerogel. BCₓ deposited on the inside of the quartz tube was scratched off the inner surface and used as a reference to compare with the BCₓ material on the Si aerogel. $^{11}$B Solid State HR-NMR was used to validate the formation of BCₓ on the Si aerogel prior to hydrogen adsorption experiments.

$^{11}$B Solid State NMR was used to determine the coordination of boron in the material. As seen in Chapter 4, BCₓ is composed of trigonally coordinated $^{11}$B compared with the common
boron-carbon material, boron carbide, which is in a tetrahedral coordination. The NMR spectrum of the BC$_x$ coated aerogel is seen in Figure 6.2. In contrast to the bulk BC$_x$, the BC$_x$ coated aerogel is composed of two nonequivalent sites as indicated by two well resolved peaks centered at ~11 ppm and ~27 ppm, respectively. The spectrum for the bulk BC$_x$ material was overlaid with the spectrum of the BC$_x$/aerogel material spectrum (Figure 6.3). The spectrum for the bulk BC$_x$ material displays one broad peak centered at ~32 ppm. The difference in peak width between the bulk BC$_x$ and the BC$_x$ coated aerogel is believed to result from a difference in structure between the two materials. Similar to graphite BC$_x$ is organized in sheets and each individual layer of this material is well ordered even though the 3D structure does not have long range order. The disordered nature of the material, therefore, causes resonances to become significantly broadened. In contrast to the bulk material, for that deposited on the aerogel, the BC$_x$ exists in well ordered sheets which have much narrower resonances. The varying chemical shift between the bulk BC$_x$ and the BC$_x$ coated aerogel is the result of varying coordination between the two materials. This indicated that the BC$_x$ coated aerogel may undergo a partial conformation change from trigonal to tetrahedral coordination.
Figure 6.2 High resolution $^{11}$B Solid State NMR Spectra of aerogel coated with BC$_x$ material.
Figure 6.3 Comparison of the two normalized spectra; the bulk $BC_x$ material and the aerogel coated with $BC_x$. Both samples were run consecutively at the same settings on the same spectrometer.

The boron nucleus is sensitive to the local electronic environment in which it resides. Therefore, when the local environment is altered, this change can be manifested in a varying chemical shift (the center of mass of the respective resonance). For nuclei experiencing a nonzero quadrupole moment or some other underlying anisotropy, there can also be a change in the symmetry of the peak or in the peak width. This can be seen explicitly in the two spectra of bulk $BC_x$ versus that of the $BC_x$ coated on the Si aerogel. When Si or O is present in the environment of the boron, a downfield shift of the peak was seen as well as a narrowing of both
peaks. The lower field peak of bulk BC\textsubscript{x} located at ~27 ppm shifts down to ~11 ppm when the material is deposited on Si aerogel. The two distinct peaks for the BC\textsubscript{x}/aerogel spectra represent trigonal boron sites with little, if any, tetrahedral sites present. As described in Chapter 4, tetrahedral boron resides at ~0 ppm. The bulk BC\textsubscript{x} displayed a tiny peak that falls where tetrahedral B sites are located, ~0 ppm.[28, 29] The BC\textsubscript{x} coating appears to only consist of trigonal boron. The narrowing of the peaks of the BC\textsubscript{x} coating is due to Si and O that make up the aerogel framework. This alters the environment of boron and changes the peak shape.

6.3.2 Hydrogen Adsorption Experiments

The hydrogen exchange ability of BC\textsubscript{x} has yet to be fully explored. Theoretical work has predicted that the heat of adsorption for H\textsubscript{2} on BC\textsubscript{x} is in the optimal range for a material to store H\textsubscript{2} reversibly at ambient conditions.[17, 30-32] However, as previously mentioned, BC\textsubscript{x} is nonporous which is why a highly porous Si aerogel was incorporated as a support. Hydrogen adsorption experiments were conducted on high surface area Si aerogels before and after coating with BC\textsubscript{x} for various times. The heat of adsorption (\(\Delta H_{\text{ads}}\)) for hydrogen on BC\textsubscript{x} was determined by measuring the hydrogen uptake at various temperatures and then applying the Claussius-Clapeyron equation.

