

**THE SELECTIVE SYNTHESIS OF AROMATICS AND FURANS FROM
BIOMASS-DERIVED COMPOUNDS**

by

Eyas Mahmoud

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

Summer 2016

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BIOMASS-DERIVED COMPOUNDS**

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ACKNOWLEDGEMENTS

I would like to thank the Department of Chemical and Biomolecular Engineering at the University of Delaware for accepting me into the program and giving me the opportunity to pursue my doctorate. I acknowledge my advisor, Professor Raul F. Lobo, for providing me with access to research equipment and the opportunity to publish my research. I would also like to thank my thesis committee members: Professors Donald Watson, Dionisios G. Vlachos, and Paul Dauenhauer for reviewing my dissertation.

The research presented in this thesis was funded by the U.S. Department of Energy under a grant given to the Catalysis Center for Energy Innovation (CCEI), an Energy Frontier Research Center. The National Science Foundation (NSF) provided funding for a graduate student fellowship.

TABLE OF CONTENTS

LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF SCHEMES	xvii
ABSTRACT	xviii

Chapter

1	INTRODUCTION AND BACKGROUND.....	1
1.1	Background and Motivation.....	1
1.2	Renewable Synthesis of Aromatics and Furans.....	2
1.3	Catalysis.....	6
1.4	Zeolites.....	8
1.5	Nuclear Magnetic Resonance Spectroscopy (NMR).....	10
1.6	Factorial Design and ANOVA.....	15
1.7	Overview of Thesis.....	20
	REFERENCES.....	23
2	EXPERIMENTAL METHODS.....	26
2.1	Overview... ..	26
2.2	Zeolite Synthesis and Ion Exchange.....	27
2.2.1	Hydrothermal Synthesis.....	27
2.2.2	Ion Exchange.....	30
2.2.3	Solid-State Ion Exchange.....	31
2.3	Materials Characterization.....	31
2.3.1	Powder X-Ray Diffraction (XRD).....	31
2.3.2	N ₂ adsorption Isotherm Measurements.....	34
2.3.3	Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).....	37
2.3.4	Inductively Coupled Plasma Analysis (ICP).....	38
2.3.5	Ultraviolet-Visible Optical Spectroscopy (UV-Vis).....	39
2.3.6	Fourier Transform Infrared Spectroscopy (FTIR).....	40
2.3.7	Temperature Programmed Desorption Thermogravimetric Analysis (TPD-TGA).....	41
2.3.8	Solid-State Nuclear Magnetic Resonance (SSNMR).....	43

2.4	Reaction Product Characterization.....	45
2.4.1	Gas Chromatography (GC).....	45
2.4.2	Mass Spectroscopy (MS).....	46
2.4.3	High-Performance Liquid Chromatography (HPLC).....	46
2.4.4	Nuclear Magnetic Resonance (NMR) Spectroscopy.....	47
2.4.5	Organic Elemental Analysis.....	47
2.4.6	Reaction Procedure.....	48
2.5	Summary.....	48
REFERENCES.....		50
3	RENEWABLE PRODUCTION OF PHTHALIC ANHYDRIDE FROM BIOMASS-DERIVED FURAN AND MALEIC ANHYDRIDE.....	52
3.1	Introduction.....	52
3.2	Experimental Methods.....	56
3.2.1	Diels-Alder Reactions.....	56
3.2.2	Dehydration Reaction.....	59
3.2.3	Polymer Separation.....	61
3.2.4	Analytical NMR Experiments.....	62
3.2.5	Attenuated Total Reflectance (ATR) Infrared Spectroscopy (IR)	62
3.2.6	Elemental Analysis.....	63
3.2.7	Karl-Fischer Titration.....	63
3.3	Results and Discussion	63
3.3.1	Diels-Alder Reaction of Furan and Maleic Anhydride	63
3.3.2	Dehydration of exo-4,10-dioxa-tricyclo[5.5.2.1.0]dec-8-ene- 3,5-dione.....	66
3.3.2.1	Mixed-Sulfonic Carboxylic Anhydrides.....	70
3.4	Conclusions.....	76
REFERENCES.....		78

4	DIELS-ALDER AND DEHYDRATION REACTIONS OF BIOMASS-DERIVED FURAN AND ACRYLIC ACID FOR THE SYNTHESIS OF BENZOIC ACID.....	82
4.1	Introduction.....	82
4.2	Experimental Methods.....	87
4.2.1	Materials Synthesis.....	87
4.2.2	Analytical Methods.....	89
4.2.3	Diels-Alder Reactions.....	89
4.2.4	Dehydration Reaction.....	92
4.2.5	TPD-TGA.....	93
4.2.6	UV-Vis Spectroscopy.....	94
4.2.7	FTIR Spectroscopy.....	94
4.2.8	Elemental Analysis.....	94
4.2.9	²⁹ Si NMR Spectroscopy.....	94
4.3	Results and Discussion.....	95
4.3.1	Materials Characterization.....	95
4.3.2	Sequential Diels-Alder-Dehydration Reaction of Furan and Methyl Acrylate.....	101
4.3.3	Diels-Alder- Reaction.....	102
4.3.4	Dehydration of the Diels-Alder Adduct.....	112
4.4	Conclusions.....	116
	REFERENCES.....	118
5	THE SOLVENT-FREE SYNTHESIS OF P-XYLENE FROM 2,5-DIMETHYLFURAN AND ETHYLENE CATALYZED BY METAL-EXCHANGED FAUJASITE ZEOLITES.....	122
5.1	Introduction	122
5.2	Experimental Methods.....	127
5.2.1	Catalyst Preparation and Characterization.....	127
5.2.2	Reaction Experiments.....	129
5.2.3	Statistical Analysis of Reaction Results: ANOVA.....	130
5.3	Results and Discussion.....	131
5.4	Conclusions	142

REFERENCES.....	144
 6 FURANS SYNTHESIS FROM GLUCOSE IN ALCOHOLIC SOLVENTS CATALYZED BY LEWIS ACIDIC BETA ZEOLITES.....	 147
6.1 Introduction	147
6.2 Experimental Methods.....	152
6.2.1 Catalyst Synthesis.....	152
6.2.2 Catalyst Characterization.....	153
6.2.3 Reaction Experiments.....	154
 6.3 Results and Discussion.....	 155
6.4 Conclusions.....	164
REFERENCES.....	165
 7 CONCLUSIONS AND RECOMMENDATIONS.....	 169
7.1 Overview.....	169
7.2 Dissertation Summary.....	171
7.3 Recommendations for Future Studies.....	180
7.3.1 Dehydration of Diels-Alder Reaction Products of Furans.....	181
7.3.2 Lewis Acid Catalysts for Diels-Alder Reaction of Furans....	183
7.3.3 Synthesis of Other Aromatic Molecules from Lignocellulosic Biomass.....	185
7.3.4 Lewis Acid Catalysts for Renewable <i>p</i> -Xylene Synthesis.....	186
7.4 Dissertation Accomplishments.....	186
REFERENCES.....	188

Appendix

A	NMR CHARACTERIZATION OF REACTION INTERMEDIATES AND ANALYSIS OF DIELS-ALDER REACTION FOR RENEWABLE PHTHALIC ANHYDRIDE PRODUCTION	191
B	CATALYST CHARACTERIZATION AND KINETIC ANALYSIS FOR BENZOIC ACID SYNTHESIS.....	203
C	STATISTICS OF P-XYLENE SYNTHESIS.....	223
D	ADDITIONAL REACTIONS FOR FURANICS SYNTHESIS FROM GLUCOSE IN ALCOHOLIC SOLVENTS CATALYZED BY LEWIS ACIDIC BETA ZEOLITES.....	225
E	REPRINT PERMISSION LETTERS.....	228

