

**STABILITY OF ACID-MODIFIED ACTIVATED CARBONS IN HOT LIQUID WATER AND
THEIR APPLICATION TO BOIMASS HYDROLYSIS REACTIONS**

A Thesis
Presented to
The Academic Faculty

By

Adam H. Van Pelt

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science in Chemical Engineering

Georgia Institute of Technology
December, 2012

Copyright © 2012 by Adam H. Van Pelt

**STABILITY OF ACID-MODIFIED ACTIVATED CARBONS IN HOT LIQUID WATER AND
THEIR APPLICATION TO BOIMASS HYDROLYSIS REACTIONS**

Approved by:

Dr. Carsten Sievers, Advisor
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Dr. Matthew Realf
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Dr. Carson Meredith
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Date Approved: TBA

ACKNOWLEDGEMENTS

As I wrap up my time here at Georgia Tech, I would like to sincerely thank my wife, family, friends, and pet bunnies for their continual support and encouragement in an otherwise turbulent time.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
LIST OF TABLES.....	iii
LIST OF FIGURES	iv
SUMMARY	v
CHAPTER 1: INTRODUCTION.....	1
CHAPTER 2: STABILITY OF ACID-MODIFIED ACTIVATED CARBON IN HOT LIQUID WATER.....	4
2.1 Introduction.....	4
2.2 Materials and Methods	8
2.3 Results	12
2.4 Discussion.....	24
2.5 Conclusions.....	31
CHAPTER 3: OLIGOSACCHARIDE HYDROLYSIS WITH SOLID ACID CATALYSTS	33
3.1 Introduction.....	33
3.2 Experimental Methods.....	34
3.5 Results and Discussion	38
3.4 Conclusions.....	56
CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS.....	58
4.1 Activated Carbon Stability.....	58
4.2 Oligosaccharide Hydrolysis.....	58
REFERENCES	61

LIST OF TABLES

1. Surface areas of activated carbons	14
2. Cellobiose hydrolysis over solid acid catalysts	43
3. CHN analysis of 30% silica niobia before and after reaction.....	47
4. Cellobiose hydrolysis reactions at various temperatures	50
5. Apparent activation energies for cellobiose hydrolysis	53
6. Cellobiose hydrolysis with reacidified activated carbon catalyst	56

LIST OF FIGURES

1. Acidic and basic functionalities of activated carbon	7
2. System used to hydrothermally treat catalysts	10
3. SEM images of activated carbon catalysts	13
4. Elemental compositions of activated carbons	15
5. PZCs of activated carbons	16
6. Acid site concentrations of acid-modified activated carbons.....	17
7. Acid site concentrations of H ₂ SO ₄ - and HNO ₃ -modified carbons	18
8. Acid site concentrations of hot air modified carbons.....	18
9. Acid site concentrations with various exposure times	19
10. Acid site concentrations with various exposure temperatures	20
11. TPD-MS curves of activated carbon catalysts	21
12. XPS spectra of HNO ₃ -modified carbons	22
13. XPS spectra of H ₂ SO ₄ -modified carbons	23
14. PFD of fixed bed reactor setup.....	37
15. Fixed bed reactor setup.....	38
16. Acid site concentrations of ASA catalysts.....	39
17. Batch cellobiose hydrolysis results with ASAs.....	40
18. Acid site concentrations of silica niobia catalysts.....	41
19. ASA(10) catalyzed cellobiose hydrolysis reaction.....	42
20. H ₂ SO ₄ - and HNO ₃ -modified activated carbons for cellobiose hydrolysis	44
21. Extended-time reaction with ASA(10).....	45
22. 30% silica niobia catalyzed cellobiose hydrolysis reaction results	46
23. IR spectra of 30% silica niobia catalyst before and after reaction	47
24. Effect of reaction temperature on cellobiose hydrolysis with ASA(2)	48
25. Cellobiose hydrolysis at various temperatures with many catalysts.....	50
26. External mass transfer limitations test.....	52
27. Arrhenius plot for cellobiose hydrolysis with ASA(2) catalyst.....	53
28. Acid site concentrations of reacidified H ₂ SO ₄ -modified carbon	55
29. Cellobiose hydrolysis with reacidified H ₂ SO ₄ -modified carbon.....	56

SUMMARY

In this work, the stability of acid-modified activated carbons is assessed in the typical biomass conversion reaction environment of 200 °C, 17 bar water. Activated carbons were modified with a variety of common liquid and gas phase methods and characterized. Acid-modified carbon catalysts were exposed to hot liquid water for 24 h and further characterized to determine the effect of this exposure on their surface chemistry. It was found that the liquid phase acidifying agents of H₂SO₄ and HNO₃ are most effective at adding acidic functionalities to the carbon. Exposure to hot liquid water was found to significantly decrease the carboxylic and sulphonic acid site concentrations on the carbons and slightly increased lactonic group concentrations. Kinetic studies indicate that these surface chemical changes occur within the first 4 h exposure to this environment, and that increased exposure temperature results in more efficient acid site removal. XPS measurements show that H₂SO₄ modification imparts partially stable sulfonic acid groups on the carbon surface while HNO₃ modification imparts nitro groups which are unstable at exposure temperatures above 150 °C.

The second part of this work focuses on the application of these acid-modified activated carbon catalysts as well as a variety of mixed metal oxide catalysts to the hydrolysis of the model biomass compound cellobiose. Catalyst screening reactions indicate that amorphous silica alumina catalysts are stable and selective but only slightly active whereas silica niobia catalysts are highly active but less selective and stable. Modified activated carbon catalysts were found to have moderate activity and selectivity. An investigation into the mechanism of silica niobia deactivation was performed and apparent activation energies were found for cellobiose hydrolysis over a variety of mixed metal oxide catalysts. Finally, a novel activated carbon synthesis mechanism was developed based on knowledge of surface site stability. This carbon catalyst was found to be highly active, selective, and stable for cellobiose hydrolysis but further characterization is required to fully understand its effectiveness as a catalyst.

CHAPTER 1

INTRODUCTION

Diminishing petroleum reserves along with the environmental and political issues involved with the use of fossil fuels and petroleum-derived chemicals is driving the development of renewable processes for their production. Biomass is considered one of the most promising sources of sustainable chemicals, materials, and fuels, and can be grown and harvested locally and converted to a variety of products in a manner that is CO₂ neutral. It has been predicted that a shift from petroleum to biomass will occur in the near future, resulting in the production of nearly 25% of transportation fuels and chemicals from biomass by the year 2030.¹ The promise of a biomass-based economy has resulted in a large body of research in the area of biomass conversion.

The largest potential feedstock for biomass-based products is lignocellulosic biomass. Lignocellulosic biomass, including agricultural residues, herbaceous crops, forestry residues, and several types of waste, is composed primarily of cellulose, hemicellulose, and lignin.² Of these components, cellulose is often present in the largest amount. It is indigestible by humans, and thus its utilization as a chemical feedstock does not compete with needs for human consumption. Due to these aspects, cellulose conversion is one of the most important processes involved in large scale biomass utilization. Cellulose is a long-chain polymer consisting of many β -1,4 glycosidic bonded glucose monomer units. These linear polymers undergo hydrogen bonding, forming crystalline structures that are both insoluble in water and chemically resistant. A key step in cellulose conversion and utilization as a chemical feedstock is the destruction of this crystalline network and subsequent hydrolysis of the glycosidic bonds to form glucose.

Due to the importance of cellulose conversion in the realization of a renewable biomass-based economy, much research has been performed in the area of cellulose hydrolysis. Enzymatic hydrolysis of cellulose has been found to selectively produce glucose, but suffers from slow reaction rates.³ Acid hydrolysis can be performed both rapidly and selectively. Cellulose hydrolysis with dilute mineral acids has been studied for nearly 70 years and has been implemented at industrial scales.⁴⁻⁵ This process, however, requires the costly separation, recycling, and treatment of the sulfuric acid remaining in the products.⁶ Recently, methods have been developed to hydrolyze cellulose in supercritical water.⁷⁻⁹ This method can completely convert cellulose to hydrolysis products with reaction times as short as 0.04 seconds. The products formed in this nature, however, are numerous. Generally, large amounts of oligosaccharides, sugar monomers, and sugar fragmentation products are formed. In order to make this process economically viable, a method must be developed to further hydrolyze the oligosaccharide products to their sugar monomer constituents.

To date, there have been great deals of literature articles that have investigated biomass hydrolysis reactions over solid acid catalysts. These catalysts have included zeolites, metal oxides, cation-exchange resins, supported metal catalysts, and heteropoly acids.¹⁰ Additionally, there have recently been a number of research groups investigating cellulose hydrolysis reactions over modified activated carbon catalysts. Activated carbon catalysts are promising for these types of reactions due to the demonstrated ability to tune their acidity through a variety of acid-modification techniques.¹¹⁻¹³ One group in particular has heavily investigated a cellulose hydrolysis reaction performed over an acid-modified activated carbon catalyst,¹⁴⁻¹⁵ reporting glucose yields of nearly 50%.

With the increase in popularity of these acid-modified activated carbon catalysts for biomass conversion processes, the issue of hydrothermal stability becomes an important one.

It has been shown for both zeolites¹⁶ and Pt/ γ -Al₂O₃¹⁷ catalysts that stability in these hot aqueous conditions is not to be ignored. It has been reported that metals sinter on activated carbon supports¹⁸ and that metal dispersion and sintering is highly dependent upon the chemistry of the support activated carbon¹⁹. While there have been a plethora of publications reporting on the effectiveness of acid-modification techniques on changing the surface chemistry of activated carbons, the stability of these imparted functionalities under biomass conversion conditions remains relatively unknown.

This work will seek to investigate the stability of acid-modified activated carbon catalysts in hot liquid water. Activated carbons will be acidified using a variety of liquid and gas phase methods and characterized extensively. These modified carbons will be subjected to simulated biomass conversion conditions (200 °C, 17 bar) and further characterized to determine the effect of this exposure on the surface chemistry of the modified carbons. Additionally, these activated carbon catalysts, along with a variety of mixed metal oxide catalysts, will be tested for cellobiose hydrolysis activity. Glucose yields and selectivities will be determined along with activation energies for each catalyst to determine how different synthesis techniques affect the effectiveness of the catalyst. Finally, knowledge gained regarding the stability of these carbon catalysts will be applied in order to synthesize an activated carbon catalyst with unusually high activity and selectivity for cellobiose hydrolysis.

CHAPTER 2

STABILITY OF ACID-MODIFIED ACTIVATED CARBON IN HOT LIQUID WATER

2.1 INTRODUCTION

One important characteristic of biomass and many biomass-derived chemicals is their extremely low vapor pressure. This property makes the liquid phase processing of biomass essential. Water is a particularly effective medium for these processes due to its availability and generally high biomass product solubility. Thus, biomass hydrolysis reactions typically occur in hot aqueous environments. This is in stark contrast to petroleum reforming conditions, and therefore particular attention must be paid to the effect of these conditions on catalyst stability. Research in the area of heterogeneous catalyst stability in biomass conversion conditions is sparse, however. Ravenelle et al. found that both zeolite Y and Pt/ γ -Al₂O₃ catalysts undergo major transformations upon exposure to hot aqueous environments – transformations that are unseen in gas phase conditions.¹⁶⁻¹⁷ Upon exposure to a hot aqueous environment, zeolite Y was found to degrade via siloxane bond hydrolysis, and the γ -Al₂O₃ support of Pt/ γ -Al₂O₃ catalysts was found to undergo hydration to form a crystalline boehmite phase. Li et al. observed similar results after exposing Ni/ γ -Al₂O₃ catalysts to hot liquid water.²⁰ In both cases, hydration of the γ -Al₂O₃ support was found to result in metal sintering and a significant decrease in surface area. Ketchie et al. utilized *in situ* x-ray absorption spectroscopy to determine that metals supported on activated carbon supports undergo sintering upon exposure to typical aqueous phase biomass conversion conditions.¹⁸ These reports, while limited, clearly demonstrate the need for research in the area of catalyst stability under typical biomass conversion conditions.

One particularly interesting catalyst for biomass conversion reactions is activated carbon. Activated carbons have been studied intensely in the past for their application in the areas of gas separation and storage,²¹⁻²² water purification,²³⁻²⁴ heterogeneous catalysis,^{11, 25-26} and electrochemistry. Activated carbons are inexpensive and can be prepared in a variety of forms including pellets, powders, extrudates, and cloths. Additionally, the surface chemistry of activated carbons can be modified easily by an assortment of techniques to adjust their hydrophobicity^{12, 27} and acidity.^{13, 28} It is well known that the physical structure of activated carbon is resistant to both highly acidic and basic conditions as well as elevated temperatures. Finally, as a catalyst support, activated carbon can be easily burnt off to recover precious metals. Due to these properties, activated carbons have received much attention as both heterogeneous catalysts and catalytic supports.

The surface chemistry of activated carbons has been studied in detail in previous works. Activated carbon structures are composed primarily of disordered graphene sheets oriented parallel to the particle surface.²⁹⁻³⁰ These graphene layers are separated by slit-shaped micropores which account for much of the large surface area of activated carbons. The edges of the graphene layers are where a majority of the surface chemistry occurs. Most of these edge sites are saturated with hydrogen, but these sites can also contain a variety of heteroatoms as a result of the carbon precursor, storage method, or specific surface modification procedures. The most important of these heteroatoms is oxygen, which has been shown to have a significant effect on the properties of activated carbons as both adsorbants²¹ and catalysts.²⁵⁻²⁶

Oxygen containing functional groups on the surface of activated carbons are generally acidic, and can be present in a variety of forms as depicted in Figure 1a. Carboxylic acid, lactone, and phenol groups are often present in the largest concentrations. These groups possess a variety of acidic strengths, with carboxylic acid groups the most acidic and phenolic

groups the least acidic. Activated carbon functional groups can also be present in a basic form, although less is understood about these species. It has been suggested long range pyrone-like structures (Figure 1b) account for the basicity of activated carbons.³¹ Additional studies have indicated that oxygen-free carbon sites located at π electron rich regions of the basal planes of an activated carbon can absorb protons from solution and thus account for the basicity of the carbon.³² The concentrations of both acidic and basic sites on an activated carbon sample are often measured by the Boehm titration.³³⁻³⁴ This technique involves the exposure of an activated carbon sample to bases of varying strengths – NaOH, Na₂CO₃, and NaHCO₃ – followed by titration, and can be used to quantify the concentrations of carboxylic, lactonic, and phenolic sites on the sample. The strongest base, NaOH, is neutralized by all acidic sites present in the activated carbon. Na₂CO₃ is neutralized by both carboxylic and lactonic sites, whereas NaHCO₃ is neutralized by only carboxylic sites. The activated carbon can also be exposed to HCl followed by titration to quantify the concentration of surface basic sites.

The surface chemistries of activated carbons are very diverse and can be modified quite easily. There exists an abundance of literature available detailing procedures for adding oxygen surface groups to activated carbons. Some modification agents that have been used include nitric acid,^{12, 27-28, 35-37} sulfuric acid,^{11-12, 26} hydrogen peroxide,^{28, 36} ammonium persulfate,^{28, 38} hot air,³⁶⁻³⁷ phosphoric acid,¹² sodium hydroxide,¹² liquid ammonia,¹² and ammonia gas.³⁵ Each of these methods has been found to impart oxygen groups onto the surface of activated carbon in slightly different manners, and this ability to tune the surface chemistry of a carbon is one of the major reasons they are viewed as such promising catalyst. For example, Huang et al.²¹ modified the surface chemistry of commercial coconut shell derived activated carbon with nitric acid, sulfuric acid, hydrochloric acid, phosphoric acid, and acetic acid to improve ammonia adsorption for air purification. This group found that the ammonia breakthrough capacity correlates directly with the total number of acidic groups on the activated carbon sample and

that an activated carbon pretreated with 12 M nitric acid provides the best ammonia adsorption. Gomes et al.¹¹ found that modification of activated carbon with H₂SO₄ greatly increases the efficiency of catalytic wet peroxide oxidation of an anionic azo dye. These examples give a small glimpse into the great body of literature that focuses on the modification of activated carbons to enhance adsorption and catalytic properties.

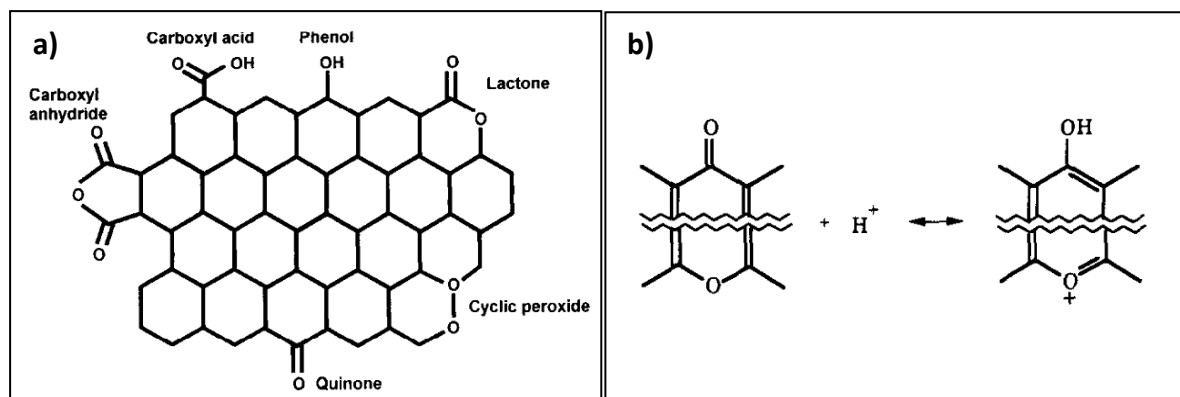


Figure 1: (a) Typical oxygen functionalities and (b) pyrone-like basic functionalities present in typical activated carbons.

There have been a limited number of research articles utilizing activated carbons in the hot aqueous environments typical of biomass conversion processes. Pigamo et al.³⁹ used activated carbons modified with hot flowing air to modify the selectivity of a cyclohexanone oxidation reaction at 140 °C and 50 bar. Guo et al.⁴⁰ found that an activated carbon catalyst greatly improved the hydrogen production from a municipal waste sludge reaction in supercritical water. While these examples may be limited, the ability to tune the acidity of activated carbon catalysts with a variety of oxidizing methods makes these catalysts prime candidates for biomass conversion reactions. To be useful as catalysts, however, the stability of these imparted oxygen functionalities, including carboxylic, lactonic, and phenolic sites, must be investigated.

In this section of my work, the stability of acid functional groups imparted on activated carbon surfaces through typical oxidation procedures is investigated. Activated carbons were acidified with both liquid and gas phase methods and characterized. These carbons were exposed to hot liquid water environments to mimic typical biomass reforming conditions. After exposure, the carbon samples were further characterized to determine the effects of the exposure on acid site concentration and morphological characteristics. Additionally, an emphasis was placed on identifying the nature and stability of surface nitrogen and sulfur-containing functional groups after oxidation with nitric and sulfuric acid, respectively.