In order to determine the optimal length of time for coating, several samples were examined with differing coating times. The samples examined were coated for 15 minutes, 30 minutes and 60 minutes. As a control, an uncoated and untreated Si aerogel was examined for hydrogen adsorption. However, it displayed such low adsorption of hydrogen that it was at the detection limits of the instrument. Figure 6.4 depicts the adsorption of hydrogen at 77K and 87K as a function of hydrogen absolute pressure for an aerogel sample that was coated for 15 minutes.
Figure 6.5 displays the data for the aerogel that was coated for 30 minutes and Figure 6.6 displays that for the aerogel that was coated for 60 minutes.

Figure 6.4 The hydrogen adsorption isotherms at 77K and 87K for an aerogel coated for 15 minutes.

For all samples, Figure 6.4, 6.5, and 6.6, the hydrogen adsorption is greater at 77 than at 87K. The sample treated for 15 minutes, Figure 6.6, displayed the highest overall uptake of hydrogen among all the samples. At the highest absolute pressure of H$_2$, ~900 mmHg, ~0.37 wt.% of hydrogen is adsorbed. The aerogel treated for 30 minutes produced the second highest uptake of hydrogen with ~0.2 wt.% at 900 mmHg. The least uptake was observed for the sample treated for 60 minutes. It’s hydrogen uptake was merely ~0.1 wt.% at 900 mmHg. This value is also near the lower limit of the instrument which makes the data less certain.
There was a pattern observed between the length of treatment time and the concentration of hydrogen adsorbed. The shorter treatment time led to a higher hydrogen uptake. If the surface area alone was the most important variable then one would have expected this result. However, it is important to recall that surface area alone is not the most important variable since the untreated aerogel had the highest surface area but also displayed little or no adsorption of hydrogen. Thus it is clear from this data that the treatment with boron carbon does have an effect and this is superimposed over the simple effect of loss of surface area. It is likely that coating the aerogel with BC₃ also resulted in some pore blocking.
Figure 6.6 The hydrogen adsorption isotherms at 77K and 87K for an aerogel coated for 60 minutes.

Although the absolute maximum amount of adsorption (wt.%) is important to consider, given the variations in the physical properties of the materials, it is not enough. An even more important consideration must involve the more intrinsic aspects of the interactions between hydrogen and the surface.
Figure 6.7 The plot of concentration of hydrogen per unit area as measured by nitrogen adsorption versus the absolute pressure of hydrogen.

In order to understand the intrinsic effects of treating the aerogel to produce a layer of BC\textsubscript{x}, a plot was made of the concentration of hydrogen adsorbed per unit area (mol/m\textsuperscript{2}) versus the absolute pressure of hydrogen. The unit area was determined from the BET nitrogen adsorption data. The plot (Figure 6.7) indicates that with longer treatment time, there is further addition of the BC\textsubscript{x} material. This leads to an increased amount of adsorbed hydrogen as is noted especially for the samples treated for 30 minute and 60 minutes. Again, it is worth pointing out that although the uncoated aerogel had the highest surface area, it displayed the lowest real adsorption of hydrogen. This is good evidence in support of the hypothesis that the chemical interactions of
hydrogen with BCx are enhanced over those with just the aerogel. A higher surface affinity for hydrogen will increase its sticking probability during the adsorption process.

The heats of adsorption for hydrogen were calculated for these adsorption isotherms (at 77 and 87K) under low hydrogen pressure. The volume adsorbed at different pressures was converted to $\Delta H_{\text{ads}}$ using the Clausius-Clapeyron equation (Equation 1). The relation of adsorption energy and hydrogen uptake for aerogels treated for 15 minutes, 30 minutes, and 60 minutes can be found in Figure 6.8.