LIST OF TABLES

Table 1.1: ^1H NMR coupling constants of selected functional groups.....	13
Table 1.2: Two-Factor ANOVA table.....	18
Table 3.1: Selectivity of Diels Alder reaction of furan (0.69 moles) and maleic anhydride (0.69 moles) to oxanorbornene (3) after 1 h of reaction.....	66
Table 3.2: Selectivity of the dehydration of substituted oxanorbornenes in neat MSA at 25 °C after 3 h.....	68
Table 3.3: Selectivity to phthalic anhydride.....	73
Table 4.1: Yield and Turnover Frequency of the Diels-Alder Reaction of Various Furans and Acrylic Acid Catalyzed by Lewis Acidic Beta and other Materials.....	107
Table 4.2: Yield and Turnover Frequency of the Diels-Alder Reaction of Various Furans and Acrylates Catalyzed by Hf-Beta Zeolite.....	111
Table 4.3: Selectivity of the Dehydration of Oxanorbornene Carboxylic Methyl Ester in Binary Mixtures of MSA and Acetic Anhydride.....	114
Table 5.1: Chemical composition and pore volume of metal-exchanged faujasite catalysts.....	134
Table 5.2: DMF conversion and p-xylene selectivity of metal-exchanged faujasites and HY zeolite for the solvent-free reaction of DMF with ethylene run at 220 °C for 6 h.....	136
Table 5.3: Selectivity and conversion for the solvent-free Diels-Alder cycloaddition and dehydration reactions of DMF and ethylene run at 250 °C for 24 h.....	143
Table 6.1: Textural properties of zeolite BEA samples.....	158
Table 6.2: Glucose, mannose, fructose, and glycoside conversion vs. HMF and IMF selectivity. Reactions were run at 110 °C with 0.02 g of Amberlyst 70 at a 150:1 molar ratio of glucose to Lewis acid in a 1	

7.5 wt.% solution of water in isopropanol.....	163
Table 6.3: Glucose, mannose, fructose, and glycoside conversion vs. HMF and IMF selectivity at 110 °C with 0.02 g of Brønsted acid catalyst and Sn-BEA catalyst (150:1 molar ratio of glucose to Sn) in a 7.5 wt.% solution of water in isopropanol.....	164
Table B1: Textural properties of catalyst samples.....	205
Table C1: TOF of <i>p</i> -xylene production rate for a two factors experiment (cation type levels 1: Na ⁺ , 2: Ag ⁺ , 3: Li ⁺ and framework type levels; 1: X and 2: Y) run with two replicates. Y zeolites have a silicon to aluminum ratio of 2.55 and X zeolites have a silicon to aluminum ratio of 1.25.....	224

LIST OF FIGURES

Figure 1.1: Schematic representing the principles underlying catalysis.....	7
Figure 1.2: Structure of zeolite Beta.....	9
Figure 1.3: Structure of faujasite zeolite.....	10
Figure 1.4: ^1H NMR chemical shift values of common functional groups.....	11
Figure 1.5: ^{13}C NMR chemical shifts of various functional groups.....	14
Figure 1.6: Example of a ^1H - ^1H NMR COSY spectrum.....	15
Figure 2.1: Schematic of a typical X-ray diffraction experiment.....	32
Figure 2.2: Examples of some adsorption isotherms for different classes of materials.....	34
Figure 3.1: Time evolution of phthalic anhydride (4) and intermediate (12) selectivity.....	71
Figure 3.2: Proposed reaction mechanism for the dehydration of the Diels-Alder product.....	74
Figure 3.3: Yield of phthalic anhydride as a function of the molar ratio of acetic anhydride and MSA.....	76
Figure 4.1: Conversion of benzoic acid to nylon 6, polycarbonates, phenolic resins, and epoxy resins.....	84
Figure 4.2: Characterization of zeolite Beta samples by (a) SEM, (b) FTIR and (c) TPD-TGA.....	98
Figure 4.3: Proposed reaction mechanism for the dehydration of oxanorbornene carboxylic methyl ester.....	115
Figure 5.1: Structure of faujasite zeolite, which consists of six-membered double rings (d6R) and sodalite cages.....	125
Figure 5.2: Powder XRD patterns of hydrated commercial or ion exchanged faujasite catalysts with silicon to aluminum ratios of 2.55.....	131

Figure 5.3: SEM images of faujasite zeolites.....	133
Figure 5.4: Effect of carbonate treatment on DMF conversion and p-xylene yield for the solvent-free reaction of DMF and ethylene catalyzed by NaX and LiX zeolites (Si/Al=1.25) at 47 bar of ethylene at 25 °C and 250 °C in the dehydration limited regime.....	135
Figure 5.5: Effect of the silicon to aluminum ratio of Na ⁺ , Li ⁺ , K ⁺ , Ag ⁺ , and Cu ⁺ ion-exchanged faujasites vs. the rate of p-xylene synthesis for the reaction of DMF with ethylene (76 bar) run at 220 °C for 6 h. Reactions were run at <15 % conversion of DMF under conditions in which the overall rate of p-xylene production was limited by the rate of the dehydration of the Diels-Alder adduct.....	141
Figure 5.6: TOFs for p-xylene production versus Na ⁺ , Li ⁺ , K ⁺ , Ag ⁺ , and Cu ⁺ ion-exchanged faujasites for the reaction of DMF with ethylene (76 bar) run at 220 °C for 6 h. TOFs were calculated at <15 % conversion of DMF under conditions in which the overall rate of p-xylene production was limited by the rate of the dehydration of the Diel-Alder adduct.....	142
Figure 6.1: Powder X-ray diffraction patterns of Si-BEA, Zr-BEA (Si/Zr=325), Sn-BEA (Si/Sn=230), and Hf-BEA (Si/Hf=219) zeolite.....	157
Figure 6.2: Powder X-ray diffraction pattern of Sn-MCM-41 (Si/Sn=50)...	158
Figure 6.3: SEM images of synthesized Sn-,Zr-, and Hf-BEA zeolites.....	159
Figure 6.4: Conversion of glucose to HMF or EMF in ethanol at different weight fractions of water.....	161
Figure 6.5: Conversion of glucose to HMF or IMF in isopropanol containing 7.5 wt.% water as a co-solvent as a function of time.....	162
Figure 7.1: SEM of ZrO ₂	185
Figure A1: NMR spectra of the reaction intermediate, (rac) (3aS,4S,5S,7aS)-1,3-dioxo-1,3,3a,4,5,7a-hexahydroisobenzofuran-4,5-diyl diacetate in CDCl ₃	196
Figure A2: (a) Temperature of the Diels-Alder reaction of furan and maleic anhydride as a function of time under solvent-free conditions (SFC)	

(b) Pressure of the Diels-Alder reaction of furan and maleic anhydride as a function of time under SFC.....	197
Figure A3: (a) Van't Hoff plot of the equilibrium constant of the Diels-Alder reaction of furan and maleic anhydride vs. $1/T$ (b) Plot of the equilibrium constant of the Diels-Alder reaction of furan and maleic anhydride in the forward direction vs. Temperature.....	198
Figure A4: Temperature of the Diels-Alder reaction of furan and maleic anhydride as a function of time under pseudo-adiabatic conditions.....	199
Figure A5: Partial pressure of furan at different temperatures in the presence and absence of water.....	201
Figure A6: ATR-IR Spectrum of the oxanorbornene polymer and furan polymer prepared by reaction at 298 K for 3 hrs followed by precipitation and washing with ice-cold water.....	202
Figure A7: Concentration of acetyl methanesulfonate as a function of the molar ratio of MSA/acetic anhydride (total solution volume kept constant at 5 mL) following 5 minutes of reaction.....	203
Figure B1: Powder X-ray diffraction patterns of Si-Beta, Zr-Beta (Si/Zr=325), Sn-Beta (Si/Sn=230), Hf-Beta (Si/Hf=219), and EF-Hf-Beta (Si/Hf=200) zeolites.....	204
Figure B2: Powder X-ray diffraction pattern of Sn-MCM-41 (Si/Sn=50)....	205
Figure B3: Nitrogen adsorption-desorption isotherm of Sn-MCM-41.....	206
Figure B4: ^{29}Si MAS NMR spectra of Hf, Sn, Zr and Si-Beta zeolites.....	206
Figure B5: Reflectance UV-Vis spectra of Si, Hf, EF-Hf, EF-Zr, and EF-Sn-Beta.....	207
Figure B6: FTIR spectra of acetonitrile- d_3 on EF-M-Beta.....	208
Figure B7: TPD-TGA of diethyl ether dosed onto EF-M-Beta samples.....	209
Figure B8: Van't Hoff plot for the Diels-Alder reaction of furan and methyl acrylate.....	210