2.2 MATERIALS AND METHODS

2.2.1 Materials

Activated carbon was purchased from Sigma Aldrich (C2889) with particle sizes of 8-20 mesh. Nitric acid (70%, 438073), hydrochloric acid (37%, 258148), and sulfuric acid (95-98%, 258105), sodium hydroxide (>97%, 221465), sodium carbonate (>99.9999%, 71347), and sodium bicarbonate (99.7-100.3%, S6014) were purchased from Sigma Aldrich. Hydrogen peroxide (35%, BDH8814-3) was purchased from BDH Chemicals. All materials were used as received.

2.2.2 Acidification Procedures

Activated carbon was modified using both liquid and gas phase methods. Details of each method are described below.

Liquid Phase Modifications

Liquid phase carbon acidifications were performed with the modifying agents H_2SO_4 , HNO_3 , and H_2O_2 . For each treatment 100-500 mL of a 10 M solution of the desired modifying agent were brought to their boiling point under vigorous stirring. Untreated activated carbon was added to the boiling solution in a ratio of 1 g carbon to 10 mL liquid solution over the course of 30 s. The slurry was stirred for 10 min while boiling and was afterwards rapidly quenched in an ice bath to room temperature. The cooled slurry was diluted with deionized water in a 3:1 water to slurry ratio. The diluted slurry was filtered and the carbon was rinsed with deionized water until the pH of the filtrate was greater than 4.5. The carbon was then dried in air at 100 °C for 4 h.

Gas Phase Modifications

Gas phase modifications were performed by exposing untreated activated carbon to flowing dry air at 300 and 400 °C. For these treatments 2 g untreated carbon were placed in each of four quartz boats. These boats were placed in a quartz tube inside of a Nabertherm RS 80/750/11 tube furnace. The furnace temperature was raised to the desired temperature at a ramp rate of 10 K/min under a 200 mL/min air flow. The temperature in the furnace was maintained at the desired value for 5 h, after which the furnace was cooled and the carbon was ground with a mortar and pestle to ensure homogeneity.

2.2.3 Treatment in Hot Water

Stability tests on activated carbon samples were performed using a 45 mL Teflon lined Parr acid digestion vessels (model 4744). For each treatment 4 g of activated carbon was suspended in 30 mL of deionized water in a digestion vessel. This vessel was then placed in a preheated oven at 175, 200, or 225 °C and agitated continuously for 1-24 h. The pressure in

the digestion vessel was maintained at the autogenic pressure of water at the specified temperature. After the desired exposure time, the digestion vessel was quenched in an ice bath, filtered with a 0.45 μm nylon filter, and dried in air at 100 $^{\circ}\text{C}$ for 4 h.



Figure 2: Acid digestion vessel and oven used to hydrothermally treat catalysts.

2.2.4 Nitrogen Physisorption

The surface areas of activated carbon samples were determined by nitrogen physisorption at 77 K using a Micromeritics ASAP 2020 automated physisorption analyzer. For these measurements 100 mg activated carbon samples were degassed at 300 $^{\circ}\text{C}$ and 10 μmHg for 5 hours prior to analysis. Surface areas were determined using a Langmuir isotherm.⁴¹ These measurements were determined to be accurate to within 2 %.

2.2.5 Scanning Electron Microscopy

Scanning electron micrographs were obtained using a JEOL JSM-6400 microscope. The samples were deposited on carbon tape supported by an aluminum stub. All images were captured at 1000x and an accelerating voltage of 15 kV using dPict32.

2.2.6 Elemental Analysis

The carbon, hydrogen, nitrogen, and sulfur contents of carbon samples were determined by Atlantic Microlab, Inc. using an automated combustion analyzer. These results were determined to be accurate to within 0.3%.

2.2.7 Point of Zero Charge

Point of zero charge measurements were obtained by suspending 1 g activated carbon in 25 mL deionized water. The slurry was stirred vigorously for 2 h after which the pH was measured with a standard pH probe.

2.2.8 Boehm Titration

The concentrations of phenolic, lactonic, carboxylic, and basic site on carbon samples were determined using a standardized Boehm titration method.³³⁻³⁴ For these experiments 1.5 g of activated carbon were added to four 50 mL aqueous solutions of either 0.5 M NaOH, NaCO₃, NaHCO₃, or HCl. These slurries were shaken on a VWR model 3500 orbital shaker at 150 RPM for 24 h. After this time, the carbon was filtered and 10 mL aliquots of the filtrate were collected. To the aliquots of the NaOH, NaCO₃, and NaHCO₃ solutions, 20 mL 0.05 M HCl were added. These solutions were back titrated with 0.05 M NaOH. HCl aliquots were titrated directly with 0.05 M NaOH. All titrations were performed to an endpoint of pH 7.

2.2.9 Temperature Programmed Desorption

The evolution of nitrogen and sulfur containing species from carbon samples was quantified with a Stanford Research Systems QMS300 Gas Analyzer. For these analyses approximately 100 mg of activated carbon were placed in a quartz tube inside of a Lindberg/Blue M model TF55035COMA-1 tube furnace. The furnace temperature was raised to

1000 °C with a ramp rate of 5 K/min under a 100 mL/min Ar flow. A mass to charge ratio of 64 (SO₂) and 30 (NO) were used to track the decomposition of sulfur and nitrogen containing groups, respectively. MS pressures were normalized by the sample mass to compare relative sulfur and nitrogen contents of the carbon samples.

2.2.10 X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were carried out with a Thermo Scientific K-Alpha, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminium anode (Al K α = 1486.6 eV) operating at 72W and a spot size of 400 μ m. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was 2 x 10⁻⁹ mbar and during measurement 3 x 10⁻⁷ mbar Argon because of the charge compensation dual beam source.

2.3 RESULTS

2.3.1 Nitrogen Physisorption

The Langmuir surface areas of activated carbon samples were in the range of 900 – 1100 m²/g (Table 1). Liquid phase and gas phase acidification procedures led to an increase of the surface area of the activated carbon. The most dramatic increase was observed for carbon modified with 400 °C air. Exposure to hot liquid water further increased the surface area of all carbons by up to 6%.

2.3.2 Scanning Electron Microscopy (SEM)

SEM images were obtained of untreated and H₂SO₄-modified activated carbons as well as H₂SO₄-modified activated carbon after 24 h exposure to water at 200 °C, 17 bar (Figure 3). These images show no distinct changes in the morphology of the activated carbon as a result of either the liquid phase acidification procedure or subsequent exposure to the hot aqueous environment.

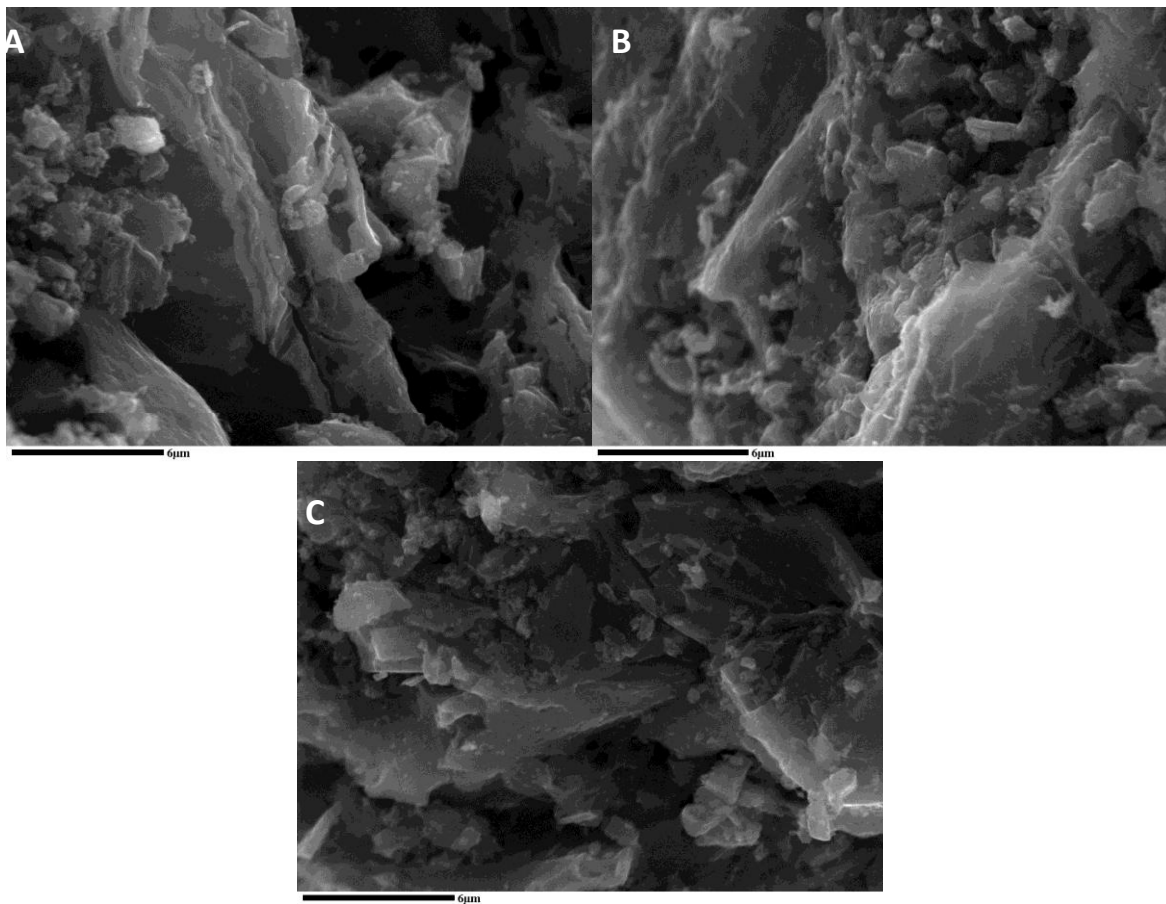


Figure 3: SEM images of A) untreated activated carbon, B) H₂SO₄-treated activated carbon, and C) H₂SO₄-treated activated carbon after exposure to 200 °C water for 24 hours.

2.3.3 Elemental Analysis

Elemental analyses were performed to determine the concentrations of hydrogen, nitrogen, and sulfur in activated carbon samples. The untreated activated carbon sample was found to contain hydrogen, nitrogen, and sulfur in concentrations below 0.5 wt% (Figure 4).

Table 1: Langmuir surface areas as obtained by N₂ physisorption of activated carbon catalysts.

Catalyst	Surface Area before exposure (m ² /g)	Surface Area after exposure (m ² /g)
Untreated	910	-
H ₂ SO ₄ -treated	951	984
HNO ₃ -treated	1000	1057
Air (400 °C)-treated	1060	1068

Modification of activated carbon with HNO₃ significantly altered the chemical composition of the carbon. The sulfur present in the untreated activated carbon was quantitatively removed in the course of the HNO₃-modification procedure. The nitrogen content increased to more than twice its original value as a result of this procedure while the hydrogen content remained constant. Exposure to liquid water at 200 °C and 17 bar for 24 h significantly increased the hydrogen content of the HNO₃-modified carbon and decreased the nitrogen concentration to a value only slightly higher than that in the untreated carbon.

H₂SO₄-modification was found to increase the sulfur content of the carbon by a factor of nine, to 1.8 wt%. The hydrogen content of the carbon approximately doubled as a result of this treatment while the nitrogen content remained constant. After exposure to water at 200 °C and 17 bar for 24 h, the sulfur content of the carbon was found to decrease to 0.65 wt%, a value three times larger than that of the untreated carbon. The hydrogen content of the carbon decreased as a result of this exposure while the nitrogen content remained constant.

2.3.4 Point of Zero Charge (PZC) Measurements

The PZCs of untreated and acid-modified activated carbon samples were obtained before and after exposure to liquid water at 200 °C and 17 bar for 24 h (Figure 5). The untreated activated carbon was found to be basic, with a PZC of over 10. All acid modifications lowered the PZC of the carbon. The most significant changes occurred during the liquid phase

modification with H_2SO_4 and HNO_3 , which resulted in carbons with PZCs of 2.58 and 3.58, respectively. Other modification procedures affected the PZC of the carbon less significantly, resulting in carbons that remained basic in nature ($\text{PZC} > 7$). Exposure to the hot aqueous environment changed the PZC of all carbon samples except for the H_2O_2 -modified carbon. In each case, the PZC of the carbon shifted towards neutrality ($\text{PZC} = 7$). The H_2SO_4 - and HNO_3 -modified carbons showed an increase in PZC as a result of this exposure, while the 300 and 400 °C-modified carbons showed a decrease in PZC.

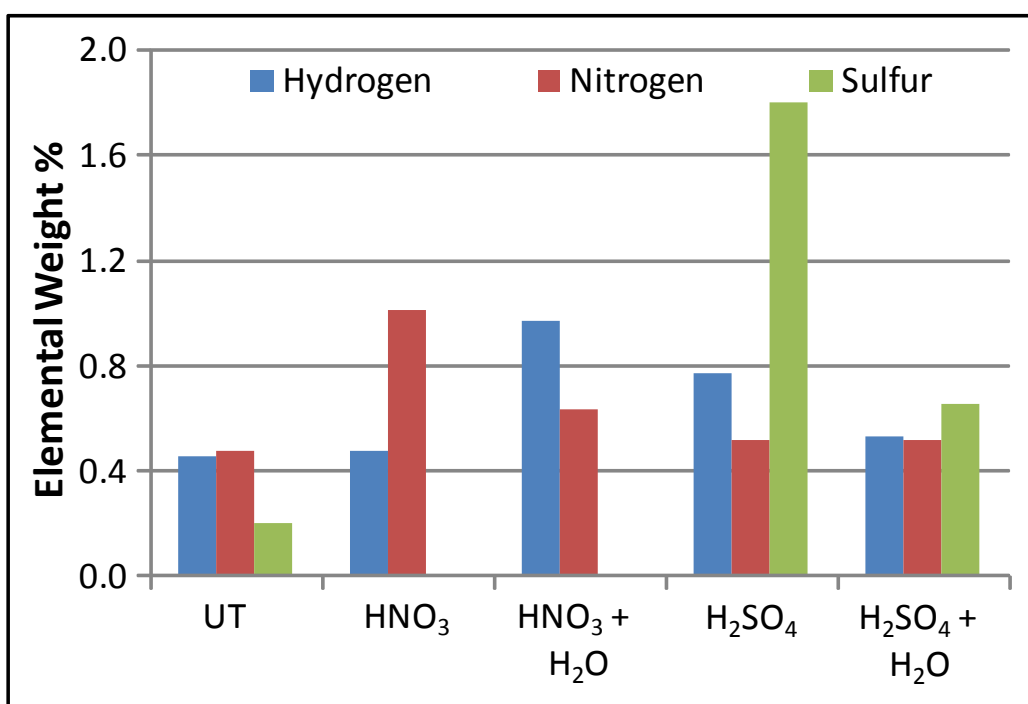


Figure 4: Elemental compositions of activated carbon catalysts.

2.3.5 Boehm Titration

2.3.5.1 Acid Modifications

Acid and base site concentrations of untreated and acid-modified activated carbons were measured with Boehm titration (Figure 6). The untreated activated carbon contained a large number of base sites and very few acid sites of any kind. All modifications methods

substantially impacted the surface chemistry of the activated carbon. Upon modification with H_2SO_4 , base sites were completely removed from the carbon, and acid sites were added largely in the form of carboxylic sites and, to a lesser extent, phenolic sites. It should be noted sulfonic acid sites would erroneously report as carboxylic in Boehm titration, and thus it is likely that at least part of these “carboxylic sites” are actually sulfonic acids. HNO_3 -modification largely removed base sites and added carboxylic, lactonic, and phenolic sites. Modification with H_2O_2 slightly decreased the concentration of base sites and slightly increased the concentration of all acid sites. The base site concentration of the carbon remained unchanged and the phenolic site concentration increased after modification with air at 300 °C. The modification with air at 400 °C significantly increased the base site concentration of the carbon and increased both the phenolic and carboxylic site concentrations.

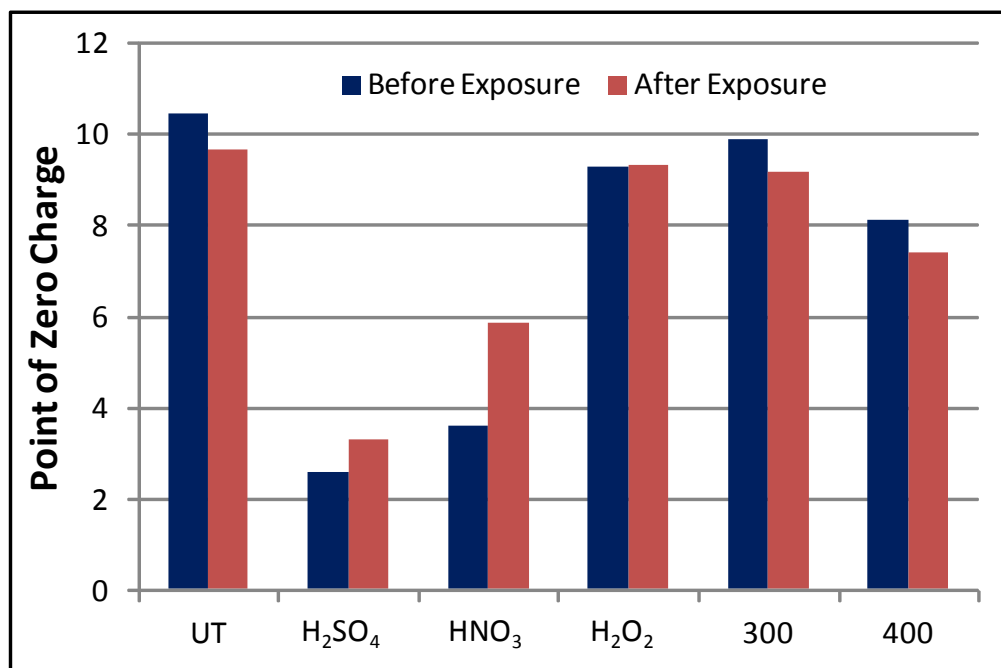


Figure 5: Point of zero charge measurements for activated carbon catalysts before and after exposure to hot liquid water at 200°C for 24 h.