The initial isosteric heat of adsorption for the 15 minute and 60 minute coated aerogels (Figures 6.8) are very similar. Both had an initial $\Delta H_{\text{ads}}$ equal to ~6 kJ/mol and displayed a similar decrease in the $\Delta H_{\text{ads}}$ as the wt. % of hydrogen increased. The final $\Delta H_{\text{ads}}$ was equal to 4 kJ/mol for the aerogel treated for only 15 minutes and 4.5 kJ/mol for the aerogel treated for 60 minutes. The aerogel treated for 30 minutes had a much higher initial $\Delta H_{\text{ads}}$, with a value of 11 kJ/mol before dropping to 7 kJ/mol at higher pressure, and which is still twice the $\Delta H_{\text{ads}}$ for the uncoated aerogel. The initial value is approaching the optimal target (15-20 kJ/mol) for a material that can be used practically as a reversible hydrogen storage material. The uncoated aerogel displayed the lowest enthalpic interactions with hydrogen with an initial $\Delta H_{\text{ads}}$ equal to 4.5 kJ/mol. This value rapidly dropped to 3.2 kJ/mol and remained constant.
Figure 6.8 The calculated heats of adsorption from the 77K and 87K isotherms for 15 minute BCx/aerogel adsorbent, 30 minute BCx/aerogel adsorbent, 60 minute BCx/aerogel adsorbent, and the uncoated aerogel.

Silica is known to have weak interactions with hydrogen, so is it not surprising to see that the lowest $\Delta H_{ads}$ obtained was for the uncoated aerogel. The aerogels treated for 15 minute and 60 minutes displayed $\Delta H_{ads}$ values that were lower than that for the aerogel treated for 30 minutes. It is within reason to surmise that the aerogel treated for only 15 minutes was not given sufficient time to coat the surface completely with BCx thus leaving some of the silica surface exposed with its much weaker interactions with hydrogen. A silica aerogel that is only partially covered with BCx will display hydrogen $\Delta H_{ads}$ between that of neat BCx and pure silica.

It was concluded that the aerogel treated for 30 minutes had sufficient time for a large portion of the surface to be covered. It had an initial $\Delta H_{ads}$ of almost twice that of the other two
coated aerogels and almost three times that of the uncoated silica aerogel. The higher $\Delta H_{\text{ads}}$ for hydrogen is due to the interactions with hydrogen and the surface of $\text{BC}_x$. Boron has one electron less than carbon and an empty $p$ orbital. Hence, it changes the electron acceptor level of bulk carbon when it is substituted in the framework. Due to the substitutional nature of boron, the $\pi$-electrons between the layer planes are redistributed and the Fermi level is lowered due to smaller number of available charge carriers.

Although the explanation for the increased enthalpic interactions of hydrogen with boron doped carbon versus undoped carbon is still debated, recent theoretical work using B doped fullerenes as a model reported that the coupling between a localized empty $p_z$ orbital on the dopant and the $\text{H}_2\sigma$ orbital does lead to the enhanced interactions.

In our composite the silica aerogel has a much weaker interaction with hydrogen, thus it is not a contributing factor in the $\Delta H_{\text{ads}}$.

The aerogel treated for 60 minutes resulted in a material that displayed enthalpic interactions similar to the aerogel treated for only 15 minutes. However, the amount of hydrogen adsorbed it is much less (max of 0.07wt.% for 60 minute coated aerogel opposed to 0.1 wt.% for the 15 minute coated aerogel). Due to the very low uptake of hydrogen, one should not draw too many conclusions about the $\Delta H_{\text{ads}}$ values it displayed. However, as mentioned earlier in this chapter, the longer the aerogel is exposed to a temperature of 900°C, the lower the surface area. It is inferred therefore with treatment for 60 minutes, the loss in surface area is enough to offset the otherwise good enhanced heat of adsorption due to the $\text{BC}_x$.

A summary of the initial hydrogen $\Delta H_{\text{ads}}$ for each sample is seen in Table 6.2.
Table 6.2 The initial hydrogen $\Delta H_{\text{ads}}$ for each aerogel sample tested.

The aerogel treated for 30 minute displayed the highest isosteric heat of adsorption for hydrogen with a value of over 11 kJ/mol. This is very close to the target value of 15 kJ/mol. With 30 minutes of treatment, the process provides a sufficient BC$_x$ coating of the aerogel, while also preserving some of the surface area and pore structure.

6.4 Conclusions

The structure and hydrogen adsorption behavior of a novel BC$_x$ coated aerogel nanocomposite has been investigated. This work shows that the hydrogen heats of adsorption for the coated aerogel with BC$_x$ are far superior to that of uncoated aerogel, presumably because of the stronger enthalpic interactions with hydrogen and BC$_x$.