Figure B9: Calculated equilibrium conversion for the Diels-Alder reaction of furan and methyl acrylate.....	211
Figure B10: Effect of catalyst amount on μmol product produced per hour.	213
Figure B11: ^1H - ^{29}Si CP-MAS NMR spectra of zeolites.....	214
Figure B12: Arrhenius plot for the reaction of furan and methyl acrylate..	214
Figure B13: Hf-Beta catalyst reusability and regeneration.....	218
Figure B14: 2D NMR COSY of dehydration intermediate.....	219
Figure B15: 2D NMR HMQC of dehydration intermediate.....	220
Figure C1: Main effects plot for the TOF of <i>p</i> -xylene production.....	225
Figure C2: Yield profile for <i>p</i> -xylene production for the solvent-free reaction of DMF and ethylene at 250 °C catalyzed by NaX zeolite.....	225
Figure D1: Glucose isomerization experiments run with Sn-beta or Sn-MCM-41.....	226
Figure D2: Glucose conversion to EMF using Sn-MCM-41 and amberlyst 15 in ethanol at 90 °C.....	227
Figure D3: Glucose conversion to EMF using Sn-MCM-41 and amberlyst 15 in ethanol at 70 °C.....	228

LIST OF SCHEMES

Scheme 1.1: Conversion of hemicellulose to furan.....	4
Scheme 2.1: Hydrolysis and crystallization of high silica zeolites using a fluoride method.....	29
Scheme 3.1: Route to renewable phthalic anhydride from biomass-derived furan and maleic anhydride.....	54
Scheme 3.2: Reaction network for the production of phthalic anhydride.....	67
Scheme 3.3: Formation of mixed sulfonic-carboxylic anhydride from MSA and acetic anhydride.....	70
Scheme 3.4: Proposed reaction mechanism for the dehydration of the Diels- Alder product.....	74
Scheme 4.1: Reaction sequence for the conversion of furan to methyl benzoate	85
Scheme 4.2: Formation of mixed sulfonic-carboxylic anhydride from MSA and acetic anhydride.....	87
Scheme 5.1: Synthesis of <i>p</i> -xylene from DMF and ethylene.....	123
Scheme 6.1: Synthesis of <i>p</i> -xylene from DMF and ethylene.....	151

ABSTRACT

Chemicals provide most of the material and energy for mankind. A majority of chemicals are produced from petroleum. The field of biomass conversion seeks to develop sustainable routes to chemicals. The commercialization of these routes improves the sustainability of the chemical industry and decreases price fluctuations. In addition, the use of biomass-derived feedstocks for chemicals and fuels production could decrease global annual CO₂ emissions. This thesis presents processes for the production of two classes of chemicals: aromatics and furans.

The economics, practicality, feedstock availability, feedstock abundance, and environmental impact of the process were considered in the lab-scale design to convert the biomass-derived molecules to chemicals. An iterative design methodology was used that begins with a low level of detail and progressively creates more and more detail. During design development, the economic viability of the scaled-up process was considered. Lignocellulosic biomass was the chosen feedstock for chemicals production because of its abundance, its high rate of production, and because it is not consumed as a food supply.

The synthesis of aromatics and furans depends on catalysts to convert biomass-derived molecules to the desired products. Catalysts materials used affected the rate of chemical reaction without being consumed by the reaction. In this thesis, zeolites Beta and faujasite, microporous molecular sieves, were the class of materials most often

used to catalyze these reactions. Some dehydration reactions were performed homogeneously.

A route for the production of phthalic anhydride from lignocellulosic biomass is described which uses the furfural-derived molecules. Furfural production was commercialized in the early 1900's and it is produced at the rate of 300,000 tons per year from biomass. Furan and maleic anhydride were converted in a two-step reaction protocol of Diels-Alder followed by dehydration reactions to phthalic anhydride. A 96% yield to the Diels-Alder product, *exo*-4,10-dioxo-tricyclo[5.2.1.0]dec-8-ene-3,5-dione, was obtained after 4 h of reaction in a batch reactor initially at 25 °C. The adiabatic temperature rise, ΔT_{ad} , was calculated to be about 150 °C. The reduction of the equilibrium constant at high temperatures prevents thermal runaway. The solvent-free reaction allows for the production of the Diels-Alder product at the hundreds of thousands of tons per year scale.

An important process discovery which is discussed in this thesis is the dehydration reaction of the Diels-Alder products of furans, or oxanorbornene molecules necessary for production of aromatics. The homogeneous dehydration reaction of the Diels-Alder product of furan and maleic anhydride, *exo*-4,10-dioxo-tricyclo[5.2.1.0]dec-8-ene-3,5-dione, yields only a 14% selectivity to phthalic anhydride at 100% conversion after 3 h of reaction in methanesulfonic acid (MSA). Nuclear magnetic resonance (NMR) experiments were used to show that the main side reaction channels for the dehydration of oxanorbornene molecules are retro-Diels-Alder and polymerization

reactions. Dehydration reactions run in a binary mixture of MSA and acetic anhydride afforded an 87% selectivity to the aromatic products phthalic anhydride and acid at 100% conversion. MSA and acetic anhydride react at 25 °C to form acetyl methanesulfonate, a strong acylating agent. In the presence of this acylating agent and acetic anhydride, it was discovered that the reaction mechanism proceeded through a different pathway when using the binary mixture of MSA and acetic anhydride as the dehydration medium as compared to reactions run in neat MSA. Following reaction, the aromatic products can be efficiently extracted using toluene as the organic phase. A technoeconomic analysis of the process demonstrated that the renewable phthalic anhydride production is cost-competitive with the synthetic route. This new chemistry can contribute to the resolution of emerging challenges in biomass conversion.

A route for the production of benzoic acid from lignocellulosic biomass is described. Benzoic acid can be industrially transformed to many consumer polymers such as nylon-6, epoxy resins, phenolic resins, and carbonates. Furan and methyl acrylate or acrylic acid were converted by Diels-Alder followed by dehydration reactions to methyl benzoate or benzoic acid. Diels-Alder reactions of furan and methyl acrylate or acrylic acid run at 25 °C yielded no detectable amounts of Diels-Alder product after 24 h of reaction. Hf-, Zr-, and Sn-containing zeolite Beta were found to provide around a 50% yield of the Diels-Alder product of furan and acrylic acid and 25% yield of the Diels-Alder product of furan and methyl acrylate after 24 h

of reaction at 25 °C, with no detected side products. The TOFs of these catalysts are one hundred times those of previously reported catalyst for this reaction.

The Diels-Alder product was dehydrated with a 96% selectivity to methyl benzoate at 100% conversion in the binary mixture for the reaction run at 25 °C for 2 h followed by a temperature increase to 80 °C for 1 h at an endo:exo ratio of 0.43. Increasing the concentration of the reactant from 0.13 to 0.65 M at the same endo:exo ratio decreased methyl benzoate selectivity from 96 to 83% at 100% conversion. Because two stereoisomers are formed after the Diels-Alder reaction, the effect of the stereochemical composition of the reactant on the selectivity was studied. Increasing the endo:exo ratio from 0.43 to 1.89 at a 0.65 M concentration of reactant led to a 89% selectivity to methyl benzoate at 100% conversion. This indicated that a change in the stereochemical composition of the reactant does not significantly affect reaction selectivity to the aromatic product. Reactions run in neat MSA resulted in a 1.7% selectivity to methyl benzoate at 100% conversion. Running the reaction using oxanorbornene carboxylic acid, the Diels-Alder adduct of furan and acrylic acid as the reactant, led to a drop in the selectivity of aromatics from 96% to 43% at 100% conversion under identical conditions of temperature, concentration and time. The process discussed for benzoic acid synthesis is a selective pathway for the production of benzene derived polymers from molecules obtained in high yield from lignocellulosic biomass.

For the solvent-free synthesis of *p*-xylene, metal-exchanged faujasite zeolites were used. Metal-exchanged faujasites are solid Lewis acids that can catalyze both Diels-Alder and dehydration reactions. It was found that at 250 °C, NaX catalyzes *p*-xylene synthesis with 96% selectivity at 10% DMF conversion. High selectivity to *p*-xylene (> 90%) is maintained at conversions greater than 30%. This result is a major improvement over the 35% selectivity to *p*-xylene obtained for HY zeolite. The experimental results indicate that the increase in *p*-xylene selectivity associated with Lewis acidic faujasite catalyst is due to a combination of the effects of Lewis acid type, strength, and extraframework position in the faujasite framework.