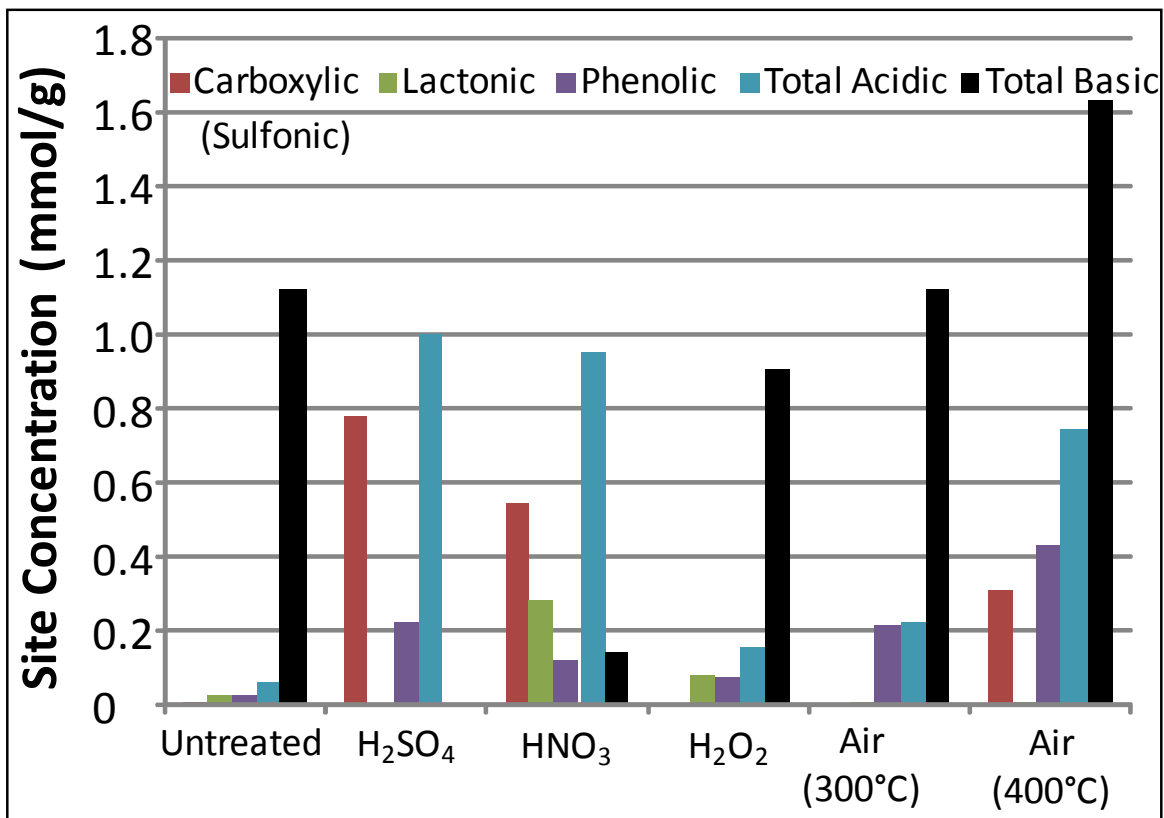


Figure 6: Acid site concentrations of acid-modified activated carbon catalysts as measure by Boehm titration.

2.3.5.2 Effect of Hot Liquid Water Exposure

The untreated and acid modified activated carbons were exposed to hot liquid water at 200 °C and 17 bar for 24 h and subsequently characterized by Boehm titration to determine the effect of the hot aqueous environment on the acid and base site concentrations. Upon exposure to hot liquid water, the concentrations of different functional groups on the untreated and H₂O₂-modified activated carbons remained unchanged. In both the H₂SO₄- and HNO₃-modified carbons, the carboxylic site concentrations decreased significantly and the base site concentrations increased during exposure. The phenolic and lactonic site concentrations in these carbons remained largely unchanged (Figure 7). The phenolic site concentration of the

carbon modified in air at 300 °C decreased as a result of the exposure to hot liquid water while the phenolic, lactonic, and basic site concentrations remained constant. During exposure of the carbon modified in air at 400 °C, the carboxylic and base site concentrations decreased, the lactonic site concentration increased, and the phenolic site concentration remained constant (Figure 8).

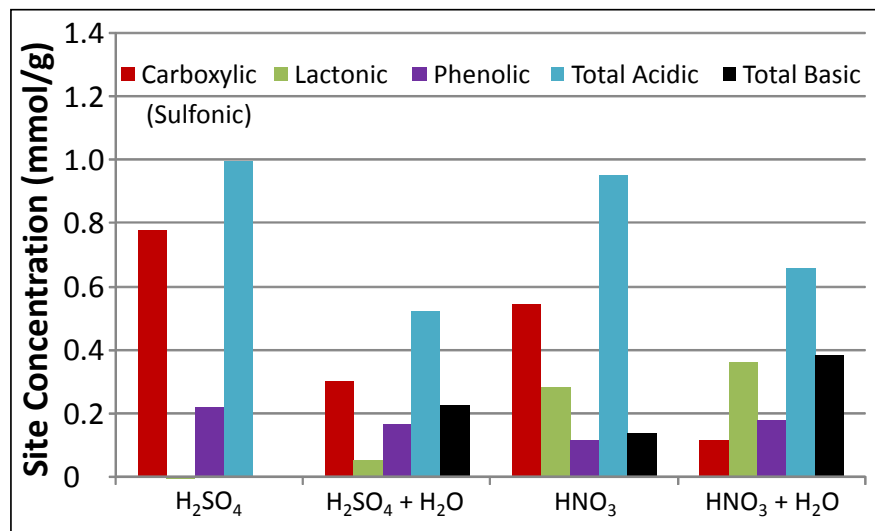


Figure 7: Acid site concentrations of H₂SO₄- and HNO₃-modified activated carbon catalyst before and after exposure to hot liquid water.

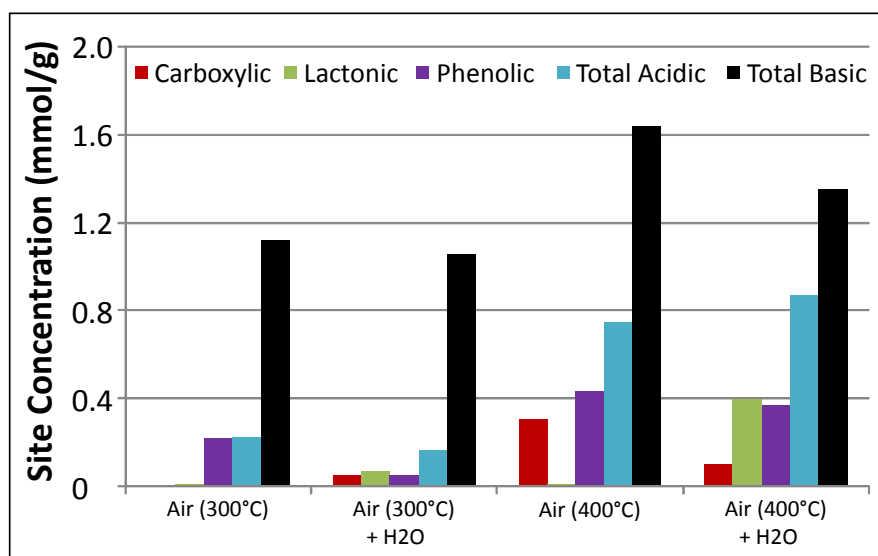


Figure 8: Acid site concentrations of activated carbon catalysts modified by air at 300 °C and 400 °C before and after exposure to hot liquid water.

2.3.5.3 Effect of Exposure Time

The H₂SO₄-modified carbon was exposed to liquid water at 200 °C and 17 bar for 1, 4, 12, and 24 h and characterized by Boehm titration to determine the effect of exposure time on the surface chemistry of the carbon (Figure 9). The H₂SO₄-treated carbon as synthesized contained 1.0 mmol/g carboxylic sites and 0.2 mmol/g phenolic sites. After a single hour of exposure to the hot liquid water, the carboxylic site concentration had decreased dramatically to 0.63 mmol/g. During this exposure time, the base site concentration of the carbon increased slightly, and the lactonic and phenolic site concentrations were unchanged. When the exposure time was increased the concentrations of each type of sites continued to change following the same trends. However, the decrease was significantly slower. Eventually constant concentrations were reached after 4-12 h.

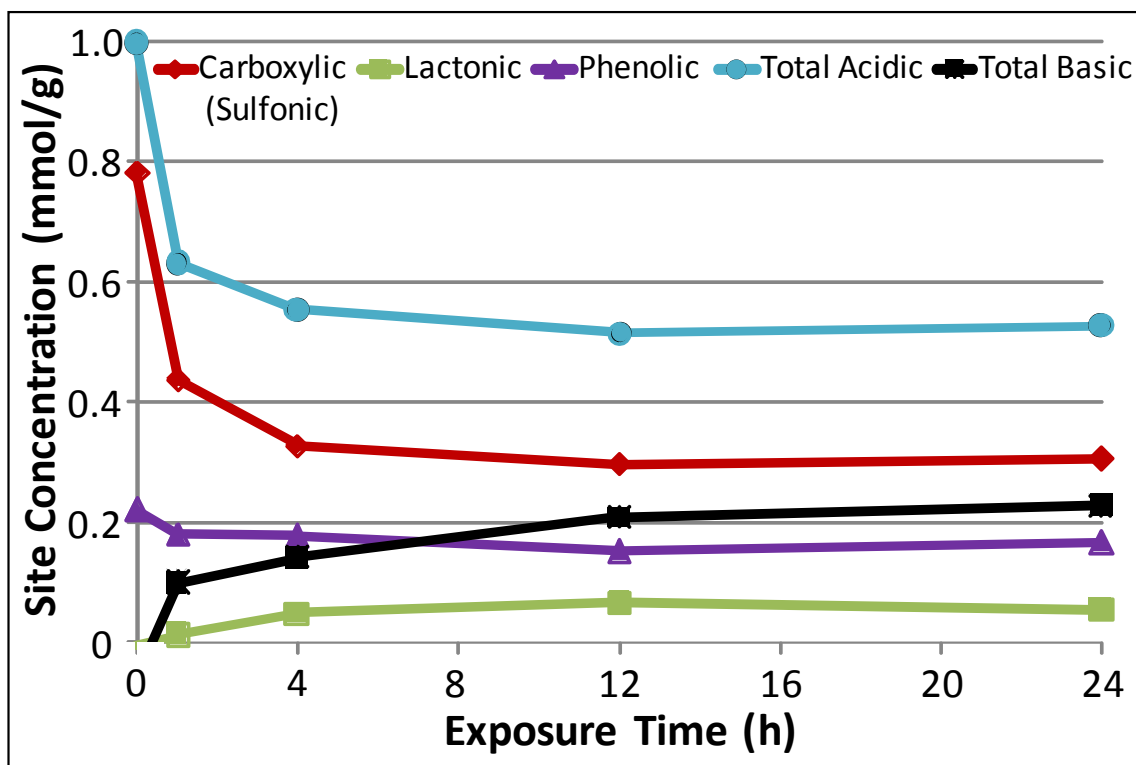


Figure 9: Acid site concentrations of H₂SO₄-modified activated carbon after exposure to hot liquid water for various time lengths at 200 °C.

2.3.5.4 Effect of Exposure Temperature

The H₂SO₄-modified carbon was exposed to hot liquid water at 150, 200 and 225 °C for 24 h and characterized by Boehm titration to determine the effect of exposure temperature on site retention (Figure 10). Exposure at the low temperature of 150 °C resulted in an increased surface concentration of all measured species, whereas exposure at the high temperature of 225 °C decreased the residual concentrations of all measured species. The most dramatic decrease in site retention after exposure to liquid water was observed for phenolic species. Their concentration decreased from 0.18 mmol/g to 0.01 mmol/g when exposure temperature was increased from 200 to 225 °C.

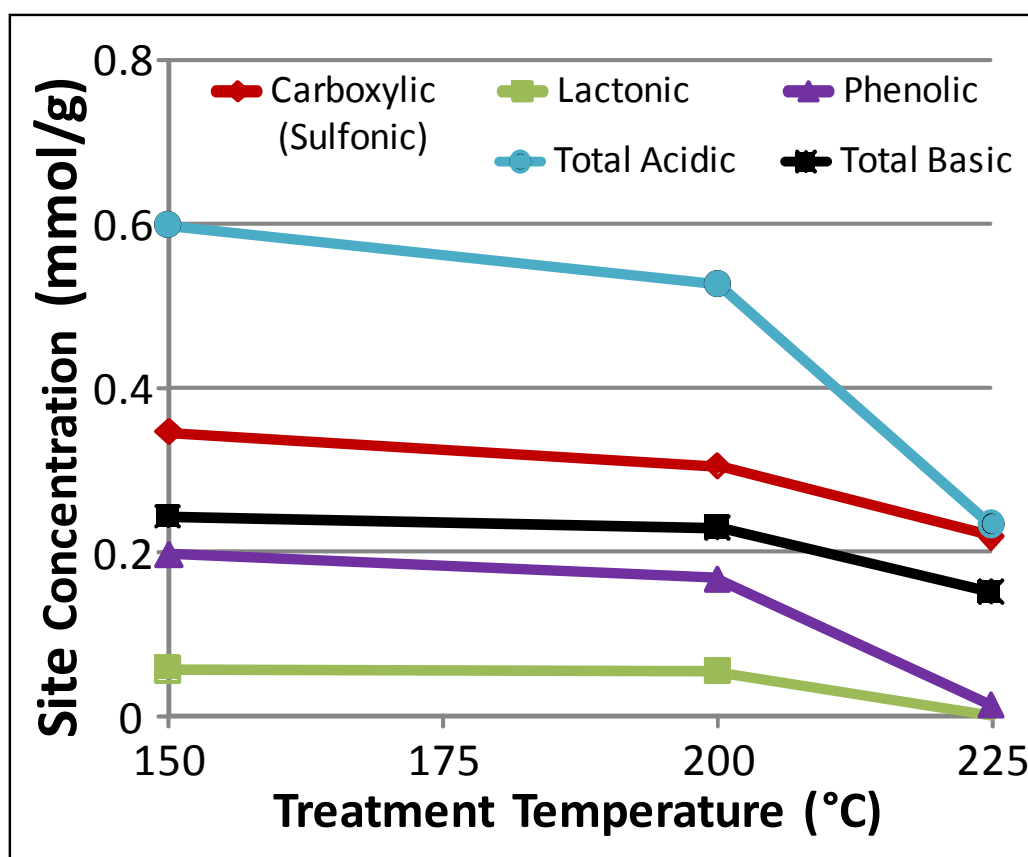


Figure 10: Acid site concentrations on H₂SO₄-modified activated carbon after exposure to hot liquid water for 24 h at various temperatures.

2.3.6 Temperature Programmed Desorption – Mass Spectrometry (TPD-MS)

The TPD of the HNO₃-modified activated carbon resulted in a MS signal at a mass to charge ratio of 30 (NO) with a maximum at 200 °C (Figure 11). After exposure to liquid water at 200 °C and 17 bar for 1, 4, 12, or 24 hours, the resulting carbon no longer evolved NO at this temperature. No MS peaks were obtained at a mass to charge ratio of 46 (NO₂) for any of these samples.

A single MS signal was found at the mass to charge ratio of 64 (SO₂) in the TPD of the H₂SO₄-modified activated carbon (Figure 11). This MS signal decreased significantly in first hour of exposure to hot liquid water. Extended exposure times resulted in a further decrease in this signal, and after 4 h exposure SO₂ evolution from the carbon appears nearly constant. No MS peaks were obtained at a mass to charge ratio of 48 (SO) for any of these samples.

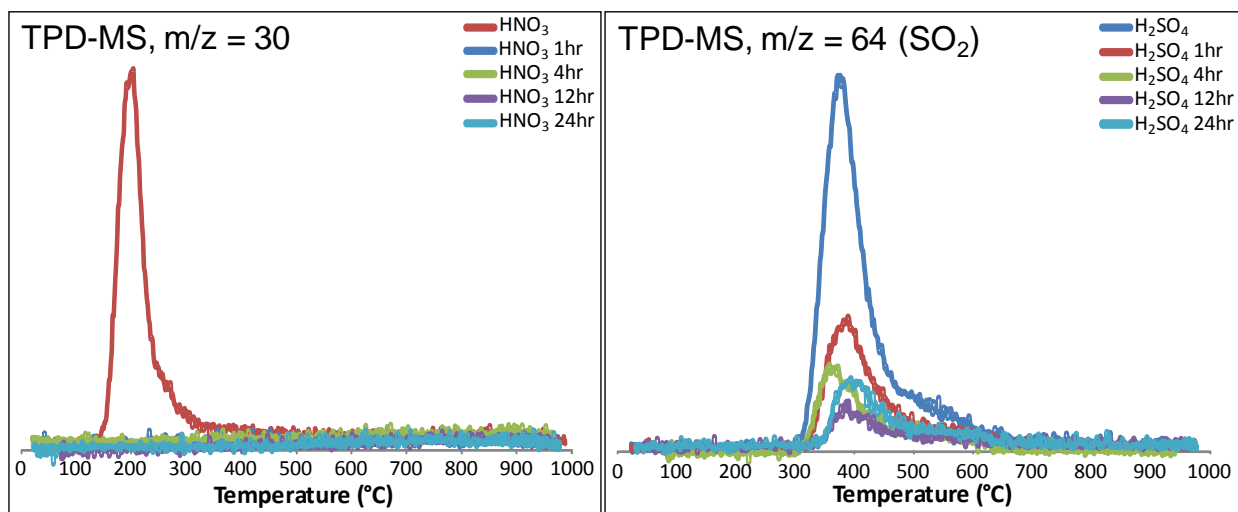


Figure 11: TPD-MS curves of HNO₃-modified activated carbons (Left) and H₂SO₄-modified activated carbons (Right).

2.3.7 X-ray Photoelectron Spectroscopy (XPS)

2.3.7.1 HNO₃-Modified Activated Carbon

XPS spectra were obtained at the binding energy of the N 1s orbital (392 – 412 eV) to analyze the chemical nature of the nitrogenous species present in HNO₃-modified activated carbon (Figure 12). The untreated activated carbon was found to possess a single absorption peak at a binding energy of 401.5 eV, which has been found to be characteristic of pyridine-like structures.⁴² After modification with HNO₃, this pyridine peak increased in intensity and shifted to a lower binding energy, indicating a decrease in oxidation state of the nitrogen atom. An additional peak at 405.9 eV was present in the spectra of the HNO₃-modified carbon sample. This peak is attributable to highly oxidized surface nitro groups. After exposure to water at 150 °C for 24 h, the nitro peak of the HNO₃-modified carbon had decreased significantly in intensity. The 401.5 eV pyridine peak present in the untreated carbon completed its shift to a 400.8 eV peak, characteristic of a pyridone, and further increased in intensity. HNO₃-modified carbons exposed to hot liquid water at 200 and 250 °C had XPS spectra with a single pyridone peak at 400.8 eV.