Solid state $^{11}$B NMR analysis of the coatings displayed very similar spectra for that of bulk BC$_x$. The environment of boron is slightly altered when it is applied to the surface of the aerogel, as is evident in the NMR spectrum. This is due to B interacting with the surface atoms of Si and O of the aerogel. After treating the aerogel for 30 minutes the resultant material displayed the highest heat of hydrogen adsorption. However, significant loss in surface area for the aerogel treated for 60 minutes resulted in a material with enhanced heat of adsorption but an overall lower
hydrogen capacity due to loss of porosity and surface area. Apparently treating the aerogel for 15 minutes was too short to adequately cover the Si surface but a treating for 60 minutes is too long because it results in a material with a very low surface area.

Further work is necessary to establish a temperature that will allow for BC₅ to be formed while the aerogel surface area remains unchanged. At the very least, the hydrogen high heats of adsorption for the nanocomposite warrant further research to explore into other possible commercial gases such as ammonia and methane.

6.5 References


Chapter 7

Conclusions and Future Directions of NPC Catalysts

Nanoporous carbon is a unique material for catalysis because it can combine the desirable properties of good metal dispersion, tunable porosity, resistance to caustic chemicals with excellent mechanical and thermal stability. The potential for this material in the field of shape selective catalytic reactions especially for more complex hydrogenations than we have examined and potentially for dehydrogenations is very high.[1] Although the work on NPC catalysts has progressed significantly throughout the past decade in terms of fundamental understanding and synthesis techniques, there are still lingering issues which have to be addressed before these carbons can be effectively implemented for real applications.

The issue of inconsistent physical characteristics of carbon in going from batch to batch has been detrimental to commercialization; namely, the lack of a uniform pore size distribution for each batch.[2] This issue must be addressed. Also, the activity of these catalysts is at least an order of magnitude lower than the commercial catalyst for the same reaction. For these types of catalysts to be cost effective, their activity should be on par with the commercial catalyst. Furthermore, the reactions provided in this thesis were implemented as models to develop a deeper understanding of the catalyst activity and novel shape selective properties. It is necessary to examine their use in commercially important reactions. Several commercial reactions for which these catalysts could provide more control of the product distribution will be discussed.
7.1 Thesis Conclusions

There were two objectives of this work. Firstly, to develop a new kind of catalyst support from nanoporous carbon derived from furfuryl alcohol for liquid-phase, shape selective catalysis, and secondly, to explore the synthesis and properties of BC, for hydrogen storage and exchange. Both objectives were met. In Chapter 2, the synthesis of a nanoporous carbon support containing Pt embedded into the matrix was characterized. The work explored possible methods of forming Pt nanoparticles as well as the effect of using multiple solvents during the polymerization. Chapter 3, went into great depth on the catalytic reactivity of the catalysts using simple alkene hydrogenations. Kinetic and mass transfer analyses combined with experiments were conducted to determine the limiting factors of the synthesized catalysts as well as to understand their selective nature. Pre-forming catalytically active Pt nanoparticles in the carbon support demonstrated high selectivities and thermal stability. Furthermore, modifying the porosity of the carbon ad layer atop the Pt allowed for control of the catalyst selectivity.

7.2 Inconsistent Physical Characteristics of Carbon

One of the conventional disadvantages of using carbon as a support is that it’s physical characteristics vary from batch to batch. For supports where a well defined pore structure is not needed, carbon has been used successfully, whereas for reactions that require the catalyst support to have a well-defined pore structure, carbon lags behind. The problem is that for reactions which potentially may produce multiple products, and for which catalytic selectivity is highly desired, alternate supports such as zeolites are better than carbon due to their narrow pore size distribution and ordered porous structure. In this work I have described a synthesis that produces well-
ordered nanoporous carbon that has been shown to not vary from batch to batch. Yet, slight alterations of the synthesis procedure will result in a carbon catalyst with significant physical differences. This is demonstrated in Table 7.1 which displays catalyst solvent ratios used in the synthesis and different catalyst pore structure properties which result.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent Type</th>
<th>Molecular Wt. (mol/g)</th>
<th>$V_{\text{micro}}$ (cc/g)</th>
<th>$V_{\text{meso}}$ (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11wt% Pt/NPC</td>
<td>THF</td>
<td>72</td>
<td>0.15</td>
<td>0.01</td>
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<tr>
<td>11wt% Pt/NPC</td>
<td>Triton X-100</td>
<td>625</td>
<td>0.18</td>
<td>0.06</td>
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<tr>
<td>6wt% Pt/NPC</td>
<td>PEG</td>
<td>8000</td>
<td>0.19</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 7.1 The effect of solvent molecular weight on the resultant catalyst pore volume