An investigation of the conversion of glucose to 5-(hydroxymethyl)furfural (HMF) was performed catalyzed by heterogeneous Lewis and Brønsted acid combinations. The addition of small weight percent of water (7.5%) increased the selectivity of the glucose isomerization reaction. It was found that glucose can be converted to furans (HMF and IMF) with a selectivity of 88% at 60% glucose conversion using mixtures of Sn-Beta zeolite (Lewis acid) and Amberlyst 15 (Brønsted acid) catalysts in isopropanol. The cascade reaction was run in ethanol and isopropanol using any of the materials: Sn-MCM-41, Sn-Beta, Hf-Beta, and Zr-Beta and polymeric Brønsted acid catalysts. At larger conversion (97%), selectivity to furans decreased to 39% due to humin formation. Increasing the temperature of reaction from 120 to 140 °C in a solution of 7.5 wt. % water in isopropanol increases glucose conversion from 52 to 63% and decreases the total carbon balance from 70 to 57% after 2 h of reaction. The

furans' selectivity also decreases from 43 to 32% when the reaction is catalyzed by Sn-Beta and Amberlyst 70.

Chapter 1

INTRODUCTION

1.1 Background and Motivation

This chapter provides background and motivation for the research presented in this thesis which focuses on biomass conversion. Chemicals production is critical in today's society and provides the material and energy to power today's world. The field of biomass conversion seeks to develop sustainable and economically competitive production routes to chemicals which are produced from petrochemicals. Two classes of chemicals discussed in this thesis are aromatics and furans. Aromatic chemicals are used for the manufacture of fibers and plastics in addition to being fuel additives. Furans, such as 5-(hydroxymethyl)furfural (HMF), are platform chemical intermediates in biorefineries used to synthesize fuels and chemicals. This thesis presents the development of lab scale processes for the conversion of lignocellulosic biomass-derived compounds to fuels and chemicals.

Lignocellulosic biomass is a promising feedstock for chemicals because of its abundance, its high rate of production, and because it is not consumed as a food supply. The synthesis and production of chemicals and fuels from biomass often depends on catalysts which help convert the starting biomass-derived molecules to the desired products. Catalysts are foreign materials which affect the rate of a chemical reaction without being consumed by the reaction. In the field of biomass conversion, side reactions, which are often prevalent, lead to undesired by-products which may

decrease the profitability of the process and increase separation costs. This makes the choice of catalyst material important. In this thesis, zeolites are the class of materials most often used to catalyze these reactions. In this introductory chapter, the fundamentals of zeolites and their applications as catalysts for biomass conversion reactions are given. To characterize the products and by-products of biomass conversion reactions, nuclear magnetic resonance (NMR) spectroscopy. In addition, this technique was used to identify unknown compounds. The information gained from the identification of reaction intermediates may be used to determine the reaction mechanism. Finally, concepts behind the statistical analysis of experiments used for the optimization of reaction yield and selectivity of the process and to determine statistically significant reaction trends of the selected catalysts are described.

1.2 Renewable Synthesis of Aromatics and Furans

The conversion of biomass into chemicals and fuels is one important scientific challenge of the 21st century [1]. Chemical and fuel production and consumption for raw materials and energy are important for mankind. Research in this field could lead to the development of alternative routes for the production of commodity chemicals produced from petroleum. The commercialization of these routes improves the sustainability of the chemical industry and decreases price fluctuations. In addition, the use of biomass-derived feedstocks for chemicals and fuels production could decrease global CO₂ emissions. The recent increase in shale gas use could also have an impact on the chemical and fuel market. Because a smaller fraction of C3/C4 olefins

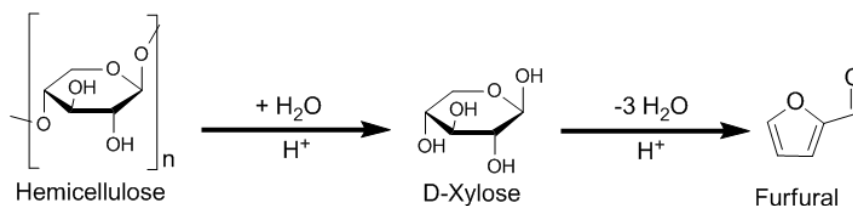
and aromatics can be derived from shale gas, biomass is a potential alternative feedstock that can produce these chemicals and fuels. This thesis discusses the production of two classes of chemicals from biomass: aromatics and furans.

Aromatic chemicals are used for the manufacture of millions of tons of consumer goods each year. These consumer goods include plastics, fibers, paints, and fuel additives. Furans can be used in the synthesis of potential biodiesel additives for fuels as well as for chemicals production [2]. This thesis focuses on the lab scale synthesis of three aromatic chemicals: phthalic anhydride, benzoic acid, and *p*-xylene. In addition, it also presents the synthesis of three furans: 5-(hydroxymethyl)furfural (HMF), 5-(ethoxymethyl)furfural (EMF), and 5-(isopropoxymethyl)furfural (IMF) in alcoholic solvents. The biomass conversion reactions to these chemicals was accomplished using both chemical and catalytic approaches. Lab scale process were designed considering process economics, process practicality, as well as feedstock availability and abundance.

Biomass-based routes to aromatic and furan chemicals and fuels may be commercially viable alternatives to conventional petrochemical routes in the future. Only 3% of the 170 billion tons of lignocellulosic biomass generated annually are used by mankind. Lignocellulosic biomass consists of three fractions: cellulose, hemicellulose, and lignin. The utilization of this non-edible feedstock for the production of fuels and chemicals traditionally obtained from petroleum could provide alternative, economically competitive routes for the production of commodity chemicals and improve the sustainability of the chemical industry. The success of such

biomass-based routes depends on the availability of the feedstock, whether it's commercially manufactured, the production rate of the feedstock, and the cost of the proposed process.

The conversion of the high-yield hemicellulose-derived molecule, furan, to aromatic chemicals by sequential Diels-Alder and dehydration reactions could be one such avenue. Hemicellulose is industrially converted to furfural at a rate of 300,000 tons per year worldwide in an aqueous phase process [3]. The process utilizes homogenous sulfuric acid catalyst to promote hydrolysis and dehydration reactions. Furfural yields of around 50% can be achieved with this process. Recent developments in the field demonstrate that furfural yields of up to 96% can be obtained from corn-stover in a one-step process [4]. Industrially, furfural is decarbonylated to furan in yields of 99% (Scheme 1.1) [5]. The overall yield for the conversion of hemicellulose to furan can be as high as 96%, making it a promising chemical for aromatics production. Furfural can also be used as a feedstock to produce maleic anhydride.



Scheme 1.1 Conversion of hemicellulose to furan

Cellulose which comprises 40-50% of lignocellulosic biomass, can be efficiently hydrolyzed to glucose with high yields. Glucose can be converted a variety of chemicals including

One important aromatic commodity chemical that could be produced from the furfural-derived molecules, furan and maleic anhydride, is phthalic anhydride. Phthalic anhydride is used for the manufacture of plasticizers, unsaturated polyesters, and alkyd resins [6]. In 2000, the worldwide production of phthalic anhydride was estimated to be 3,232,000 tonnes per year [7]. Currently, phthalic anhydride is produced from crude oil by the vapor phase oxidation of *o*-xylene *via* the Gibbs phthalic anhydride process [8].

Another aromatic chemical that could be produced using the approach of sequential Diels-Alder and dehydration reactions of lignocellulose-derived furan and acrylic acid is benzoic acid. Benzoic acid is produced at the rate of 130,000 tonnes per year for the manufacture of therapeutic drugs, food and industrial preservatives, and plasticizers mainly by the oxidation of petroleum-derived toluene. Benzoic acid can be industrially converted to produce many of the monomers typically manufactured from benzene such as phenolic resins, epoxy resins, polycarbonates, and Nylon-6 [9].

The synthesis of the third aromatic commodity chemical in this thesis is *p*-xylene. *p*-Xylene was synthesized by the sequential Diels-Alder and dehydration reactions of lignocellulose-derived 2,5-dimethylfuran (DMF) and ethylene. *p*-Xylene is an important commodity chemical used as raw material for the production of terephthalic acid, and by further condensation with ethylene glycol into polyethylene terephthalate (PET). PET is a polyester produced at a rate of over 31 million tons per year primarily for plastic bottle and clothing manufacture [10].

The conversion of glucose to 5-(hydroxymethyl)furfural (HMF) and the potential biodiesel additives 5-(ethoxymethyl)furfural (EMF) and 5-(isopropoxymethyl)furfural (IMF) is investigated. EMF has an energy density of 30.3 MJ/L which is similar to that of gasoline (31.1 MJ/L) [11]. In engine tests, Avantium reported that tested engines ran smoothly when using EMF blended in commercial diesel as the fuel [12]. IMF has similar chemical properties as EMF making it another viable biodiesel additive though not much has been reported about its synthesis to date.