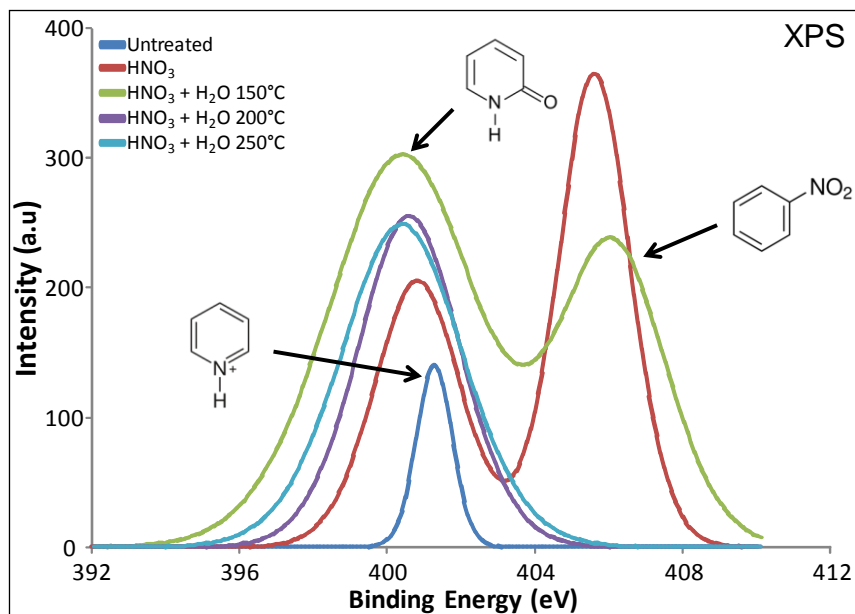


Figure 12: XPS spectra of HNO₃-modified activated carbon catalysts.

2.3.7.2 H₂SO₄-Modified Activated Carbon

The chemical nature of the sulfurous species present in the H₂SO₄-modified activated carbons was analyzed with XPS spectra at the binding energy of the S 2p orbital (158 – 175 eV). The untreated activated carbon spectrum was found to contain a single peak at 170.0 eV (Figure 13). This high binding energy is indicative of a highly oxidized sulfur species and thus this peak is likely attributable to a metal sulfate or sulfonic ester. Modification with H₂SO₄ removed this high binding energy peak and created an additional intense peak at a binding energy of 168.8 eV that has been found to be characteristic of sulfonic acids.⁴² This sulfonic acid peak decreased in intensity when the H₂SO₄-modified carbon was exposed to hot liquid water at 150, 200, and 250 °C for 24 h, with a larger intensity decrease present in carbons exposed to water at higher temperatures.

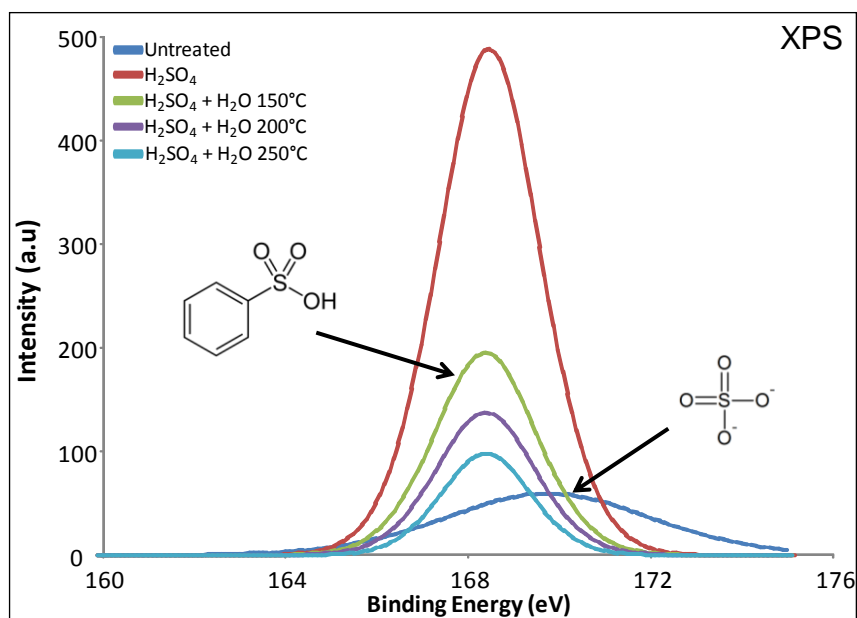


Figure 13: XPS spectra of H₂SO₄-modified activated carbon catalysts.

2.4 DISCUSSION

2.4.1 Structural Changes of Activated Carbon

The extremely low vapor pressure of most biomass and biomass-derived chemicals necessitates liquid phase processing. It has been found that heterogeneous catalyst stability under these conditions is an important issue. Upon exposure to hot liquid water, Zeolite Y was shown to degrade via siloxane bond hydrolysis¹⁶ and the γ -Al₂O₃ support of both Pt/ γ -Al₂O₃ and Ni/ γ -Al₂O₃ was found to undergo hydration to form a crystalline boehmite phase^{17, 20}. Activated carbon stability under these conditions, however, remains relatively understudied. The BET surface area of an activated carbon catalyst was found to remain constant after exposure to supercritical water at 400 °C for 3 h but decrease significantly upon exposure to similar lignin gasification conditions.⁴³ Additionally, in the wet oxidation of phenol, an activated carbon catalyst was found to experience a significant reduction in micropore volume upon repeated exposure to 160 °C, 16 bar aqueous reaction conditions.⁴⁴ It has been determined, however, that surface areas as determined by the Langmuir equation are more valid for microporous activated carbons, thus bringing these results into question.⁴¹

SEM images and Langmuir surface areas obtained in this work suggest that both the liquid and gas phase activated carbon modification methods used had no significant impact on the structural morphology of the materials. SEM images obtained before and after modification with H₂SO₄ show no significant morphological changes (Figure 3 A, B). Nitrogen physisorption data processed with the Langmuir equation indicate a slight increase in surface area of the activated carbon after modification with H₂SO₄, HNO₃, and 400 °C air (Table 1). The most significant of these changes occurred with the 400 °C air modification, resulting in an activated carbon with a 16% increased surface area. After exposure to hot liquid water at 200 °C and 17 bar, the structural morphology of the H₂SO₄-modified activated carbon as represented in SEM

images (Figure 3 B, C) was found to remain relatively unchanged. This is supported by additional Langmuir surface area measurements, indicating an addition slight increase in surface area of the H₂SO₄, HNO₃, and 400 °C air treated activated carbons.

The SEM images and N₂ physisorption data obtained indicate that both the acid modification and hot water exposure have only a small affect on the physical morphology of the activated carbons. The small relative increase in Langmuir surface area after acid modification and exposure to hot water is likely beneficial in the areas of heterogeneous catalysis and adsorption. These results are supported by a variety of previous studies which have found that surface area changes as a result of acid modification are relatively small^{11, 13, 26, 28} and are dependent on the type of activated carbon used.²⁸ The increase in surface area of the modified activated carbon after exposure to hot liquid water aligns with the results of a previous group that reported a slight increase in Ru/C surface area after exposure to supercritical water at 400 °C for 3 h.⁴³

2.4.2 Acid-Modification of Activated Carbon

Chemical agents have been used to modify the surface chemistry of activated carbons for many decades. Early studies utilized a variety of acids and hydroxides to increase the adsorption of a variety of environmental contaminants such as germanium and mercury vapor.⁴⁵⁻⁴⁶ Since that time, there have been a plethora of studies published utilizing activated carbon modification methods in the areas of gas separation,^{12, 21} water purification,⁴⁷⁻⁴⁸ heterogeneous catalysis,^{11, 25-26, 37, 49} and electrochemistry.⁵⁰⁻⁵¹ Modifications have typically been performed in the liquid phase using chemicals such as nitric acid, sulfuric acid, hydrogen peroxide, phosphoric acid, sodium hydroxide, and liquid ammonia. Additionally, gas phase modifications have been performed in previous works using hot air and ammonia gas.

Each acid-modification procedure was found to increase the overall acidity of the carbon as indicated by decreased PZCs (Figure 5). The surface chemistries of the H₂SO₄, HNO₃, and 400 °C air modified carbons were found to change most significantly as a result of the functionalization procedures. After modification, The H₂SO₄-modified carbon had a considerably lower PZC and a greatly increased sulfur content. Previous works have identified and quantified the concentration of sulfur-containing species on the surface of carbon treated with H₂SO₄ to be in the form of sulfonic acid and thiol groups^{11, 26, 35, 42} using XPS and TPD-MS. In XPS spectra, sulfonic acid groups provide a peak at 169.0 eV and thiol groups provide a peak in the range of 163.5 – 163.7 eV.⁴² The S2p XPS spectrum of the untreated activated carbon in this work contains a single broad peak located at H₂SO₄-modified activated carbon in this work contains a single broad peak centered at 169.8 eV (Figure 13). The high binding energy of this peak is indicative of a highly oxidized sulfur species, and is thus likely representative of either a sulfonic ester or metal sulfate. After modification with H₂SO₄, this peak is replaced with one at 169.0 eV corresponding to sulfonic acid groups. There is a notable lack of thiol groups present in the H₂SO₄-modified carbon which can be explained by the differences in carbon chemistry associated with the use varying carbon sources. This lack of thiol groups as determined with XPS signifies that both the 385 °C peak and 500 °C shoulder of the SO₂ evolution TPD curve of the H₂SO₄-treated carbon are associated with sulfonic acid groups (Figure 11). This is indicative of the presence of two types of sulfonic acid sites. The first type evolves SO₂ at 385 °C and is present in larger concentrations than the second, more thermally stable type, which evolves SO₂ at 500 °C. Upon H₂SO₄ modification, the activated carbon was found via Boehm titration to contain a significant increased concentration of highly acidic (sulfonic) acid sites, slightly increased concentration of phenolic sites, and no significant amount of basic sites (Figure 6). These results are in line with previous literature reporting a general increase in acidity and decrease in basicity after an activated carbon has been modified with H₂SO₄.

The low PZC of the HNO₃-modified carbon indicates a significant increase in surface acidity as a result of the treatment. A doubling in the nitrogen content of the carbon as a result of the treatment is due to the presence of surface nitrogen functional groups, identifiable by XPS. The N1s XPS spectrum of the untreated activated carbon contains a single peak at a binding energy of 401.3 eV. Peaks at this binding energy have been attributed to pyridine-like structures⁴² in previous literature. After HNO₃ treatment, this peak shifts slightly to a lower binding energy. This is likely due to the partial transformation of pyridines to pyridones, which are reported to have binding energies of 400.5 eV,⁵² as a result of the treatment procedure. In addition to this shift, the HNO₃ modification procedure imparts nitro groups on the carbon surface, as indicated by an XPS peak at a binding energy of 405.6.^{42, 52} The TPD-MS curve of the HNO₃-modified activated carbon possesses a single NO evolution peak at 200 °C which is attributable to the nitro groups, as the relatively thermally stable pyridine and pyridone structures have been shown to evolve NO at much higher temperatures. Treatment with HNO₃ was found to impart carboxylic, lactonic, and phenolic groups and remove nearly all of the basic groups from the carbon. These results are in line with other reports.¹³⁻²⁸

Modification with both H₂O₂ had just a minimal impact on the surface chemistry of the carbon, a result that has been found in a previous study.³⁶ The 300 °C air treatment was also found to have just a slight impact on the carbon, whereas the effects of the 400 °C treatment were more profound. This treatment imparted a significant amount of carboxylic, phenolic, and basic groups on the carbon surface. Interestingly, this modification method was the only one found in this study to increase the concentration of surface basic sites, thus making this catalyst preparation procedure potentially relevant for the synthesis of an effective solid base catalyst.

2.4.3 Stability of Activated Carbon Functional Groups in Hot Liquid Water

While information regarding the morphological stability and effect of acid pretreatments on the surface chemistry activated carbons has been published widely, research in the area of acid site stability is relatively sparse. A large number of groups have published TPD-MS curves for acid-modified carbons.^{11, 26, 28, 35, 38-39, 53} De la Puente et al. reports three major decomposition stages in the TPD profiles of their activated carbons.⁵³ The first stage, in the range of 400 – 623 K, is associated with the decomposition of carboxylic acid groups. The second stage, at 623 – 823 K, is associated with the decomposition of lactone groups and the final stage above 823 is associated with the decomposition of remaining, more stable groups. While these results give some indication of the thermally stability of different functional groups, they are often performed under inert atmospheres that are atypical of catalytic processes. Nevertheless, it is likely that acid site stability in hot aqueous conditions follow a similar trend.

Acid-modified activated carbon catalysts were exposed to hot liquid water at 200 °C and 17 bar for 24 h and characterized by point of zero charge measurements and Boehm titration to determine the effect of this hot aqueous exposure on their surface chemistries. After exposure to hot liquid water, point of zero charge measurements for all modified carbons were found to shift towards neutrality (Figure 5). This is an indication of the cleaning of the carbon surface of both acidic and basic functionalities. Boehm titrations give a more in depth look into the aqueous stability of specific functional groups (Figure 7, 8). Both carboxylic and sulfonic functional groups were found to be relatively unstable under these conditions. Hot liquid water exposure was found to significantly decrease these site concentrations for all modified carbons. It is interesting to note that the percentage of carboxylic and sulfonic functional groups remaining after hot liquid water exposure is around 20 – 30% for each of these carbons. This is an indication that sulfonic and carboxylic acid site stabilities are not related to the modification

method. Lactonic group concentrations were found to increase slightly upon hot liquid water exposure for all carbons while phenolic group concentrations were relatively constant. Basic site concentrations were found to increase with exposure to hot liquid water for the H₂SO₄- and HNO₃-modified carbons and decrease with exposure for the hot air modified carbons.

To elucidate information on the kinetics of acid site removal, a H₂SO₄-modified carbon was exposed to 200 °C water for 1, 4, 12 and 24 hours and characterized with Boehm titration and TPD-MS. The most significant changes in the surface chemistry of the carbon were found to occur in the first four hours of exposure (Figure 9). Further exposure was not found to significantly alter the functional group concentrations of the carbon, and both the acid and base site concentrations measured after 24 hours exposure were found to be nearly identical to those measured after 4 hours exposure. TPD-MS curves of the H₂SO₄-modified carbon after exposure for various time lengths shows similar results (Figure 9). The area of the sulfur desorption peak is found to decrease significantly in the first four hours, after which it remains relatively constant. These results suggest that acid modified activated carbon catalysts will undergo a four hour period in which their surface chemistries and reactivities will change dramatically, after which they will exhibit an extended period of on-stream stability.

Carbon modified with sulfuric acid was subjected for 24 hours to hot liquid water environments at 175 °C and 225 °C in addition to 200 °C to determine the effect of exposure temperature on the surface chemistry changes of the activated carbon. Boehm titration results after exposure indicate that acid site retention is highly dependent on exposure temperature (Figure 10). At the lower temperature of 175 °C, the retained concentrations of all sites measured were at their highest. When the exposure temperature was raised to 200 °C and 225 °C, all measured site concentrations decreased. This effect is more pronounced between 200 °C and 225 °C. This data suggests that an increased exposure temperature more efficiently

“cleans” the carbon surface, resulting in lower concentrations of all surface species. This effect could have an impact on reactor design and optimization, as steady state acid site concentrations on activated carbon catalysts are clearly dependent on reaction temperature and must be considered when choosing reaction parameters.

Some literature suggests that modification of activated carbons with nitric acid and sulfuric acid can impart nitrogen and sulfur based functionalities on the carbon surface.^{19, 37} In the interest of this project, it was thus important to both identify these species, if present, and determine how stable they are in hot liquid water. Initially, CHNS analyses were performed on samples of untreated, sulfuric acid modified, and nitric acid modified activated carbons both before and after exposure to 200 °C water for 24 hours (Figure 4). These results indicated that the nitrogen and sulfur content of the carbons increased substantially upon modification with the respective acid. After exposure to the 200 °C aqueous environment for 24 hours, the nitrogen and sulfur content of the carbons decreased, but remained larger than in the untreated carbon sample. To understand these results, identification of the sulfur and nitrogen functionalities in the carbons was necessary. In previous literature, x-ray photoelectron spectroscopy (XPS) has been shown to be an effective method for this identification.³⁷ The quantitative nature of XPS was particularly useful for this application, as analysis of carbon samples both before and after exposure to the 200 °C water environment allows for evaluation of the stability of the identified nitrogen and sulfur containing groups under these conditions.

Samples of the aforementioned carbons were sent to collaborators at the Eindhoven University of Technology in the Netherlands for XPS analysis. For the nitric acid modified carbon, XPS scans at the nitrogen 1s energy (392 - 410 eV) were performed to identify the nitrogen groups present in the carbon (Figure 12). The XPS spectrum of the untreated activated carbon contains a single peak attributable to a pyridine-like structure. Upon oxidation

with nitric acid, XPS spectra indicate that these structures are partially converted into pyridones. Additionally, after modification with nitric acid, a large concentration of nitro groups is found to be present on the carbon surface. After exposure to hot liquid water at 150 °C, these nitro groups are partially removed and complete nitro group removal is seen after exposure at higher temperatures. Exposure at 150, 200, and 250 °C was found to completely convert pyridines to pyridones.

In the untreated activated carbon, it was found that sulfur is present in a highly oxidized form which is likely attributable to either a metal sulfate or sulfonic ester (Figure 13). Upon oxidation with sulfuric acid, these highly oxidized groups are removed and the sulfur content of the carbon is found to be entirely attributable to sulfonic acid groups. This data confirms the hypothesis presented earlier that the carboxylic acid site concentration measured in Boehm titration is partially attributable to sulfonic acids. When the sulfuric acid modified carbon is exposed to hot liquid water, it is found that the sulfonic acids are partially removed. The relative concentration of sulfonic acid before and after hot liquid water exposure as measured by XPS agrees well with that measured by Boehm titration and discussed earlier. Furthermore, it is found that sulfonic acid site retention is temperature dependant, with more sulfonic acid groups being retained at lower exposure temperatures. These findings are again in agreement with those determined through Boehm titration measurements.

2.5 Conclusions

The results obtained in this research project indicate that acid-functionalized activated carbons are unstable under typical biomass reforming conditions. The data obtained via Boehm titration suggests that severe deactivated of these carbons can occur within just one hour when

exposed to a hot aqueous environment at 200 °C and that deactivation is even more severe at higher temperatures. The sulfuric and nitric acid modified carbons were found to be the most acidic, and thus likely the most effective as solid acid catalyst. XPS data indicated that acid functionalization with nitric acid imparted a large number of nitro groups on the carbon surface. These nitro groups were found to be partially stable at 175 °C and completely unstable at higher temperatures. Sulfuric acid modified carbons were found to possess large amounts of highly acidic sulfonic acid groups. These groups were found to be partially stable under the conditions tested, and may prove to be promising solid acid catalysts or biomass conversion reactions.