(Note: Pore volumes measured by methyl chloride adsorption)

The higher the molecular weight of the solvent used during the polymerization process the more porous the carbon. The amount of volume in porosity for the THF catalyst and Triton X-100 is relatively similar, yet the activities of the catalysts are significantly different. Remember the THF catalyst was for all intents and purposes not active for the hydrogenation of 1-hexene.

The pore size distribution for catalysts made with different solvents is pictured in Figure 4.5 of Chapter 4. Regardless of the solvent, the micropore size is narrow for the resultant carbon. It is noticeable that the solvents with higher molecular weight formed a broader pore size distribution in the resultant carbon. This is evident for the PEG-synthesized carbon noted in Figure 4.5 of Chapter 4. Using tetrahydrofuran as a solvent resulted in the carbon with the most narrow pore size. That of the carbon made with Triton X-100 was somewhat broader, and that produced with PEG was the broadest.
Another detail that has to be considered in preparing consistent catalysts is the curing process. Burket explored the effect on surface area for cured PFA compared to non-cured PFA.[3] He found that curing the polymer in a silicon mold resulted in a polymer that had a surface area of ~300 m$^2$/g compared to a surface area of 60 m$^2$/g when the polymer was immediately pyrolyzed. Hence, the catalysts prepared in this work were always cured prior to pyrolysis. This created a solid, homogeneous mixture of solvent and polymer with a high degree of cross-linking and it insured that each polymer had very close to the same degree of polymerization prior to pyrolysis. If one skips the step of curing the polymer before pyrolysis, the result is pyrolysis of polymers that vary in their degree of cross-linking and extent of polymerization which changes the properties of the resultant carbon.

7.3 Enhancing Catalyst Activity

As discussed throughout this thesis, the porosity control of the synthesized platinum-containing NPC catalysts directly correlates to the total number of active sites that are accessible. This has been shown in going from an NPC catalyst being synthesized with Triton X-100 compared to one being synthesized with THF. The overall volume increased when Triton X-100 was incorporated from 0.15 cc/g to 0.21 cc/g. For the hydrogenation of 1-hexene the $r_{obs}$ increased from $10^{-5}$ to $10^{-1}$ mols/g*hr when THF was replaced with Triton X-100.

Because these two properties, porosity and accessible active sites, are intimately intertwined resulting in a balancing act that must be considered in the preparation of these catalysts. Increasing the porosity by too much will result in a loss of selectivity, while not having enough porosity results in low activity. Based on this knowledge, several paths can be taken to bring up the activity while retaining the selectivity one of which is activation of the NPC catalyst.
Activation of carbon is a process whereby the surface area and pore volume of the solid is enhanced. Activation is most commonly conducted either by a physical activation or chemical activation. Physically activated carbons are produced by heating the carbon material under an oxidizing atmosphere (carbon dioxide, oxygen, or steam) at temperatures in excess of 250°C. Chemical activation requires the carbon material to be impregnated with an oxidizing chemical, typically an acid or base, followed by carbonization of the impregnated carbon. However, it is common that contaminants remain in the carbon which are left over from the decomposed oxidizing chemical. Both methods oxidize carbon to produce gaseous byproducts (carbon monoxide, and carbon dioxide) which results opening of new channels and fractures that have surface area. With these methods in mind a preliminary study was conducted on the outcome of physical activation of the NPC catalyst.