1.3 Catalysis

The catalytic conversion of biomass-derived compounds to aromatic compounds and furans is critical for their efficient and economical production. Catalysts accelerate the rate of reaction by decreasing the activation energy of reaction without themselves being altered or consumed in the reaction (Figure 1.1) [13]. Catalysts may be in the same phase (homogeneous) or in a different phase (heterogeneous). Catalysts increase the relative rate of desired reaction. At the same time, these materials may be selected to decrease the ratio of the rate of undesired to desired reactions and therefore, the selectivity of the reaction. The use of catalysts in this thesis allows for Diels-Alder, dehydration, and isomerization reactions to proceed at appreciable rates at the chosen reaction temperatures. Some reactions investigated, would not proceed at appreciable rates without catalysts. Side reactions catalyzed by the chosen catalysts include hydrolysis, alkylation, Friedel-Crafts type, and

oligomerization side reactions which were observed though at much lower rates as compared to the rate of product formation.

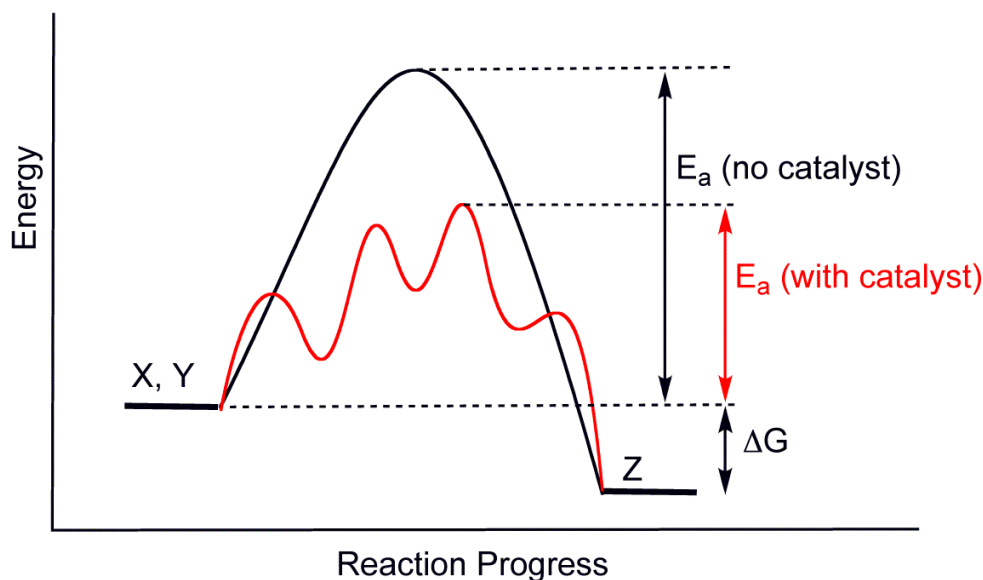


Figure 1.1 Schematic representing the principle behind catalysis. A catalyst decreases the activation energy of reaction (E_a) and therefore increases the rate of the reaction. The relative stability of the reactants and products is unchanged by the presence of the catalyst.

For example, the Diels-Alder reaction of furan and acrylic acid does not proceed thermally at low temperatures ($< 358\text{ }^{\circ}\text{C}$) [14]. At temperatures greater than $35\text{ }^{\circ}\text{C}$, the reaction becomes thermodynamically limited. Therefore, a catalyst is required to speed up the rate of reaction at low temperatures while minimizing possible side reactions.

In the case of the sequential Diels-Alder and dehydration reactions of DMF and ethylene, there are two kinetic regimes governing the rate of reaction: a

dehydration and Diels-Alder reaction limiting regime [15]. In the dehydration limiting regime, the rate of *p*-xylene synthesis increases with increasing acid site concentration. The rate of *p*-xylene synthesis then plateaus with increasing Brønsted acid concentration in the Diels-Alder cycloaddition limited regime. Lewis acidic catalysts could potentially increase the rate of both the dehydration and Diels-Alder reactions.

1.4 Zeolites

Zeolites are three dimensional microporous molecular sieves that are constituted by combining oxide tetrahedral such as SiO_4 and AlO_4^- to form a number of different building blocks called secondary building units (SBU) [16]. The SBUs consist of different units such as squares, pentagons, hexagons, and octagons. SBUs can form cages and channels in which the substrate, active site, and framework interact. Catalytically active centers can be introduced into the zeolite framework during synthesis, by post-synthesis modification, or by ion exchange.

Of particular interest for these biomass conversion reactions is zeolites Beta (International Zeolite Association structure code-BEA) and Faujasite (FAU). Zeolite Beta consists of two intersecting polymorphs (A and B) made of 12-ring pores, 6.68 Å wide (Figure 1.2). In the high silica form, silicon atoms can be isomorphously substituted for tetravalent framework Lewis acids such as tin, zirconium, and hafnium in the zeolite Beta framework. These active centers catalyze a variety of reactions by in principle coordinating with oxygen atoms in the biomass-derived molecules. For example, Sn-Beta zeolite can catalyze the Baeyer-Villiger [17], Meerwein-Ponndorf-Verley [18], isomerization [19], Diels-Alder [14, 20], and retro-aldol reactions [21].

For these reactions, catalytic activity originates from the coordination of the oxygen atoms of the carbonyl groups of the reacting molecules with the Lewis acid metal center.

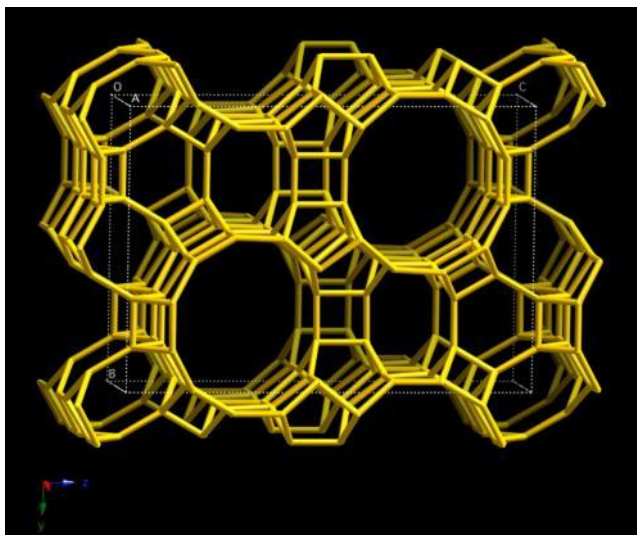


Figure 1.2 Structure of zeolite Beta which is made up of two intersecting polymorphs consisting of 12-ring pores 6.68 Å wide.

Faujasite is a molecular sieve consisting of sodalite cages connected in a cubic manner over six-membered double rings forming wide intersecting channels with an apertures of 7.4 Å (Figure 1.3). Charge imbalance is introduced by replacing Si^{4+} with Al^{3+} atoms in the FAU framework and is compensated by the positive charge of extraframework cations. Extraframework cations can be Brønsted or Lewis acidic and occupy various sites interspersed in the zeolite framework some of which are shown in Figure 1.3. Approximately half of the cations reside in the sodalite cage and are bonded to three framework oxygens of the six-membered rings. The activity and

selectivity of extraframework Lewis acid active centers is determined by the silicon to aluminum ratio, nature of the acidic cation, and the zeolite-specific channel and pore size arrangement.

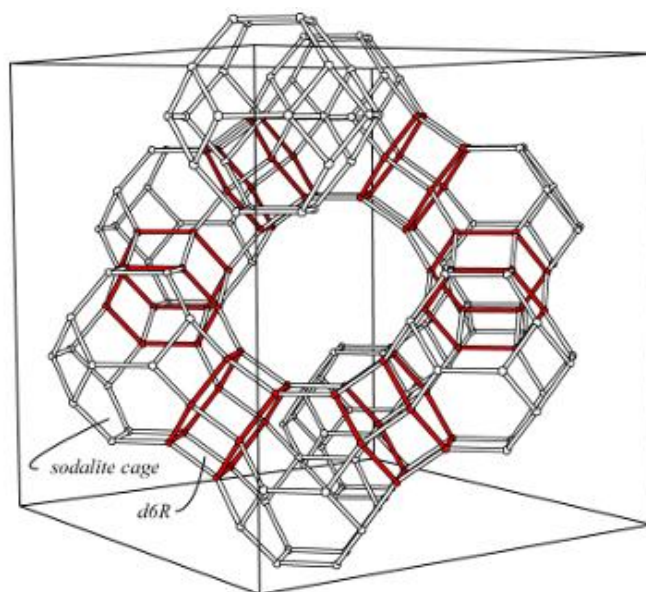


Figure 1.3 Structure of faujasite zeolite. Sodalite cages and six-membered double rings (d6R) are labelled in the figure.