The specifics of acid site stability as discovered in this project could potentially be applied to catalyst design in order to develop highly active and stable catalysts. Knowledge of the relative stability of moderately-acidic lactonic functional groups indicates that an activated carbon modification method in which lactonic groups are formed in large concentrations could produce a promising catalyst. Additionally, the stability of around 25% of carboxylic and sulphonic acid groups could provide another pathway for catalyst design. If the differences between stable and unstable sulphonic groups were fully understood, a highly acidic and stable H₂SO₄-modified carbon could theoretically be produced and utilized for a variety of aqueous phase biomass conversion processes.

CHAPTER 3

CELLOBIOSE HYDROLYSIS WITH SOLID ACID CATALYSTS

3.1 INTRODUCTION

Oligosaccharides are sugar polymers containing a relatively small number of monomer units. In the field of biomass conversion oligosaccharides are often considered an undesirable intermediate in the conversion of cellulose to glucose, which has been shown to be a very versatile reagent. Aqueous phase reforming of glucose can form either hydrogen gas or large alkanes for fuel use depending on the catalyst used.⁵⁴⁻⁵⁵ Additionally, a variety of products can be formed through the fermentation of glucose, including ethanol for liquid fuel use⁵⁶ and lactic acid for bioplastic production.⁵⁷

In the area of biomass conversion, oligosaccharides are most often formed as a result of the rapid hydrolysis of cellulose in near-critical and supercritical water.⁷⁻⁹ This reaction, performed in the absence of a catalyst, has been shown to result in nearly complete conversion of cellulose in as little as 0.04 seconds.⁷ This rapid conversion, however, is accompanied by a very diverse product mixture, including organic acids, erythrose, HMF, oligosaccharides, and glucose. Oligosaccharide yields of nearly 40% have been reported from these processes⁸ along with glucose yields of nearly 30%.⁹ From these reaction products, it would be economically desirable to completely convert the residual oligosaccharides to glucose as a feedstock for further biomass conversion processes.

Oligosaccharide hydrolysis research to date has been quite limited. One important characteristic of oligosaccharides is their solubility in water, making conversion with heterogeneous catalysis possible. Shanks et. al. utilized propylsulfonic acid-functionalized

mesoporous silica to perform the hydrolysis of oligosaccharides formed in the hydrothermal pretreatment of distiller's grains, reporting sugar yields of around 60%.⁵⁸ Ladisch et al. used Amberlyst 15 to study the hydrolysis of oligosaccharides.⁵⁹ This group reported glucose yields of as high as 90%, but catalyst deactivation due to autohydrolysis of the resin was found to be a major issue. Marzo et al. investigated the hydrolysis of sucrose, maltose, and cellobiose with acidic resins and mixed metal oxides at mild temperatures, finding the γ - β -1-2-glycosidic bond of sucrose to be most reactive over solid acids.⁶⁰

In this section of my work, catalysts were tested for the hydrolysis of the model oligosaccharide cellobiose. A large series of activated carbon, amorphous silica alumina (ASA), and silica niobia catalysts were synthesized and characterized. These catalysts were chosen due to the ability to tune their acidity either by varying the composition (ASA, silica niobia) or modification method (activated carbon) before reaction. These catalysts were screened for cellobiose hydrolysis activity in a fixed bed reactor. Stable catalysts were evaluated further to determine kinetic parameters for cellobiose hydrolysis and a novel, highly active activated carbon catalyst was synthesized and tested for hydrolysis activity.

3.2 EXPERIMENTAL METHODS

3.2.1 Catalyst Synthesis

ASA catalysts were prepared with Si/Al ratios of 2, 5, and 10 by a cogelation method.⁶¹ To prepare the samples, the required amount of aluminum chloride hexahydrate was added to 600 g water and 75 g acetic acid. To this solution, a solution of sodium silicate in 2000 g water was added under vigorous stirring. The pH of the solution was adjusted to 7 through the addition of concentrated ammonia. After stirring for an hour, the product was filtered and ion-exchanged

with 800 mL 0.1 M ammonium acetate. The samples were then dried at 80 °C and calcined at 650 °C for 5 h.

SiO₂-Nb₂O₅ catalysts were prepared by a coprecipitation method⁶² with concentrations of 10%, 30%, and 50% niobia. To prepare the samples, an aqueous solution of ammonium niobium oxalate was dropped into tetraethyl orthosilicate which had been previously hydrolyzed with a HCl solution for 1 h with a HCl/TEOS molar ratio of 4. A 28% ammonia solution was then added dropwise until complete precipitation. This solution was filtered, aged for 24 h, and dried under vacuum at 70°C for 4 h. Finally, the solid was calcined at 550 °C for 8 h.

Activated carbon catalysts were prepared as described in Chapter 2. A reacidified H₂SO₄-modified catalyst was prepared by performing the H₂SO₄-modification procedure on an activated carbon that had been previously H₂SO₄-modified and subsequently exposed to 200 °C, 17 bar water for 24 h.

3.2.2 Stability Studies

Stability studies of ASA and silica niobia catalysts were performed in Parr acid digestion bombs. For ASAs, 0.7 g catalyst was placed with 20 mL water in a teflon-lined acid digestion bomb (Figure 2). For silica niobias, 1 g catalyst was placed with 30 mL water in identical teflon-lined vessels. Each bomb was then closed and placed on a rotating rack in a 200 °C preheated forced convection oven. ASAs were exposed to the 200 °C and 17 bar water for 24 h, whereas silica niobias were exposed for 96 hours. After the required time, the acid digestion vessels were removed from the oven and quenched rapidly under flowing water. The catalyst was filtered and dried before further characterization or reaction.

3.2.3 Modified Boehm Titration Method

The aqueous acidities of both ASA and silica niobia catalysts were obtained using a modification of the Boehm titration method described in detail in Chapter 2. For ASAs, 100 mg catalyst were added to 20 mL 0.001 M NaHCO₃ and stirred vigorously for 2 h and filtered. For silica niobias, 200 mg catalyst were added to 40 mL 0.001 M NaHCO₃ and stirred vigorously for 2 h and filtered. For each, a 10 mL aliquot of the filtrate was added to 20 mL 0.001 M HCl and back titrated with 0.001 M NaOH. The titration endpoint was determined by the first derivate method.⁶³

3.2.4 Hydrolysis Reactions

Hydrolysis reactions were performed in a fixed bed flow reactor designed and built for this very project (Figures 14 and 15). This reactor system features an Agilent quaternary HPLC pump, which is able to supply up to four different liquid reagents to the reactor simultaneously. Air, H₂, and He can be supplied to the reactor through individual Brooks mass flow controllers. Each reagent flows through a check valve and a six-inch preheating section. The reactor itself consists of 1/4" Swagelok tubing heated by a home-built furnace, which is controlled by an Omega PID controller. There is a two foot section of 1/8" Swagelok tubing after the reactor, which serves to cool the reaction products to a temperature acceptable for the backpressure regulator. After the backpressure regulator, the products flow into a Valco 16-way selector valve, controlled by a microelectric actuator. This valve allows up to 15 liquid samples to be deposited in HPLC vials automatically. The waste products flow through a simple gas/liquid separator, allowing for gas sampling and analysis through GC/MS if deemed necessary. The entire reactor system is controlled through Labview, including the mass flow controllers, PID furnace temperature controller, and selector valve.

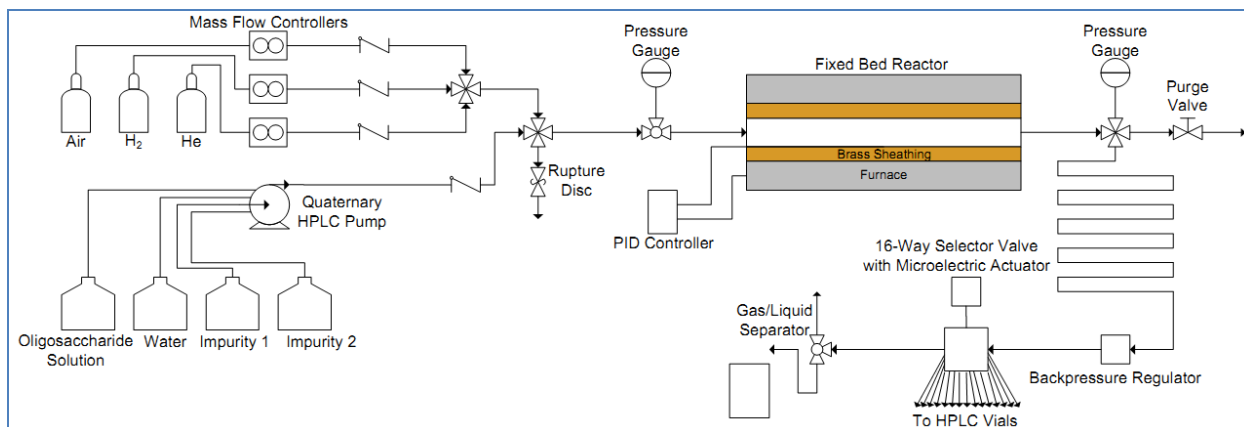


Figure 14: Process flow diagram of fixed bed reactor setup.

Before reaction, all catalysts were sieved to a particle size less than 75 μm . 100 mg catalyst was added to the reactor atop a quartz wool layer. The reactor was then sealed and the N_2 pressure behind the backpressure regulator was increased to a value slightly above the autogenic pressure of water at the desired reaction temperature. 2 mL/min 1 wt% cellobiose solution was mass flow over the catalyst bed until the desired pressure was reached, after which the flow rate was decreased to the value desired for the specific experiment. At this point, both the preheater variac and reactor furnace PID were set to the desired reaction temperature. Once the desired temperature was reached, autosampling was begun. At the desired time intervals, 1.5 mL liquid samples were automatically collected in HPLC sample vials for later analysis. After the completion of the reaction the cellobiose flow was ceased and the temperature setpoints of both the preheater and furnace PID were decreased to room temperature. The reactor was allowed to cool under air flow while the sample vials were collected.

3.2.5 IR Spectroscopy

For the IR experiments, the catalyst was diluted with spectroscopic grade KBr to make a 1 wt% mixture of catalyst in KBr. This mixture was pressed in a Pike brand evacuable pellet press to 6 tons of pressure to form a uniform wafer with a diameter of 13 mm and thickness

around 2 mm. This wafer was placed in a vacuum IR cell at 0.001 mbar, and a spectrum was recorded after one hour.



Figure 15: Fixed bed reactor setup.

3.3 RESULTS AND DISCUSSION

3.3.1 Catalyst Stability

As described earlier, catalyst stability under hydrolysis reaction conditions is something that has been mostly overlooked and is very important to consider when designing a catalyst for oligosaccharide hydrolysis reactions. Activated carbon stability was discussed in depth in the previous chapter, but ASA and silica niobia stability under these conditions has yet to be studied in much detail.

3.3.1.1 ASA Stability

A thorough investigation into the stability of ASAs was performed by a previous group member, who found that exposure to a hot aqueous environment significantly decreased the surface area of ASA catalysts and modified the aluminum coordination environment.⁶⁴ The acidity of ASA catalyst prepared via the cogelation method, measured by a modified Boehm titration method, however, was found to remain relatively unchanged after exposure to 200 °C, 17 bar water for 24 h (Figure 16). This is reinforced by batch cellobiose hydrolysis reaction data, which indicates that the activity of an ASA catalyst with a Si/Al ratio of 4 is nearly identical before and after exposure to the hot aqueous environment for 24 h (Figure 17). These results are promising for ASAs as an oligosaccharide hydrolysis catalyst.

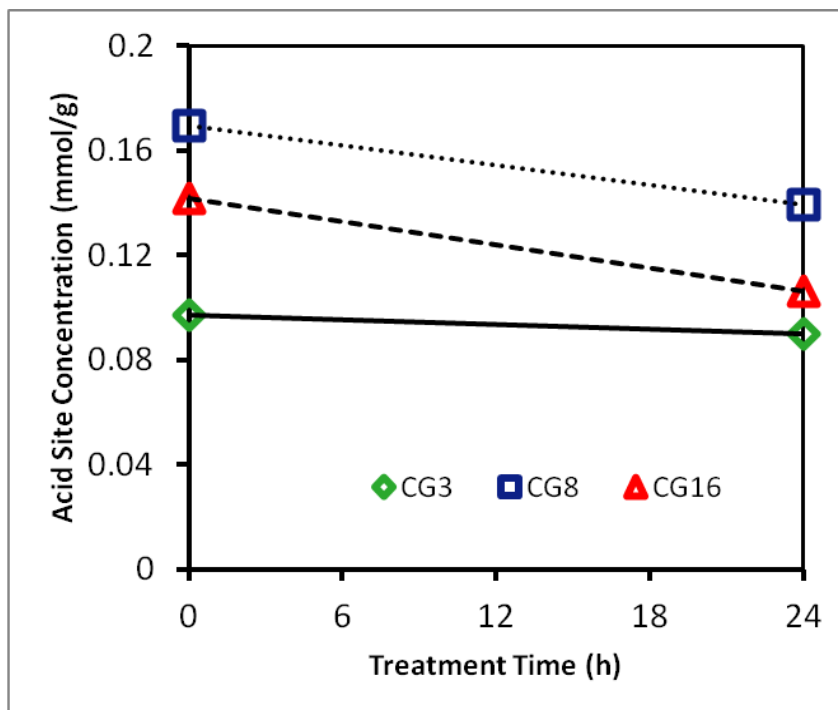


Figure 16: Acid site concentration of ASA catalysts before and after exposure to 200 °C water.

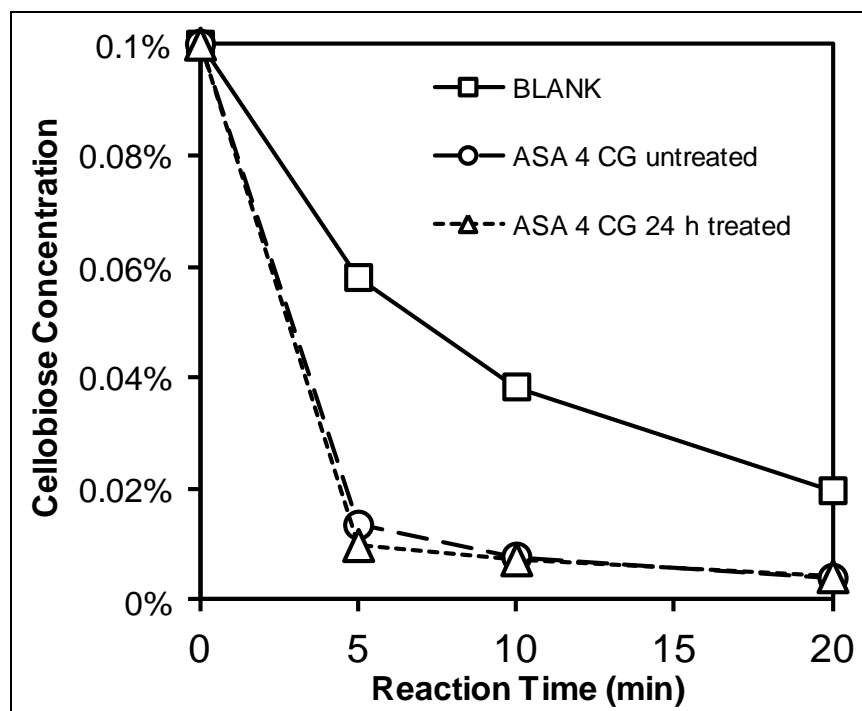


Figure 17: Batch reactor results for cellobiose conversion with ASA(4) catalysts before and after hot aqueous treatment.

3.3.1.2 Silica Niobia Stability

The acidity of the silica niobia catalysts was characterized by a modified Boehm titration method before and after exposure to 200 °C, 17 bar water for 96 hours (Figure 18). For the catalysts as synthesized, the 10% silica niobia was found to have the lowest acidity whereas the 30% silica niobia was found to have the highest. After exposure to the hot aqueous environment, the acid site concentration of each of the silica niobia catalysts increased substantially. This increase may be due to a leaching of the silica. In the silica niobia catalysts, the weakly acidic silica serves to moderate the acidity of the strongly acidic niobia. Leaching silica would result in a more niobia rich, acidic catalyst. Further experiments, including the utilization of ICP to determine silicon concentration in the water after hot aqueous exposure, would be required to confirm this hypothesis.

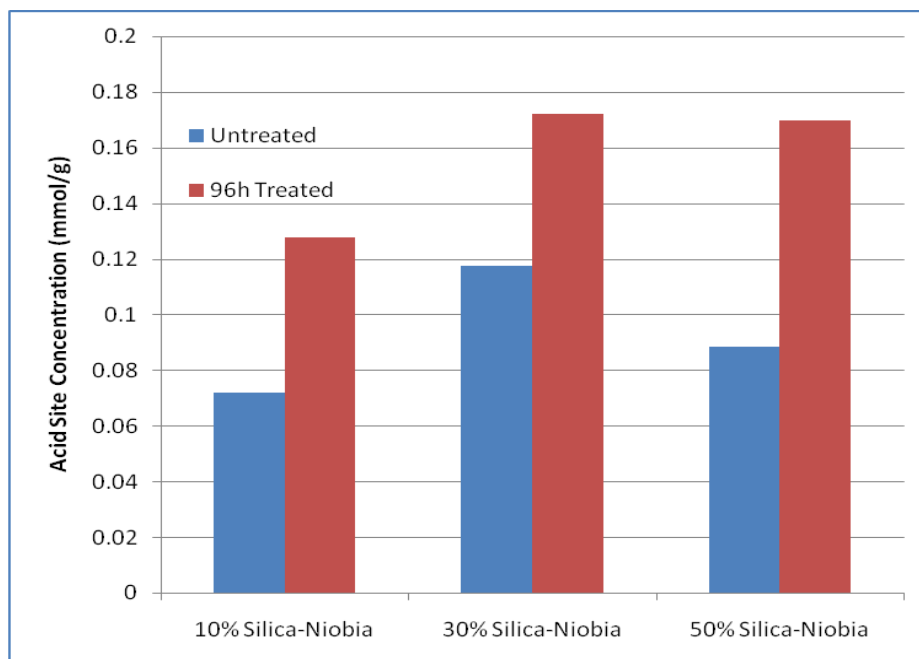


Figure 18: Acidity of silica niobia catalysts before and after exposure to 200 °C, 17 bar water for 96 hours.