A 10wt.% Pt/NPC-THF catalyst was activated under flowing carbon dioxide at 600°C for two different lengths of time; X-ray diffraction and the hydrogenation of 1-hexene were conducted on the catalysts and compared to the unactivated catalysts (Table 7.2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Temp. (°C)</th>
<th>Activation Time (min)</th>
<th>% Burnoff</th>
<th>Metal Dispersion (%) (^1)</th>
<th>% Conversion of 1-hexene (^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/NPC-THF</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.5</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Pt/NPC-THF</td>
<td>600</td>
<td>15</td>
<td>3</td>
<td>6.5</td>
<td>99</td>
</tr>
<tr>
<td>Pt/NPC-THF</td>
<td>600</td>
<td>30</td>
<td>9</td>
<td>6.2</td>
<td>56</td>
</tr>
</tbody>
</table>

Table 7.2 Summary of the effect of activation on a 10wt.% Pt/NPC-THF catalyst. (Note: \(^1\)The metal dispersion calculated by CO chemisorption. \(^2\)The percent conversion of 1-hexene is at the end of two hours.)
The activation of Pt/NPC-THF displayed a significant increase in activity, going from less than 3% conversion to 99% conversion. This increase came about even with only a minimal amount of carbon burnoff (3%). However, when the burnoff was increased to 9%, the metal dispersion decreased and the percent of 1-hexene converted at the end of two hours at the same conditions dropped by half.

Based on these preliminary results, it is possible to increase the activity of the NPC catalysts. However, the exact amount of burnoff needed to find the highest activity is still unknown. A systematic test needs to be completed examining different activation times so that a maximum in metal dispersion is found as well as a maximum in catalytic activity with optimal shape selectivity.

7.4 Exploration of New Catalytic Reactions

Dehydrogenation is the reverse hydrogenation process and, theoretically, the same catalyst could be used for either direction of reaction, however, the operating processes are extremely different. The dehydrogenation of alkenes is a highly endothermic reaction and thus is favorable at higher temperatures. So although it is true that the same catalysts used for hydrogenation could be used in dehydrogenation, based on the principles of chemical equilibrium and microscopic reversibility, the reality is that different materials are used for catalysis done at much higher temperatures (500-700°C). When the temperature is so high one also has to manage the problem of lost selectivity due to activation of additional reactions. To create catalysts which can withstand high temperatures and which limit multi-reaction pathways is the art of preparing what are usually highly proprietary catalysts with complex promoters. Particular problems that arise in the catalyzed dehydrogenation of alkanes include coke formation, and formation of
products that are skeletal isomers or dienes. The most widely practiced commercial dehydrogenation is the formation of styrene from ethylbenzene.[4] The commercial process involves temperatures above 650°C and the use of steam in the feed to carry heat into the reactor and to slow the rate of coke formation on the catalyst. Standard catalysts used contain a mixture of iron oxide with potassium carbonate and one or more promoters. Other notable dehydrogenations that enjoy wide commercial application include the formation of light alkenes from light alkanes, especially ethylene from ethane and the conversion of C_{10}-C_{14} alkanes to C_{10}-C_{14} alkenes.

While the steps leading to the dehydrogenation of ethane and propane are mechanistically straightforward, forming, those leading to the dehydrogenation of butane and pentane are much more complex; a host of products form at the reaction temperatures used (550-700°C).[5] Beyond forming products such as terminal alkenes, other products include different skeletal isomers, dienes, and some cracked products as well. The production of propene, isobutene, and butadiene is done on a large scale to supply the subsequent production of poly propylene, propylene oxide and isooctene.

The dehydrogenations of C_{10}-C_{14} alkanes to C_{10}-C_{14} alkenes is done to produce akylnbenzenes for detergents. Thus it is necessary to have C_{10}-C_{14} alkenes for the alkylation process. The major route for this dehydrogenation is a proprietary process by UOP called “Palcol-Olex”. This process has been used to yield alkenes as low as C_6.[6] The dehydrogenation of higher alkanes is a very complex with several pathways possible that can contribute to a wide product distribution (Figure 7.1).
Carbon supported catalysts are not currently used in commercial dehydrogenations, because as a conventional support carbon is unable to prevent aggregation of dispersed metals, especially at temperatures above 400°C which are necessary for dehydrogenation. The catalysts that have been synthesized and characterized in this thesis could prove to be excellent dehydrogenation catalysts. They have several properties that current carbon and commercial dehydrogenation catalysts do not have, namely they are inherently non-acidic which reduces cracking and coke formation, they have excellent thermal stability, and they have high selectivity for non-branched hydrocarbons. Current commercial dehydrogenation catalyst supports, such as alumina, have to be made basic in order to diminish cracking rates and they must contain only macropores to provide for fast diffusion away from the surface and its active sites. A slow diffusion time has shown that reactants react further to form unwanted species as well as an increase in cracked species and especially coke.[4] With the platinum active sites for dehydrogenation embedded within the carbon, shape selective effects could act to provide mainly terminal alkenes. Also, since platinum is known to be highly active metal for dehydrogenation, this could allow for a much less complex catalyst and no need for promoters. In addition, a more
active catalyst would result in a lower operating temperature and the lack of acidity would prevent cracking and coking.