1.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy (NMR) is a critical tool used in the development of new routes for the conversion of biomass to aromatics, as it can be used to identify the structure of unknown organic compounds. As compared to other spectroscopies, the information obtained from NMR spectra is more abundant and interpretable [22]. ^1H NMR spectra can be acquired more easily than other NMR

techniques, is more sensible, and when combined with ^{13}C NMR and mass spectroscopy, may be used to deduce the structure of simple unknown compounds.

The main parameters found in ^1H NMR spectra are chemical shifts (δ), coupling constants (J), and peak areas. Chemical shifts represent peak positions of functional groups relative to a standard chemical shift applied most frequently, which is most frequently tetramethylsilane (TMS). Chemical shifts of the most common functional groups, whose values are measured in parts per million (ppm), can be found to the left of the standard and have positive values. The value of the chemical shift represents the density of electrons around the hydrogen atom. The greater the density of electrons around the nucleus the smaller the chemical shift value (Figure 1.4). Chemical shift values are mainly determined by the type of functional group.

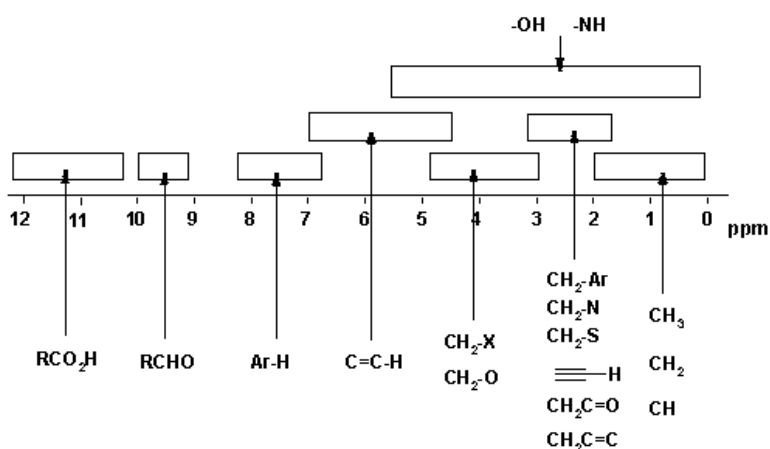
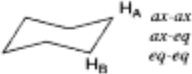
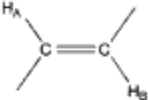
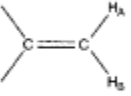
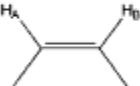
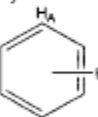
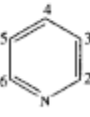


Figure 1.4 ^1H NMR chemical shift values of common functional groups.

Coupling constants are determined by peak splittings. Magnetic nuclei with non-zero magnetic quantum numbers, such as ^1H , ^{19}F , and ^{31}P , have coupling effects. For ^1H NMR spectra, an $n+1$ rule governs the observed peak splittings. The peak set

of a functional group which is connected to another functional group containing n hydrogen atoms will be shown as a multiplet with the peak number of $n+1$. The coupling constant, J , measures the magnitude of the coupling effect which depends on the number of chemical bonds through which the coupling effect is transferred. Values of typical coupling constants can be found in Table 1.1 ^1H NMR coupling constants of selected functional groups..

Table 1.1 ^1H NMR coupling constants of selected functional groups.

Structural unit	Typical coupling constant J_{AB} (Hz)
	-10–-15
$\text{CH}_\text{A}\text{CH}_\text{B}$	7
	8–11 2–3 2–3
	15–17
	0–2
	10–11
	$J(\text{ortho})$ 8
	$J(\text{meta})$ 2
	$J(\text{para})$ 0.3
	$J(2-3)$ 5
	$J(3-4)$ 8
	$J(2-4)$ 1.5
	$J(3-5)$ 1
	$J(2-5)$ 0.8
	$J(2-6)$ 0
	$J(2-3)$ 1.8
	$J(3-4)$ 3.6
	$J(2-4)$ 0.8
	$J(2-5)$ 1.5

The relative areas of peaks in a molecule indicate the relative proportion of the number of protons belonging to a particular functional group. When used in conjunction with mass spectroscopy, the relative peak areas help to deduce the structure of an unknown molecule. ^{13}C NMR spectra provide chemical shift values δ

of carbon atoms which are determined by the electronegativity of substituents and steric effects (Figure 1.5).

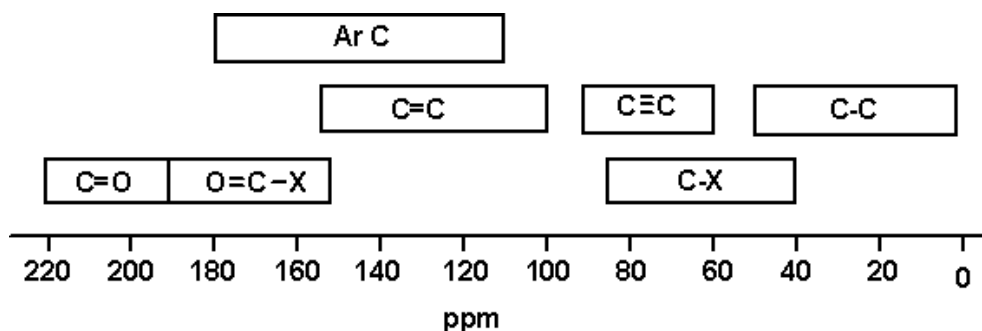


Figure 1.5 ^{13}C NMR chemical shifts of various functional groups.

To determine the structure of more complicated biomass-derived compounds, 2D NMR spectroscopy is utilized. 2D NMR spectra correlate two kinds of NMR spectra with the abscissa or the ordinate corresponding to the ^1H NMR or ^{13}C NMR spectrum of the compound. 2D NMR spectra appear as contour plots with useful information coming from cross peaks, which denote a correlation between those two chemical shift values (Figure 1.6). Homonuclear Shift Correlation Spectroscopy (COSY) projects the ^1H NMR spectrum of the sample on both ω_2 (F_2 , horizontal) and ω_1 (F_1 , vertical) axes. Heteronuclear Shift Correlation Spectroscopy (HMQC) projects the ^1H and ^{13}C NMR spectra of the sample on both ω_2 (F_2 , horizontal) and ω_1 (F_1 , vertical) axes. Long-range heteronuclear shift correlation spectroscopy (HMBC)

correlates the long-range couplings between carbon atoms and hydrogen atoms across three chemical bonds.

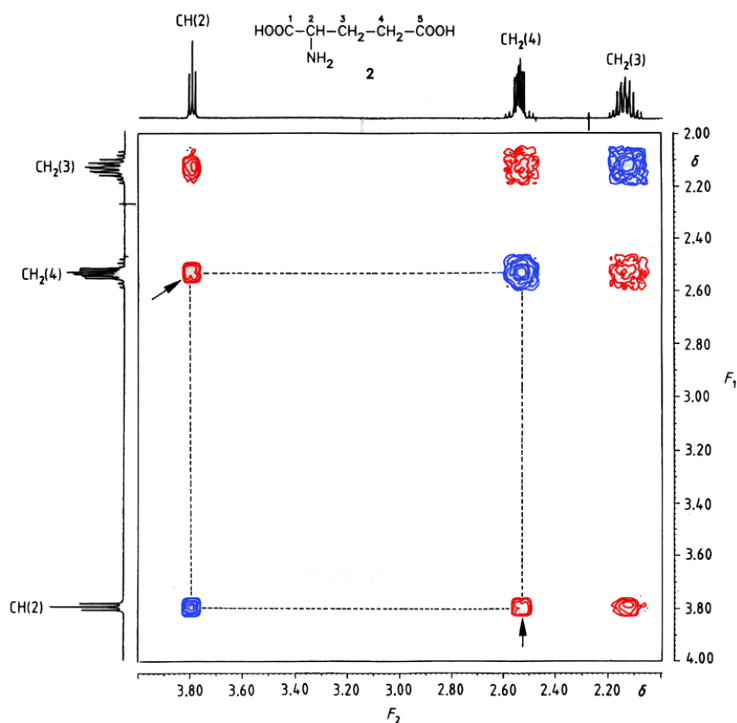


Figure 1.6 Example of a 2D NMR ^1H - ^1H NMR COSY spectrum.