3.3.2 Catalyst Screening

Each of the activated carbon, ASA, and silica niobia catalysts were tested in the flow reactor for cellobiose hydrolysis. Initial data showed that at these conditions, steady state product formation occurs after 30 minutes (Figure 19), and thus all data reported was determined after that 30 minute initiation period. Reactivity data for all catalysts is shown in Table 2. For the activated carbon catalysts, it can be seen that the glucose yield increases for each acidification method. With the untreated activated carbon, cellobiose conversion is quite low at just 23.9%, but the fractional yield of glucose is high, at 80.6%. This conversion is similar to that obtained in the absence of a catalyst but the glucose fractional yield is slightly lower. After each acidification method, both the maximum glucose concentration in the product stream and cellobiose conversion were found to increase. In each case, however, the glucose fractional yield was found to decrease significantly, indicating that increasing acidity promotes

side reactions which form undesired byproducts. The ASA catalysts were found to give quite high product glucose concentrations with relatively high glucose fractional yields. ASA(5) was found to give the highest glucose production out of the catalysts tested, with a maximum glucose concentration of 0.4%, while ASA(10) resulted in a relatively high glucose production (0.32% concentration) with a very high fractional yield of 99.49%. The silica-niobia catalysts were found to give glucose yields similar to those in the activated carbon catalysts. At the higher niobia contents of 30 and 50%, there was a decrease in glucose yield accompanied by an increase in cellobiose conversion. The 30% silica niobia catalyst was found to result in a slightly higher cellobiose conversion than the 50% silica niobia, which is likely due to its increased acid site concentration as determined by the modified Boehm titration method and discussed earlier (Figure 18). While the cellobiose conversion decreased with an increase from 30% to 50% niobium content, the maximum glucose concentration and glucose fractional yield were found to decrease. It is hypothesized that with the increase in highly acidic niobium

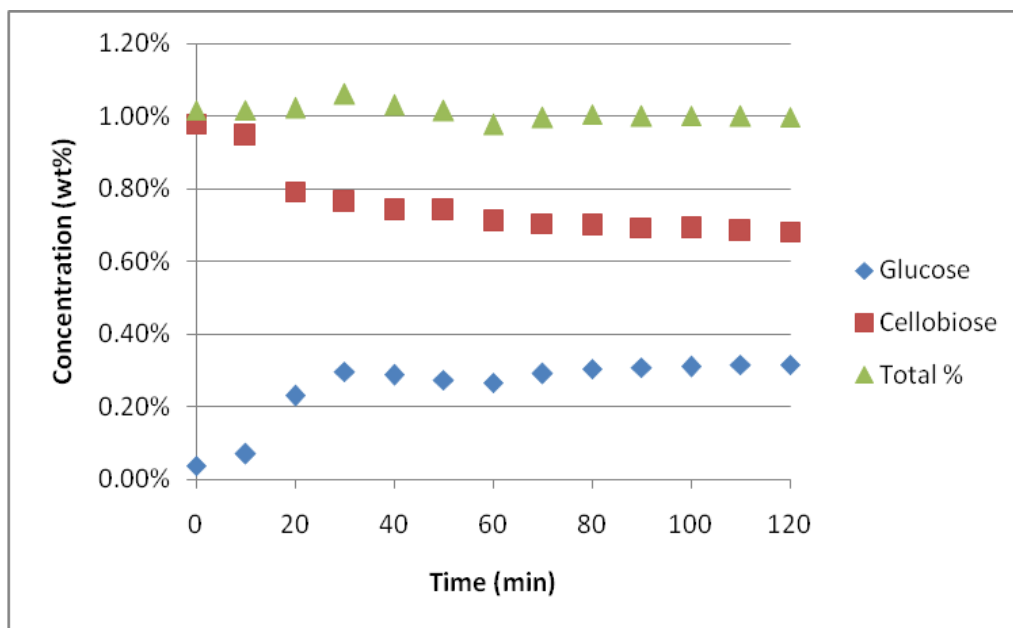


Figure 19: Glucose and cellobiose concentrations obtained for ASA(10) catalyzed cellobiose hydrolysis reaction.

Table 2: Performance of solid acid catalysts for hydrolysis of cellobiose in packed bed reactor. Reaction conditions – 0.5 mL/min 1 wt% cellobiose, 200 °C, 100 mg catalyst.

Catalyst	Max Glucose Concentration	Cellobiose Conversion	Glucose Fractional Yield
Blank	0.24%	23.37%	102.51%
Untreated AC	0.19%	23.91%	80.64%
H ₂ SO ₄ AC	0.29%	48.85%	58.83%
HNO ₃ AC	0.33%	56.47%	59.27%
H ₂ O AC	0.26%	46.45%	56.98%
Air (300 °C) AC	0.26%	54.25%	48.52%
Air (400 °C) AC	0.29%	63.75%	45.99%
ASA(2)	0.35%	58.01%	60.71%
ASA(5)	0.40%	54.46%	74.21%
ASA(10)	0.32%	31.78%	99.49%
10% SN	0.33%	39.17%	84.04%
30% SN	0.27%	72.34%	37.16%
50% SN	0.23%	68.92%	33.16%
Al ₂ O ₃	0.23%	19.76%	113.90%
SiO ₂	0.32%	33.00%	96.97%
Nb ₂ O ₅	0.28%	39.00%	71.79%

content in the 50% silica niobia, the average acid site strength is higher than that of the 30% silica niobia and thus glucose is more rapidly degraded into undesirable side products. The pure metal oxides of alumina and silica were found to give high glucose fractional yields but low cellobiose conversions. Niobia, however, gave both a low cellobiose conversion of 39% and a relatively low glucose fractional yield of 72%.

3.3.3 On-Stream Stability

3.3.3.1 Activated Carbons

As discussed extensively in the second chapter of this thesis, acid-modified activated carbons are likely to undergo significant surface chemical changes when exposed to typical

biomass conversion reaction conditions. Thus, it is expected that these acidified carbon catalysts will exhibit deactivation over the course of an extended cellobiose hydrolysis reaction. This was, indeed, determined to be the case with the H_2SO_4 -modified carbon but not for carbons acidified with other methods. In the short two hour reaction time, the glucose product yield from the H_2SO_4 -modified activated carbon was found to decrease significantly. All other activated carbon catalysts tested, however, were found to exhibit a stable glucose yield after the 30 minute initiation period (Figure 20). This could be due to significantly slower kinetics of chemical changes in non H_2SO_4 -modified activated carbons. In Chapter 2, it was found that for H_2SO_4 -modified carbons, surface chemical changes occur primarily in the first four hours of exposure to hot liquid water (Figure 9). If this rapidity is characteristic of sulfonic acid sites only, it is possible that the chemical changes found to occur in other carbon species (e.g. HNO_3 -modified) occur at much slower rates and thus cannot be seen in a short 2 hour reaction. This hypothesis remains unconfirmed, however, and would require additional stability studies to verify.

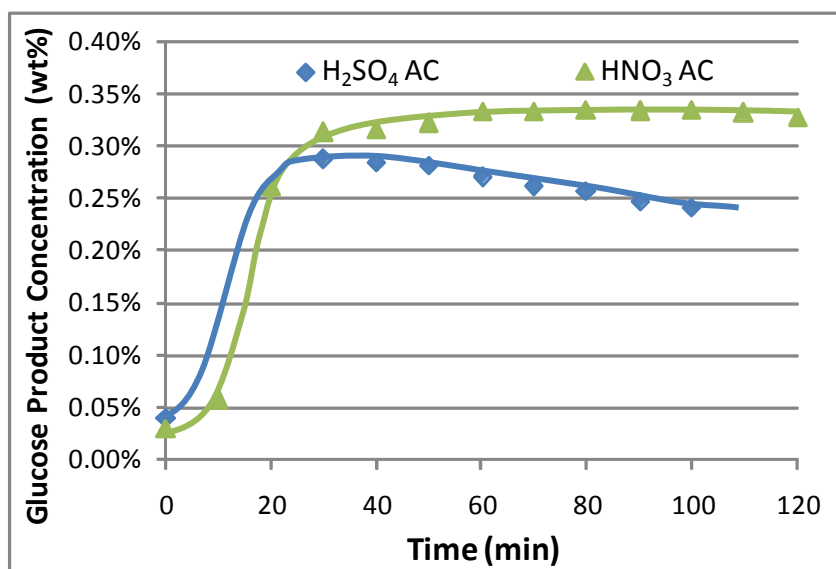


Figure 20: H_2SO_4 -modified activated carbon exhibiting deactivation over the course of a two hour reaction, HNO_3 -modified carbon stable.

3.3.3.2 ASAs

ASA stability studies indicated that catalysts prepared via the cogelation method exhibit stability in terms of acidity and reactivity upon exposure to hot liquid water. Short-term reactivity data for cellobiose hydrolysis under flow conditions reaffirms this. Each of the ASAs tested showed excellent stability over the course of the two hour screening reactions. Additionally, a 24 h reaction was performed using an ASA(10) catalyst (Figure 21). This catalyst exhibited stability throughout this reaction, resulting in a consistent 32% cellobiose conversion and nearly 100% glucose selectivity over the course of the entire extended reaction.

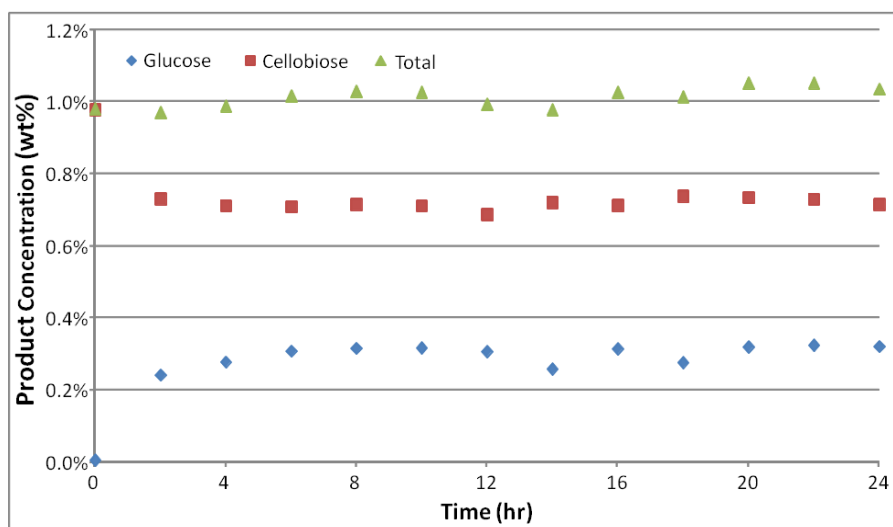


Figure 21: Extended-length reaction results indicating stability of ASA(10) catalyst.

3.3.3.3 Silica Niobias

Previous results indicate that silica niobia catalysts increase in acid site concentration after exposure to hot aqueous conditions for extended periods (Figure 18). This transformation can be seen in the product yields of just a two hour reaction product plot (Figure 22). The 30% silica niobia catalyst is highly acidic as synthesized, as can be seen by the initially high cellobiose conversion of around 80%. While the conversion is high, the glucose selectivity is

quite low, with glucose yields being only around 25%. This low selectivity is an indication of the prevalence of glucose degradation side reactions catalyzed by the overly-acidic 30% silica niobia catalyst. After two hours of reaction, the cellobiose conversion increases to over 90% while the glucose yield decreases to just 20%, changes which, although subtle, are likely due to the acid site concentration increase as determined by the modified Boehm titration method.

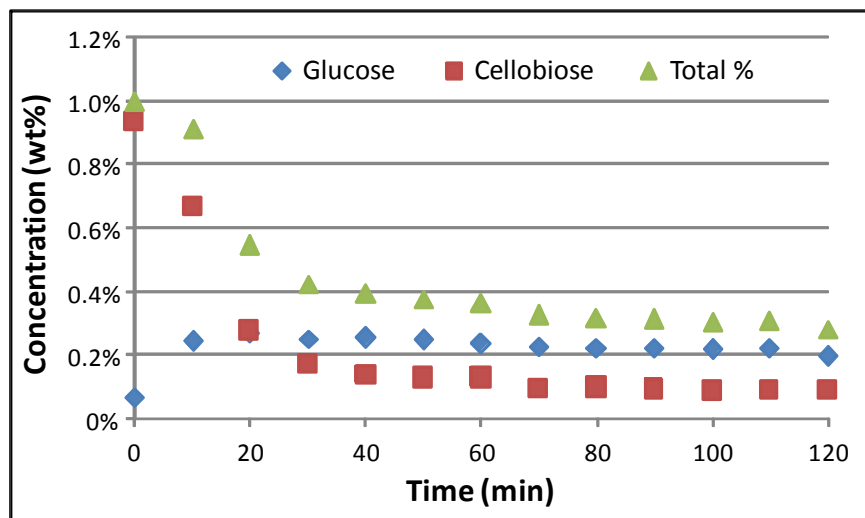


Figure 22: Glucose and cellobiose concentrations after obtained for a 30% silica niobia catalyzed cellobiose hydrolysis reaction.

With the high acidity of the 30% silica niobia catalyst, the potential for coke formation during the course of a reaction is high. For the development of an industrially-relevant catalyst, coke formation and its effect on catalyst reactivity are very important. The 30% silica-niobia catalyst was evaluated before and after reaction to determine if carbonaceous deposits were formed under these reaction conditions. The catalyst was found to change color from white to brown, and CHN analysis indicated that some carbonaceous deposits were formed on the catalysts (Table 3). The FT-IR spectra of the fresh and spent catalysts were quite similar. However, the spent catalyst was found to have an additional peak around 1700 cm^{-1} , indicating that carbonyl groups are present as part of the deposit (Figure 23). The changes in carbon and

hydrogen content of the spent catalyst as determined by CHN analysis (3.04% C, 0.12% H) indicate that the carbonaceous species on the spent catalyst have a C:H ratio of nearly two, which is much higher than that of cellobiose (~0.5). While physisorbed water may have an effect on the hydrogen content of the two samples, this ratio still provides evidence that dehydration reactions on the catalyst surface are playing a role in carbon species deposition. Going forth, if the 30% silica niobia catalyst is to be considered as a potential oligosaccharide hydrolysis catalyst, it will be important to further investigate this coke formation by determining its effect on reactivity and developing an efficient and non-destructive regeneration technique.

Table 3: CHN analysis of 30% silica niobia catalyst before and after 4 h reaction.

Catalyst	C (wt%)	H (wt%)	N (wt%)
30% s-n Fresh	0	0.55	0
30% s-n Spent	3.04	0.67	0

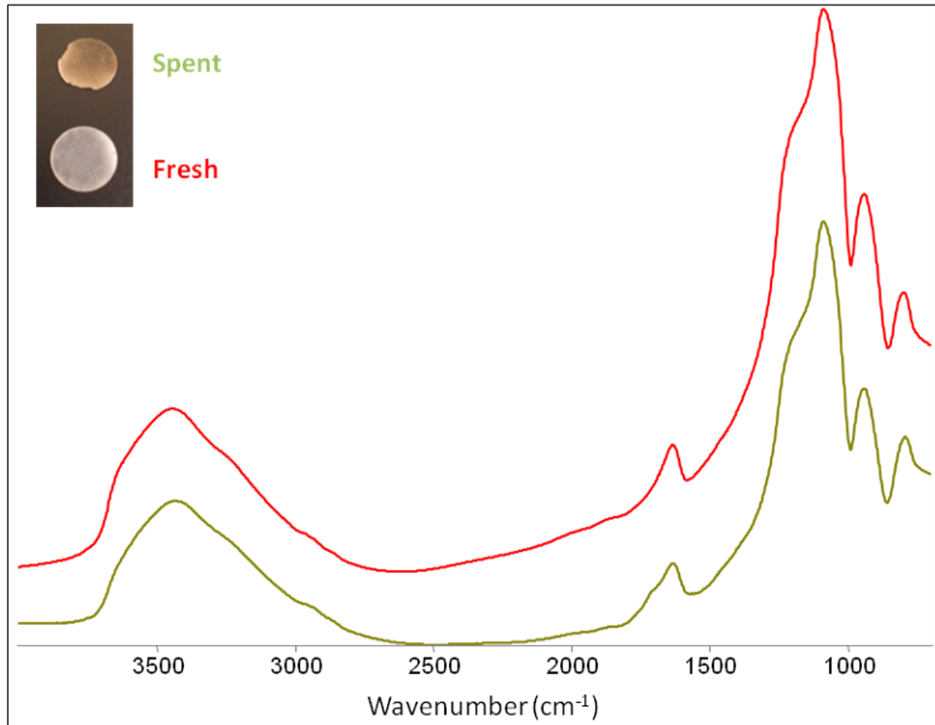


Figure 23: IR spectra of 30% silica-niobia catalyst before and after reaction.

3.3.4 Kinetics of Cellobiose Hydrolysis over Mixed-Metal Oxide Catalysts

In order to optimize the conditions for cellobiose hydrolysis over amorphous silica alumina (ASA) and silica-niobia catalysts, a series of reactions were performed varying temperature to determine apparent activation energies for cellobiose hydrolysis. Cellobiose hydrolysis experiments were performed at 175, 200, and 225°C over each of the mixed metal oxide catalysts. The results of this experiment for the catalyst ASA(2) are shown in Figure 24. At the relatively low temperature of 175 °C, the cellobiose conversion decreases significantly, resulting in a dramatic decrease in glucose production. When the temperature of the reaction is increased to 225 °C, the glucose yield approaches that seen at the reaction temperature of 200 °C. The cellobiose conversion at this temperature, however, is much higher than that seen at 200 °C, indicating that the glucose formed in the reaction at this temperature is being further degraded into undesired side products which are not quantified via HPLC.

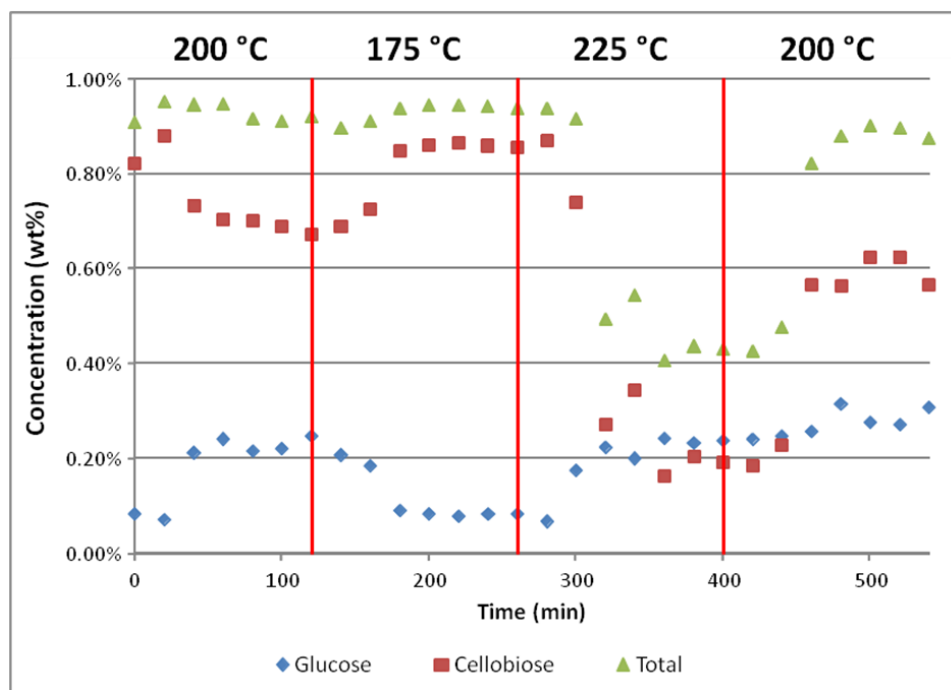


Figure 24: Effect of reaction temperature on product concentrations for 1 wt% cellobiose hydrolysis in a packed bed reactor with 100 mg ASA(2) catalyst.