It is with these properties in mind, low acidity, shape selectivity and highly active metals, that a modified reaction scheme for the dehydrogenation of higher alkenes is proposed using the synthesized Pt/nanoporous carbon catalyst (Figure 7.2).

![Diagram of reaction scheme](image)

Figure 7.2 Modified reaction scheme for dehydrogenation of higher alkanes using the Pt/NPC catalyst.

7.5 Formation of Pt/BCx/NPC Catalyst

The structure of boron substituted carbon is similar to that of micro-crystalline carbon, however the electronic and physical properties are quite different.\cite{4-7} It has been theoersized that boron doped carbons lead to increased interaction between the metal and the carbon material,
stabilizing atomic-sized particles. With this in mind, the use of BC₅ to atomically disperse platinum is considered.

In the past, several researchers have explored the use of a support to disperse the active metal followed by forming a thin layer of nanoporous carbon around the support to act as a selective membrane. This is considered in the synthesis of a novel NPC/Pt/BC₅ catalyst.

As reported in this work, the number of active sites is low, with measurable metal dispersions >5%. This is one of the current drawbacks of the synthesized NPC catalyst. One method to increase the number of active sites is to create much smaller metal particles. As previously mentioned, BC₅ can act as a support that stabilizes atomic Pt. Once that Pt is deposited on BC₅ the support would be coated with PFA, followed by curing. After the polymer had solidified the composite material would be pyrolyzed to yield a catalyst with a selective layer, NPC, surrounding highly active, atomically dispersed platinum nanoparticles. An illustration of the procedure is presented in Figure 7.3. In detail, the synthesis starts with BC₅ having platinum deposited on it which can either be done by wet synthesis or vapor deposition. This is followed up with soaking the Pt/BC₅ material in polyfurfuryl alcohol solution and then cure in an oven. Once the film of polymer has solidified the material is pyrolyzed. This method has several parts that will need to be experimentally optimized, such as the method for platinum deposition, and the viscosity of the polymer solution the Pt/BC₅ material is soaked in. This method has the advantage of controlling the diffusion path length to the platinum active sites. The NPC film thickness directly translates to the approximate diffusion path length traversed by reactants. By noting the amount of PFA is added (weight) and the thickness of the coating, the catalyst could be tailored to have a thin layer of NPC to be a selective barrier. A more in-depth study could be conducted where the thickness of the NPC is altered followed by 1-hexene hydrogenation. It is hypothesized that as the thickness increases the activity decreases and, to a first approximation, the tortuosity of PFA-derived nanoporous carbon could be calculated. Having the ability to
understand the interconnectivity of the pore structure, as well as, the length of the path traversed to the active sites enable a very selective and engineered catalyst to be produced. The potential for a heterogeneous catalyst with such a high degree of engineering is infinite.

Figure 7.3 Step-by-step process of how to create NPC catalyst using BC$_x$ as a metal support to enhance the number of active sites
7.6 References


VITA

Billy-Paul Matthew Holbrook

Billy-Paul Matthew Holbrook was born in Fort Campbell, Kentucky on December 20th, 1980. After graduating high school from Rowan County Senior High School in 1999, he joined Morehead State University in Morehead, Kentucky, where he was a four year letterman in Cross Country and Track & Field. He obtained his B.S. degree in Chemistry in the Spring of 2004. He entered the Pennsylvania State University in August of 2004, where he began his PhD studies in the Department of Chemistry under the guidance of Prof. Henry C. Foley. Future plans are to continue his studies at Université de Lyon 1, in Lyon France as a post doctoral student.