1.6 Factorial Design and ANOVA

Factorial design allows the investigator to study postulated effects of various experimental variables and their interactions on the response variable [23]. To carry out such an experimental design, one identifies variables that could potentially influence the response variable and then selects the desired number of "levels" of each factor to be studied. With this design, one can then run experiments in all possible combinations. In principle, the experimenter can choose any number of factors or

levels within these factors for the study. Since the experimental design encompasses all factor-level combinations, one is able to precisely determine which experimental conditions optimize the outcome of the response variable. Then, using ANOVA, one can orthogonally decompose the total variation observed in the response variable into various constituent components, and thus determine the significance of each contribution to the total variation. Main effects describe the individual impacts of each factor on the response variable, while interaction effects describe the combinatorial impacts of multiple factors.

The correct execution of a factorial design requires the replication of data points at each factor-level combination. One can determine the number of replicates needed based on the signal-to-noise ratio, defined as:

$$\rho_{SN} = \frac{\delta^*}{\sigma} \quad (\text{Eq. 1.1})$$

In Eq. 1.1, σ , δ^* , and ρ_{SN} represent the standard deviation, smallest magnitude of the effect desired to be detected, and signal-to-noise ratio, respectively. Eq. 1.2 relates the signal-to-noise ratio to the appropriate sample size range, where n represents the total sample size. One desires a high signal-to-noise ratio in order to confidently attribute the results to important experimental effects rather than to experimental noise.

$$\left(\frac{7}{\rho_{SN}}\right)^2 < n < \left(\frac{8}{\rho_{SN}}\right)^2 \quad (\text{Eq.1.2})$$

ANOVA is employed to analyze the results from a factorial design. ANOVA acts as an extension of the t-test, since it can examine the difference of means between more than two groups. Because of the high alpha risk associated with multiple pair-wise t-tests, ANOVA is the preferred method of analysis. ANOVA uses the fundamental approach of orthogonal decomposition to partition the total variance of the response variable into components that reflect the different sources of variation. The magnitude of each component quantifies the relative importance of each source of variation. The decomposition of the sum of squared deviations for a two factor experiment is given as:

$$SS_Y = SS_A + SS_B + SS_{AB} + SS_E \quad (\text{Eq. 1.3})$$

In Eq. 1.3, SS_Y , SS_A , SS_B , SS_{AB} , and SS_E represent the total variability, variability due to factor A, variability due to factor B, variability due to the AB interaction, and variability due to pure error, respectively. The mean error sums are determined as the ratio of the sum of squares terms divided by the degrees of freedom associated with each source of variation. Table 1.2 presents a typical ANOVA table for a two-factor design.

Table 1.2 Two-Factor ANOVA Table. Degrees of Freedom correspond to "a" levels of factor A, "b" levels of factor B, and "r" replicates.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F	P
Main Effect A	a-1	SS_A	MS_A	MS_A/MS_E	
Main Effect B	b-1	SS_B	MS_B	MS_B/MS_E	
Interaction Effect AB	$(a-1)(b-1)$	SS_{AB}	MS_{AB}	MS_{AB}/MS_E	
Error	$ab(r-1)$	SS_E	SS_E		
Total	abr-1	SS_Y			

Taking the ratio of each mean error sum term with respect to the MS_E term, one calculates an important statistic, known as the F-statistic. This ratio, generally defined as the ratio of between-group variability to within-group variability, is the key piece of information ascertained from the ANOVA analysis. A larger F-value indicates a significant difference between the means of groups, and thus distinguishes the important main and interaction effects from those that are unimportant. Determining the critical F-values for the specified degrees of freedom at a certain significance level (95% is most common) enables one to compare the calculated F-value to this range and decide whether or not to accept or reject the null hypothesis at that particular significance level.

Additionally, the two-factor design has an associated postulated model to define the response variable:

$$Y_{ij} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \varepsilon_{ijk} \quad (\text{Eq. 1.4})$$

In Eq. 1.4, α_i is the main effect of the i^{th} level of factor A, β_j is the main effect of the j^{th} level of factor B, γ_{ij} is the interaction effect between the i^{th} level of factor A and the j^{th} level of factor B, and ε_{ijk} is the random error. The null hypothesis states that the main and interaction effects are not important, so that all of the α , β , and γ terms equal zero. The alternative hypothesis is that these terms are significant, and thus not equal to zero. The associated F-statistic and p-value of each coefficient indicate whether or not the effect is significantly different from zero at a particular significance level.

In order for the ANOVA analysis to be applicable, two major assumptions must be satisfied: (1) normality of the response variable, and (2) independent observations. The first assumption requires that for each treatment, the response variable be a random variable with a normal distribution and the same variance. Normal probability plots are used to confirm this assumption. In these plots, the data is rank ordered and then plotted in that order versus the expected value from a normal distribution. If the assumption holds, this plot should be linear and the associated p-value should be greater than 0.05. The assumption of independence is met by ensuring that the experimental setup is completely randomized, so that each response is measured in random order. This step in the experimental design ensures that any extraneous influences do not propagate systematically through the observations.

1.7 Overview of Thesis

The conventional routes to phthalic anhydride, benzoic acid, and *p*-xylene comprise the catalytic reforming of crude oil, separation, and in the cases of phthalic anhydride and benzoic acid production, oxidation of the aromatic precursors. The shale gas revolution will likely not provide enough aromatics to compensate the withering petroleum-based routes [24]. In this project, we aimed to establish alternative routes to these aromatic chemicals which are based on renewable resources and are highly selective. The aim of this work is to fundamentally understand the conversion of furans to aromatics by gaining a sound understanding of by-product formation and the underlying mechanism of the conversion.

In Chapter 2, the experimental methods and analytical techniques used in this thesis are outlined. The chapter begins with a description of the zeolite synthesis and post-synthesis modifications used to prepare the catalysts used in this thesis. Following this section a description is given of the materials characterization techniques used to characterize these catalysts which include powder X-ray diffraction (XRD), N₂ adsorption, scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), temperature programmed desorption thermogravimetric analysis (TPD-TGA), and solid-state (SS) nuclear magnetic resonance spectroscopy (NMR). A description of the reaction product characterization tools is also given which is critical for the development of the reaction network. These include gas chromatography (GC), mass spectroscopy (MS),

high performance liquid chromatography (HPLC), nuclear magnetic resonance spectroscopy (NMR), and organic elemental analysis.

A route to phthalic anhydride from biomass-derived furan and maleic anhydride was first investigated. Furan and maleic anhydride were reacted in a two-step reaction protocol by sequential Diels–Alder cycloaddition followed by dehydration. The Diels–Alder reaction of furan and maleic anhydride was run under solvent-free conditions (SFC) and an investigation into possible thermal runaway of the reaction was taken. The dehydration of the Diels-Alder adduct (oxanorbornene) including side reactions and the mechanism of reaction was studied. (Chapter 3).

Subsequently, a route to benzoic acid from biomass-derived furan and acrylic acid was investigated to serve as a potential drop-in replacement for benzene-derived monomers. The Diels-Alder reaction was catalyzed by Lewis acidic molecular sieves of the zeolite Beta topology. The effect of concentration and stereochemistry on the dehydration of the Diels-Alder adduct (oxanorbornene) was investigated. (Chapter 4).

In the subsequent chapter, a route to *p*-xylene from biomass-derived DMF and ethylene catalyzed by metal exchanged faujasites is investigated (Chapter 5). A statistical analysis is undertaken studying the effect of active site concentration, location, and framework composition on *p*-xylene selectivity. Structure activity relationships are made and an investigation into possible Diels-Alder catalysis was undertaken.

In Chapter 6, the conversion of glucose to HMF and the potential biodiesel additives, EMF and IMF, was studied. Co-solvent effects in binary mixtures of water and alcohols are studied and related to the activity of Lewis acids in various molecular sieves in catalyzing the glucose isomerization reaction. A possible low-cost route for HMF production is discussed.