Table 4 and Figure 25 display the results of these experiments for the selected catalyst. It can be seen that in general the glucose yield increases with an increased reaction temperature. The highest glucose yield as determined in these experiments is 47% with the 10 % silica-niobia catalyst at 225 °C. A similar yield was seen with ASA(10) at 225 °C. As expected, cellobiose conversions were found to increase with increasing reaction temperature. It is interesting to note from Figure 2 that an increase in reaction temperature from 175 – 200 °C results in only a small increase in cellobiose conversion in the case of the ASA catalysts and a large increase in cellobiose conversion in the case of the silica-niobia catalysts. The opposite trend was found to occur from 200 – 225 °C, however, where the higher temperature results in a significant increase in cellobiose conversion for ASA catalysts and only a slight increase in cellobiose conversion for silica-niobia catalysts. When the reaction temperature was returned to 200 °C at the end of the experiment, the cellobiose conversion was found to increase slightly for the ASA catalysts. This increase in conversion was accompanied by either no change in the glucose yield (ASA(10)) or a slight increase in glucose yield (ASA(2)). This is an indication that over the course of the temperature cycle the ASA catalysts become slightly more active for cellobiose hydrolysis. For the silica-niobia catalysts, however, significantly different results were found. Upon returning to a reaction temperature of 200 °C, the cellobiose conversion over the silica-niobia catalysts was found to decrease significantly, associated with either a slight increase (30% silica-niobia) or decrease (10% silica-niobia) in glucose yield. The decrease in cellobiose conversion over these catalysts is a clear indication of catalyst deactivation in the course of the experiment. After just two hours on stream, it was found that a significant amount of carbonaceous deposits were present on the 30% silica-niobia catalyst, and thus it is likely that coking is a major mechanism for this observed catalyst deactivation.

Table 4: Glucose and cellobiose concentrations in the product solution of 1 wt% cellobiose hydrolysis reaction at various temperatures.

	200 °C		175 °C		225 °C		200 °C	
Catalyst	Glucose	Cellobiose	Glucose	Cellobiose	Glucose	Cellobiose	Glucose	Cellobiose
ASA(2)	0.24%	0.69%	0.08%	0.86%	0.24%	0.20%	0.28%	0.63%
ASA(5)	0.22%	0.76%	0.06%	0.91%	0.28%	0.26%	-	-
ASA(10)	0.31%	0.68%	0.08%	0.93%	0.45%	0.23%	0.30%	0.63%
10% SN	0.36%	0.28%	0.17%	0.67%	0.47%	0.18%	0.28%	0.62%
30% SN	0.27%	0.11%	0.23%	0.48%	0.26%	0.06%	0.30%	0.45%

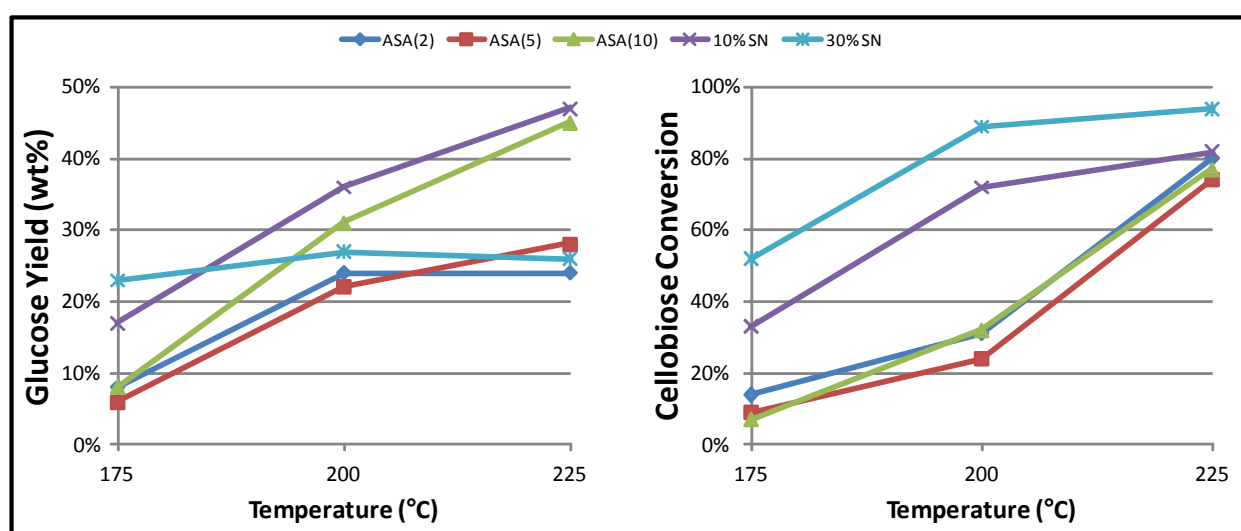


Figure 25: Glucose yield and cellobiose conversions for 1 wt% cellobiose hydrolysis reaction at various temperatures.

In order to determine meaningful kinetic parameters from this system, both internal and external mass transfer limitations must be considered. To determine the extent of external mass transfer limitations in our reaction system, a series of experiments were performed to compare the activity of the 30% silica-niobia catalyst for cellobiose hydrolysis at different flowrates and identical resident times. The 30% silica-niobia catalyst was used for these experiments because it was found to have the highest activity for cellobiose hydrolysis and thus would be the catalyst most susceptible to mass transfer limitations. Therefore, ensuring that our system is

not mass transfer limited under typical reaction conditions for the 30% silica niobia catalyst will allow us to assume that this is the case for all of our silica-niobia and ASA catalysts. For these experiments, typical two hour reactions were performed with a 1 wt% cellobiose feed at 200 °C with a 30% silica-niobia catalyst bed of mass 50, 100, or 200 mg and cellobiose solution flowrate of 0.25, 0.5, or 1 mL/min, respectively. In each experiment, liquid samples were collected for a total time length necessary for 60 mL of feed solution to flow over the catalyst bed. The cellobiose concentrations in the reaction products, as measured by HPLC, are presented in Figure 26. It can be seen that in the case of the lowest flowrate, 0.25 mL/min, the steady state cellobiose product concentration is around 27%. This is much higher than the values obtained for both the medium flowrate of 0.5 mL/min and the high flowrate of 1.0 mL/min. This is an indication that external mass transfer limitations are significant at this low flowrate. The steady state cellobiose concentrations in the product of the medium and high flowrate reactions are nearly identical, and therefore it is safe to say that external mass transfer limitations are not significant at these flowrates. This set of experiments has thus allowed us to verify that kinetic parameters obtained at flowrates of 0.5 mL/min and above are valid. Internal mass transfer limitations could be tested by varying catalyst particle size and comparing reactivity. Due to the extremely small particle size of less than 75 μm, internal mass transfer limitations have been assumed to be insignificant for this reactive system.

The cellobiose conversion data obtained for the mixed metal oxide catalysts in the previous experiments can be used to determine the apparent activation energies for cellobiose hydrolysis over each catalyst. An Arrhenius plot can be created utilizing the following equation:

$$\ln k\tau = -\frac{E_a}{RT} + \ln A\tau$$

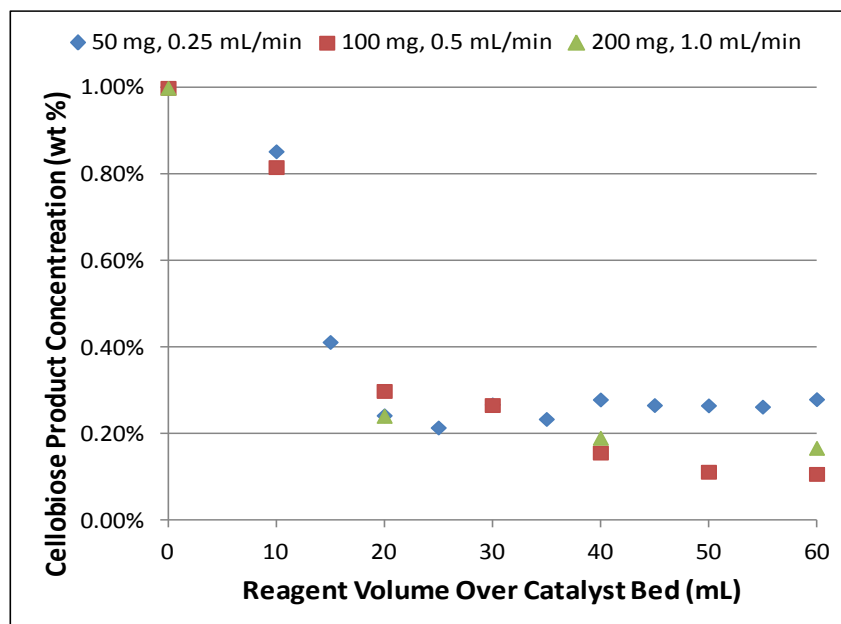


Figure 26: Cellobiose concentrations in hydrolysis reaction products over a 30% silica-niobia catalyst bed of various mass with a 1 wt% cellobiose reagent at various flowrates.

where k is the reaction rate constant, A the pre-exponential factor, E_a the apparent activation energy, R the gas constant, and T the reaction temperature. For reactions in a fixed bed reactor the term $k\tau$ is calculated using the final concentration of cellobiose in the reaction product by the following equation:

$$k\tau = \ln \frac{C_{A0}}{C_A}$$

where C_{A0} is the initial cellobiose concentration and C_A is the final cellobiose concentration. Using this method, Arrhenius plots have been prepared, (Figure 27) and apparent activation energies have been calculated (Table 5) for each catalyst. The activation energies as calculated in Table 2 lie within a range of 75 – 100 kJ/mol, similar to values reported for cellobiose hydrolysis mineral acids in previous literature.⁶⁵⁻⁶⁶ In general, ASA catalyst were found to have higher apparent activation energies for cellobiose hydrolysis than silica-niobia catalysts. Of the ASA catalysts, ASA(2) was found to have the lowest and ASA(5) was found to

have the highest apparent activation energy for cellobiose hydrolysis. The apparent activation energy for 30% silica-niobia was found to be slightly lower than that of 10% silica-niobia. It should be noted that only the cellobiose conversion data at 175 and 200 °C were used to determine the apparent activation energies for the silica-niobia catalysts due to the obvious deactivation that was observed over the course of the experiment.

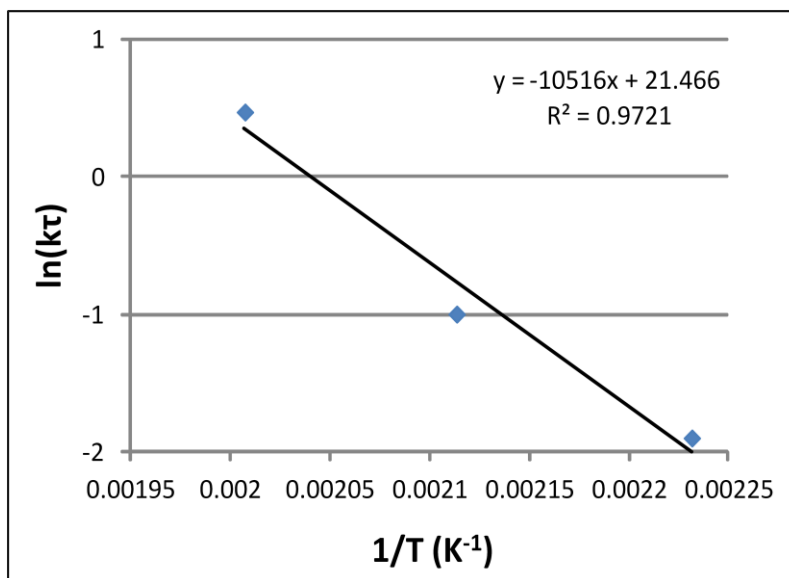


Figure 27: Arrhenius plot for conversion of 1% cellobiose solution to glucose in a fixed bed reactor over a 100 mg ASA(2) catalyst bed.

Table 5: Calculated apparent activation energies of tested catalysts for cellobiose hydrolysis.

Catalyst	E_A (kJ/mol)
ASA(2)	87.43
ASA(5)	98.28
ASA(10)	94.33
10% SN	81.55
30% SN	77.64

3.3.5 Reacidification of H₂SO₄-Modified Activated Carbon

While the activated carbon catalysts were found, in general, to result in only moderate cellobiose hydrolysis activity and glucose selectivity, it was desired to determine a method by which to produce an effective activated carbon catalyst for this cellobiose hydrolysis reaction. The stability study described in Chapter 2 provided some information on how that could be accomplished. As shown by Boehm titration in Figure 7 and XPS spectra in Figure 13, H₂SO₄-modified activated carbon retains around 30% of its highly acidic sulfonic acid groups even after prolonged exposure to a hot aqueous environment. This is an indication that this portion of sulfonic acid groups imparted upon acidification are stable under these conditions. In order to produce a stable, highly active catalyst it is thus desirable to increase the concentration of these stable sulfonic acid sites on the carbon. It was hypothesized that repeated cycles of acidification and hydrothermal treatment would result in an increase in stable sulfonic acid sites. In order to produce these carbons, it was desired to impart the maximum amount of sulfonic acid sites on the carbon surface, and thus the acidification conditions were changed slightly. The untreated activated carbon was crushed to a particle size of ~75 μm before use and the carbon was allowed to contact the boiling H₂SO₄ for 30 minutes instead of 10 minutes.

Boehm titrations were performed on this H₂SO₄-modified carbon as synthesized, after hydrothermal treatment, reacidification, and subsequent hydrothermal treatment (Figure 28). It was found that this modified synthesis method imparted slightly higher acid site concentrations on the carbon surface (compare with Figure 7). As expected, heat treatment in water dramatically decreased the sulfonic acid site concentration and slightly increased the basic site concentration on the carbon surface. Reacidification was found to return the surface chemistry of the activated carbon to a state nearly identical to that of the carbon before hydrothermal

treatment and additional thermal treatment was found to result in a carbon with a surface chemistry nearly identical to that before reacidification.

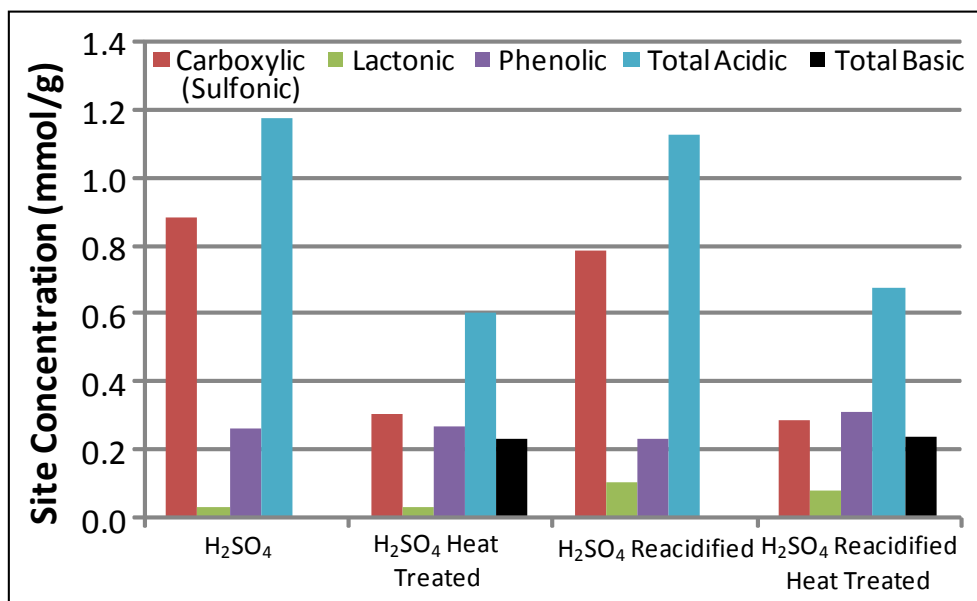


Figure 28: Acid site concentrations on activated carbons prepared from crushed carbon with a 30 minute H₂SO₄ exposure time, measured by Boehm titration.

While the acid site concentrations as measured by Boehm titration suggested that reacidification has a negligible effect on the surface chemistry of the carbon, reaction data suggests otherwise. Each of these carbons was test for cellobiose hydrolysis activity (Table 6 and Figure 29). It can be seen that the reacidification process has a significant effect on both the activity and selectivity of the H₂SO₄-modified carbon. Upon reacidification, the cellobiose conversion increased slightly and glucose selectivity increased to nearly 100%. This reacidified H₂SO₄-modified carbon thus represents the most effective catalyst found in this work for the cellobiose hydrolysis reaction. In addition to its high conversion and selectivity, this catalyst was found to be stable over the course of an 8 h reaction. This increase in activity, selectivity, and stability is remarkable, and cannot be explained with the acid site concentration measurements reported in Figure 28. Thus, additional work is required to determine how each of the synthesis

variables – carbon particle size, H₂SO₄ exposure time, and reacidification – affect the surface chemistry and reactivity of the activated carbon catalyst.

Table 6: Cellobiose hydrolysis results using H₂SO₄-modified carbon catalysts - 100 mg catalyst, 0.5 mL/min 1 wt% cellobiose, 200 °C.

Catalyst	Max Glucose Concentration	Cellobiose Conversion	Glucose Fractional Yield
Blank	0.24%	23.37%	102.51%
H ₂ SO ₄ AC	0.29%	48.85%	58.83%
H ₂ SO ₄ Heat Treated	0.27%	44.00%	61.36%
H ₂ SO ₄ Reacidified	0.50%	51.00%	98.04%
H ₂ SO ₄ Reacidified, Heat Treated	0.49%	69.00%	71.01%

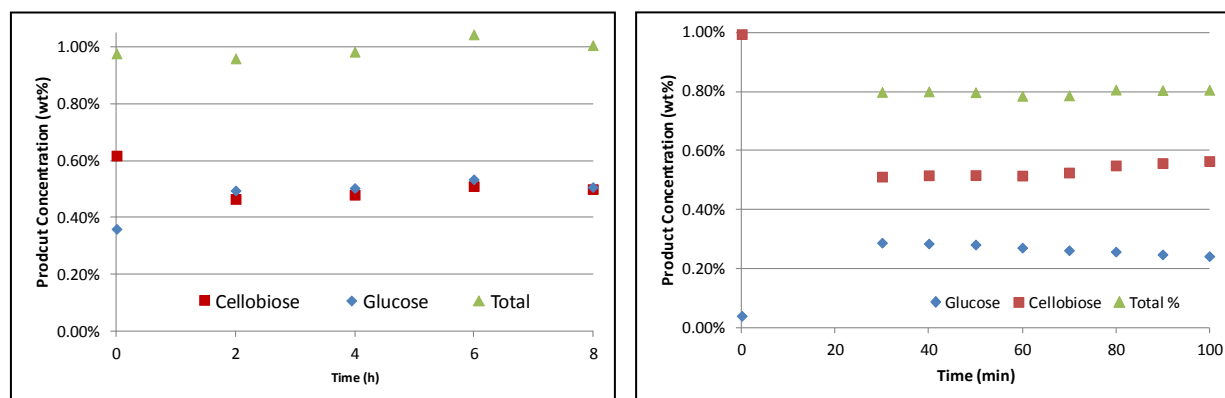


Figure 29: Cellobiose hydrolysis reaction results with “reacidified” H₂SO₄-modified carbon (left) and traditionally synthesized H₂SO₄-modified carbon (right) catalysts.

3.4 CONCLUSIONS

In this work, a large number of activated carbon, ASA, and silica niobia catalysts were synthesized. These catalysts were characterized and their stability in the hot aqueous environments typical of biomass conversion reactions was assessed. ASAs were found to be stable in acidity whereas silica niobias were found to increase in acidity upon exposure to these conditions. Each of these catalysts was tested for cellobiose hydrolysis activity and glucose selectivity using a fixed bed flow reactor designed and built for this project. Acid-modification

procedures were found to increase the cellobiose conversion but decrease the glucose fractional yield of the carbons. ASAs showed fairly low conversion but high glucose selectivities, whereas silica niobias showed high conversions and low selectivities.

Activated carbon catalysts, with the exception of the H₂SO₄-modified carbon, and ASAs were found to be fairly stable over the course of two hour reactions. Silica niobias were found to increase in cellobiose conversion and decrease in glucose selectivity after prolonged reaction, and coking was found to be significant on a 30% silica niobia catalyst. The mixed metal oxide catalyst were tested for cellobiose hydrolysis at various temperatures and Arrhenius plots were prepared to determine effective activation energies for cellobiose hydrolysis. A reacidification procedure was performed on a H₂SO₄-modified activated carbon, resulting in significantly improved conversion, selectivity, and stability.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 ACTIVATED CARBON STABILITY

It is clear from this work that activated carbon stability in biomass conversion conditions is an important issue. The surface chemistry of the carbon was found to change significantly after short exposure to hot liquid water and thus as this class of catalyst becomes more popular for these types of reactions stability must be considered closely. There are many directions in which this project could continue, the most obvious of which revolve around using knowledge of activated carbon stability to enhance its properties for specific applications. An example of such work was presented in the 3rd chapter of this work, where information regarding the stability of imparted sulfonic acid groups on H₂SO₄-modified carbon was utilized to synthesize a highly active, selective, and stable catalyst for a highly relevant biomass hydrolysis reaction. Additionally, procedures such as this reacidification could be useful in the area of carbon supported metal catalysts. It has been shown extensively that the surface chemistry of the support activated carbon has a significant effect on the properties of metal particles deposited on it.⁶⁷⁻⁷² While much further research is required, the demonstrated ability to manipulate the surface chemistry of activated carbons in novel ways has the potential to enhance the properties of these metal supported catalysts.

4.2 OLIGOSACCHARIDE HYDROLYSIS

In this work, a series of initial mixed metal oxide and activated carbon catalysts were synthesized and tested for cellobiose hydrolysis activity. A reacidified H₂SO₄-modified activated carbon was found to be the most successful, possessing remarkable activity, selectivity, and stability. At the time, however, it is unclear why exactly that is the case and thus additional work

is required in the area to identify the catalytic properties that are responsible for these positive reactivity parameters. Knowledge in this area will allow for the directed and systematic development of even more effective biomass hydrolysis catalysts.

Much work still remains in order to develop a commercial catalyst with the ability to selectively hydrolyze oligosaccharide solutions resulting from the rapid hydrolysis of cellulose in supercritical water. A commercially viable catalyst must be able to withstand exposure to the impurities present in non-model oligosaccharide feedstocks generated by rapid cellulose hydrolysis in supercritical water. Previous literature indicates that there are a wide variety of impurities in these oligosaccharide solutions. Zhao et al. identified glyceraldehyde, erythrose, 1-6-anhydroglucose, dihydroxyacetone, and HMF in oligosaccharide solutions obtained by cellulose hydrolysis in 378-382 °C water for 15-18 seconds⁸. Sasaki et al. identified organic acids and pyruvaldehyde in addition to these species for a similar reaction⁷. Furfural was found to be present in the reaction product solution by Kumar et al. after the hydrolysis of microcrystalline cellulose in subcritical and supercritical water⁹. Additionally, it is reasonable to expect a variety of metal ions to be present in product solutions of the hydrolysis of non-model cellulosic biomass.

There is limited literature available on the effects of these types of products on cellulose or oligosaccharide hydrolysis and catalyst stability. Ravenelle et al. discovered recently that Pt/ γ -Al₂O₃ deactivation by boehmite formation occurs at much lower levels in hot aqueous sorbitol and glycerol solutions than in hot liquid water.⁷³ This increased stability was attributed to the formation of carbonaceous species on the catalyst surface which blocked the alumina hydroxyl groups which were found to be the point of attack for alumina hydration.¹⁷ While this carbon deposition was found to have a positive impact on Pt/ γ -Al₂O₃ stability, a similar process would likely be detrimental to a metal oxide's catalytic activity. These results indicate that

catalyst stability can be greatly affected by the presence of biomass molecules such as those present in cellulose hydrolysis product solutions. Additionally, metal ions have been shown to be slightly Lewis acidic in aqueous solutions,⁷⁴ and thus it is reasonable to believe that both metal ion and organic acid impurities would have a reactivity effect in oligosaccharide hydrolysis.

In order to ensure that a catalyst will be effective for industrial oligosaccharide hydrolysis reactions, it must be determined how each of the major feedstock impurities affects the catalyst's stability and reactivity. Systems must then be designed to mitigate the effects of major impurities found to deleteriously affect catalyst properties. Finally, this system must be tested for hydrolysis of non-model oligosaccharide feedstocks and implemented at an industrial scale.

REFERENCES

- 1) Biomass Research and Development Technical Advisory Committee, Roadmap for Biomass Technologies in the U.S., U.S. Government, **2002**.
[http://www.bioproducts-bioenergy.gov/pdfs/Final Biomass Roadmap.pdf](http://www.bioproducts-bioenergy.gov/pdfs/Final_Biomass_Roadmap.pdf).
- 2) Lee, A.; Owens, V.N.; Boe, A.; Jeranyama, P., Composition of Herbaceous Biomass Feedstocks, South Dakota State University, **2007**.
- 3) MacLellan, J., *MMG 445 Basic Biotech eJournal* **2010**, 3:3.
- 4) Sherrard, E. C.; Kressman, F. W. *Ind. Eng. Chem.* **1945**, 37, 5–8.
- 5) Faith, W. L. *Ind. Eng. Chem.* **1945**, 37, 9–11.
- 6) Suganuma, S.; Nakajima, K.; Kitano, M.; Yamaguchi, D.; Kato, H.; Hayashi, S.; Hara, M. *J. Am. Chem. Soc.*, **2008**, 130 (38), 12787-12793.
- 7) Sasaki, M.; Kabyemela, B.; Malaluan R.; Hirose, S.; Takeda, N.; Adschiri, T.; Arai, K. *Journal of Supercritical Fluids* **1998**, 13, 261-268.
- 8) Zhao, Y.; Lu, W.; Wang, H. *Chemical Engineering Journal* **2009**, 150, 411-417.
- 9) Kumar, S.; Gupta, R.B. *Ind. Eng. Chem. Res.* **2008**, 23, 9321-9329.
- 10) Guo, F.; Fang, Z. Charles Xu, C.; Smith Jr., R.L. *Process in Energy and Combustion Science* **2012**, 38, 672-690.
- 11) Gomes, H.T.; Miranda, S.M.; Sampaio, M.J.; Silva, A.M.T.; Faria, J.L. *Catalysis Today* **2010**, 151, 153-158.
- 12) Li, L.; Liu, S.; Liu, J. *Journal of Hazardous Materials* **2011**, 192, 683-690.
- 13) Noh, J.S.; Schwarz, J.A. *Carbon* **1990**, 28, 675-682.
- 14) Onda, A.; Ochi, T.; Yanagisawa, K. *Top Catal* **2009**, 52, 801-807.
- 15) Onda, A. *Journal of the Japan Petroleum Institute* **2012**, 55, 73-86.
- 16) Ravenelle, R.; Schubler, F.; D'Amico, A.; Danilina, N.; van Bokhaven, J.A.; Lercher, J.A.; Jones, C.W.; Sievers, C. *J. Phys. Chem. C* **2010**, 114, 19582-19595
- 17) Ravenelle, R.; Copeland, J.; Kim, W.; Crittenden, J.C.; Sievers, C. *ACS Catalysis* **2011**, 1, 552-561.
- 18) Ketchie, W.C.; Maris, E.P.; Davis, R.J. *Chem. Mater* **2007**, 19, 3406-3411.
- 19) Prado-Burguete, C.; Linares-Solano, A.; Rodriguez-Reinoso, F.; Salinas-Martinez de Lecea, C. *Journal of Catalysis* **1989**, 115, 98-106.
- 20) Li, H.; Xu, Y.; Gao, C; Zhao, Y. *Catalysis Today* **2010**, 158, 475-480.
- 21) Huang, C.; Li, H.; Chen, C. *Journal of Hazardous Materials* **2008**, 159, 523-527.
- 22) Zini G.; Marazzi, R.; Padrazzi, S.; Tartarini, P. *Int. J. Hydrogen Energy* **2010**, 35, 4909-4917.
- 23) Konsowa, A.H.; Ossman, M.E.; Chen, Y.; Crittenden, J.C. *Journal of Hazardous Materials* **2010**, 176, 181-185.
- 24) Foo, K.Y.; Hameed, B.H. *Journal of Hazardous Materials* **2010**, 175, 1-11.
- 25) Santiago, M.; Stuber, F.; Fortuny, A.; Fabregat, A.; Font, J. *Carbon* **2005**, 43, 2134-2145.

- 26) Gomes, H.T.; Miranda, S.M.; Sampaio, M.J.; Figueiredo, J.L.; Silva, A.M.T.; Faria, J.L. *Applied Catalysis B: Environmental* **2011**, *106*, 390-397.
- 27) Soria-Sanchez, M.; Maroto-Valiente, A.; Guerrero-Ruiz, A.; Nevskaja, D.M. *Journal of Colloid and Interface Science* **2010**, *343*, 194-199.
- 28) Moreno-Castilla, C.; Lopez-Ramon, M.V.; Carrasco-Marin, F. *Carbon* **2000**, *38*, 1995-2001.
- 29) Yang, Y.; Chiang, K.; Burke, N. *Catalysis Today* **2011**, *178*, 197-205.
- 30) Boehm, H.P. *Carbon* **1994**, *32*, 759-769.
- 31) Voll, M.; Boehm, H.P. *Carbon* **1971**, *9*, 481-488.
- 32) Leon y Leon, C.A.; Solar, J.M.; Calemma, V.; Radovic, L.R. *Carbon* **1992**, *30*, 797-811.
- 33) Goertzen, S.L.; Theriault, K.D.; Oickle, A.M.; Tarasuk, A.C.; Andreas, H.A. *Carbon* **2010**, *48*, 1252-1261.
- 34) Oickle, A.M.; Goertzen, S.L.; Hopper, K.R.; Abdalla, Y.O.; Andreas, H.A. *Carbon* **2010**, *48*, 3313-3322.
- 35) Terzyk, A.P. *Journal of Colloid and Interface Science* **2003**, *268*, 301-329.
- 36) Polovina, M.; Babic, B.; Kaluderovic, B.; Dekanski, A. *Carbon* **1997**, *35*, 1047-1052.
- 37) Bouchenafa-Saib, N.; Grange, P.; Verhasselt, P.; Addoun, F.; Dubois, V. *Applied Catalysis A: General* **2005**, *286*, 167-174.
- 38) Li, N.; Ma, X.; Zha, Q.; Kim, K.; Chen, Y.; Song, C. *Carbon* **2011**, *49*, 5002-5013.
- 39) Pigamo, A.; Besson, M.; Blanc, B.; Gallezot, P.; Blackburn, A.; Kozynchenko, O.; Tennison, S.; Crezee, E.; Kapteijn, F. *Carbon* **2002**, *40*, 1267-1278.
- 40) Guo, Y.; Want, S.; Gong, Y.; Xu, D.; Tang, X.; Ma, H. *Journal of Hazardous Materials* **2010**, *180*, 137-144.
- 41) Gomez-Serrano, V. Gonzalez-Garcia, C.M., Gonzalez-Martin, M.L. *Powder Technology* **2001**, *116*, 103-108.
- 42) Terzyk, A.P. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2001**, *177*, 23-45.
- 43) Osada, M.; Sato, O.; Arai, K. Shirai, M. *Energy and Fuels* **2006**, *20*, 2337-2343.
- 44) Cordero, T.; Rodriguez-Mirasol, J.; Bedia, J.; Gomis, S.; Yustos, P.; Garcia-Ochoa, F.; Santos, A. *Applied Catalysis B: Environmental* **2008**, *81*, 122-131.
- 45) Matsumura, Y. *Atmospheric Environment* **1974**, *8*, 1321-1327.
- 46) Evdokimo, D.Y.; Kogan, E.A.; Sheikina, Z.P. *Zhurnal Prikladnoi Khimii*. **1973**, *46*, 1409-1413.
- 47) Monser, L.; Adhoum, N. *Separation and Purification Technology* **2002**, *26*, 137-146.
- 48) Jiang, Z.; Liu, Y. Sun, X.; Tian, F.; Sun, F.; Liang, C.; You, W.; Han, C.; Li, C. *Langmuir* **2003**, *19*, 731-736.
- 49) Gomes, H.T.; Miranda, S.M.; Sampaio, M.J.; Figueiredo, J.L.; Silva, A.M.T.; Faria, J.L. *Applied Catalysis B: Environmental* **2011**, *106*, 390-397.
- 50) Swiatkowski, A.; Pakula, M.; Biniak, S.; Walczyk, M. *Carbon* **2004**, *42*, 3057-3069.
- 51) Chen, J.; Yang, G.; Li, W.; Sun, J. *Russian Journal of Electrochemistry* **2009**, *45*, 908-912.
- 52) Pels, J.R.; Kapteijn, F.; Moulijn, J.A.; Zhu, Q.; Thomas, K.M. *Carbon* **33**, **1995**, 1641-1653.

- 53) de la Puente, G.; Menendez, J.A.; Grange, P. *Journal of Analytical and Applied Pyrolysis* **1997**, 43, 125-138.
- 54) Davda, R.R.; Dumesic, J.A. *Chem. Commun.* **2004**, 36-37.
- 55) Huber, G.W.; Chheda, J.N.; Barrett, C.J.; Dumesic, J.A. *Science* **2005**, 308, 1446-1450.
- 56) Alvira, P.; Tomas-Pejo, E.; Ballesteros, M.; Negro, M.J. *Bioresource Technology* **2010**, 101, 4851-4861.
- 57) Hirata, M.; Gao, M.; Toorisaka, E.; Takanashi, H.; Hano, T. *Biochemical Engineering Journal* **2005**, 25, 159-163.
- 58) Bootsma, J.A.; Entorf, M.; Eder, J.; Shanks, B.H. *Bioresource Technology* **2008**, 99, 5226-5231.
- 59) Kim, Y.; Hendrickson, R.; Mosier, N.; Ladisch, M.R. *Energy & Fuels* **2005**, 19, 2189-2200.
- 60) Marzo, M.; Gervasini, A.; Carniti, P. *Carbohydrate Research* **2012**, 347, 23-31.
- 61) Xu, B.; Sievers, C.; Lercher, J.A.; Rob van Veen, J.A.; Giltay, P.; Prins, R.; van Bokhoven, J. *J. Phys. Chem.* **2007**, 111, 12075-12079
- 62) Carniti, P.; Gervasini, A.; Marzo, M. *J. Phys. Chem.* **2008**, 112, 14064-14074.
- 63) Marasinghe, P.A.B.; Mollerud, K.J.; Carlson, B.D. *Microchemical Journal* **1996**, 53, 225-229.
- 64) Hahn, M.W.; Copeland, J.R.; Van Pelt, A.H.; Sievers, C. *Manuscript in preparation*.
- 65) Bootsma, J.A.; Shanks, B.H. *Applied Catalysis A: General* **2007**, 327, 44-51.
- 66) Mosier, N.S.; Ladisch C.M.; Ladisch, M.R. *Biotechnology and Bioengineering* **2002**, 79, 610-618.
- 67) Du, J.; Song, C.; Zhao, J.; Zhu, Z. *Applied Surface Science* **2008**, 255, 2989-2993.
- 68) Kholodovich, A.N.; Simonov, P.A.; Kvon, R.I.; Vukhtiyarov, A.V.; Zaikovskii, V.I.; Chesalov, Y.A.; Romanenko, A.V. *Kinetika i Kataliz* **2008**, 49, 936-943.
- 69) Radkevich, V.Z.; Senko, T.L.; Wilson, K.; Grishenko, L.M.; Zaderko, A.N.; Diyuk, V.Y. *Applied Catalysis A: General* **2008**, 335, 241-251.
- 70) Salgado, J.R.C.; Quintana, J.J.; Calvillo, L.; Lazaro, M.J.; Cabot, P.L.; Esparbe, I.; Pastor, E. *Physical Chemistry Chemical Physics* **2008**, 10, 6796-6806.
- 71) Yu, X.; Ye, S. *J. Power Sources* **2007**, 172, 133-144.
- 72) Jia, R.; Wang, C.Y.; Way, S. *J. Mater. Sci.* **2006**, 41, 6881-6888.
- 73) Ravenelle, R.M.; Copeland, J.R.; Van Pelt, A.H.; Crittenden, J.C.; Sievers, C. *Top. Catal.* **2012**, 55, 162-174.
- 74) Richens, D.T. *The Chemistry of Aqua Ions: Synthesis, Structure, and Reactivity*, Wiley, **1997**.