Chapter 7 presents conclusions and suggestions for future work.

Two appendices are included to document NMR results for stable reaction intermediates formed during the dehydration of Diels-Alder adducts in binary mixtures of MSA and acetic anhydride. Appendix A describes results for the dehydration of the Diels-Alder adduct of furan and maleic anhydride (oxanorbornene dicarboxylic anhydride). Thermodynamics of the reaction are also provided. Appendix B describes results for the dehydration of the Diels-Alder adduct of furan and methyl acrylate. Kinetic and thermodynamic data of the reaction as well as a temperature program are provided.

The last two appendices include catalyst characterization and glucose isomerization studies. Appendix C includes catalyst characterization results of metal-exchanged faujasites as well as parameters for statistical analysis. Appendix D includes results for glucose isomerization studies run in ethanol.

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Chapter 2

EXPERIMENTAL METHODS

2.1 Overview

In this chapter, the most important experimental methods used in this dissertation are described. The section begins with a description of the hydrothermal method used to synthesize the zeolites used as catalysts in this research as well as the liquid and solid-state ion exchange procedures to prepare Lewis acidic zeolites. Next, materials characterization techniques used to study the crystal structure, particle morphology, and composition of samples are described. Techniques for the characterization of these materials such as X-ray diffraction (XRD), N₂ adsorption, scanning electron microscopy (SEM), ultraviolet/visible optical spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), temperature programmed desorption thermogravimetric analysis (TPD-TGA) and solid-state NMR spectroscopy (SSNMR), were used to evaluate catalyst active site structure and the strength of Lewis acid sites. A description of the analytical techniques used to characterize the liquid products such as gas chromatography (GC), mass spectroscopy, high performance liquid chromatography (HPLC), NMR, and elemental analysis is also given.

2.2 Zeolite Synthesis and Ion Exchange

2.2.1 Hydrothermal Synthesis

Hydrothermal synthesis involves crystallizing substances, such as inorganic reactants containing silica often in presence of an organic structure directing agent, from basic aqueous solutions heated between 100-200 °C in sealed autoclaves [1]. After heating for a few hours to a few weeks, a crystalline zeolite product precipitates from solution, which can be recovered by filtration. The filtered product is then washed with deionized water, dried, and calcined in air to remove any occluded organic molecules used for the zeolite synthesis. Following calcination the zeolite is ready for application as a catalyst.

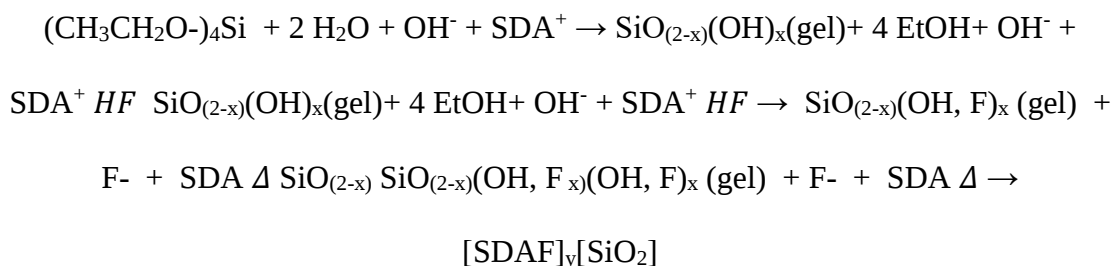
The preparation of the first synthetic zeolites in the 1940's and 50's was an advance in the field of hydrothermal synthesis. Since then, researchers have investigated the crystallization process of these materials to gain a better understanding of their preparation. Zeolite preparation can be a very complicated process, especially at the molecular level. Zeolite crystallization occurs in three defined time periods. In the first period, the amorphous phase dissolves and soluble intermediates condense in the solution phase. In the second period, stable nuclei grow into larger crystals. In this period, stable nuclei grow into larger crystals. Dissolved silicate and aluminate ions undergo a polymerization process which is affected by the presence of hydroxide ions which help to dissolve the gel material. Aluminosilicate or polysilicate species may regroup around hydrated cations such as the tetraethylammonium ion to form nuclei of the ordered zeolite [2]. Structure directors

such as tetraethylammonium hydroxide (TEAOH) which can be added to the synthesis media to aid in the organization of the building units that form the framework. Since the bond type of the precursor oxides is similar to the bond type of the product, the overall free energy change of the zeolite synthesis reaction is small and the product is frequently kinetically controlled. In this thesis, synthesis methods were altered by the addition of seed crystals. The addition of seed crystals helps to bypass the nucleation step and the induction period and increases the crystallization rate [3].

The third time period is defined as crystal growth. During this step, three phases coexists: an amorphous phase, a solution phase, and a crystalline phase and concludes with the complete depletion of the amorphous phase. This is accompanied by a decrease in the solution pH during the crystal growth. Crystal growth occurs by two mechanisms: nanoparticles aggregation and monomers or oligomers addition. The incorporation of aluminosilicate or polysilicate species continues in the crystallization period results in the formation of the zeolite crystal lattice. Ripening of crystal-monomer-oligomer dissolution and attachment to crystal surfaces results in crystals having smooth surfaces.

High silica zeolites, which are used extensively in this thesis as catalysts for biomass conversion reactions, can be synthesized in a fluoride media. Synthesis of high silica zeolites in basic media without the addition of fluoride compounds has been associated with more framework defects in aluminum free zeolites containing heteroatoms such as Ti and Zr. In a typical experimental method, tetraethylorthosilicate (TEOS) is hydrolyzed at room temperature in a basic aqueous

solution containing an organic structure-directing agent for a few hours (Scheme 2.1). Following hydrolysis, the mixture is heated to 80 °C to evaporate the formed ethanol (under stirring in a heating plate) [4].



Scheme 2.1. Hydrolysis and crystallization reactions of high silica zeolites using a fluoride method.

After the solution reaches the correct weight, a fluoride-containing mineralization agent, most commonly an aqueous solution containing 48 wt. % HF or less commonly NH_4F or NaF , is added resulting in a thick paste that is mixed using a metal spatula. The thick paste is then heated in a Teflon-lined stainless steel autoclave (Parr). The paste becomes the gel material which crystallizes to form the zeolite crystal.

Following zeolite crystallization, the suspension is filtered, washed using deionized (D.I.) water, and calcined in air to remove any occluded structure-directing agent used for zeolite synthesis. The calcination procedure, which may be performed in a furnace or in a plug flow reactor, typically consists of a controlled ramp to a ‘lower temperature’ (around 120 °C) to dehydrate the sample followed by a ramp and hold at a higher temperature to completely burn away any organic material on the

sample. This calcination procedure helps to minimize dealumination of the zeolite and helps to maintain the structural integrity of the microporous material. High silica frameworks prepared using this method have less framework defects ($\text{Si(OSi)}_3\text{OH}$ groups or Q_3 species) as compared to materials prepared in alkaline media. Because of the slow nucleation step of zeolites prepared by the fluoride route, zeolite particles prepared by this method are usually larger.

2.2.2 Ion Exchange

Zeolites may be subject to post-synthesis modification to alter their catalytic properties. For example, ion exchange can be used to displace the charge compensating cation present in the intercrystalline pore system of the zeolite with desired cations originally present in the aqueous phase. This process can only occur if the cation is replaced by its electrochemical equivalent to maintain charge neutralization. This process depends on the nature of the zeolite, the ion, and temperature. Ion exchange is governed by an ion exchange isotherm [5]. A commercial application of the process is the use of zeolites for their ion exchange capacities to soften the wash water by reducing the activity of hard ions such as Ca^{2+} and Mg^{2+} .

In a typical ion exchange procedure, the solid zeolite is added to an aqueous solution at a solution to solid mass ratio of at least 20. Ion exchange procedures may be performed at temperatures between 25-95 °C with at least a 5-fold excess of the desired cation in a solution at an optimal concentration. Following exchange the suspension is filtered and the product is washed with D.I. water. The exchange

procedure may be repeated at varying concentrations. Changes in ionic composition of the zeolite may produce changes in the properties of the sample such as its thermal stability, sieving, sorptive as well as catalytic functions.

2.2.3 Solid-State Ion Exchange

Solid-state ion exchange (SSEI) is based on similar principles as aqueous ion exchange but occurs when reacting two solids at elevated temperature, thereby eliminating washing, filtration, and drying steps typically required in aqueous ion exchange. In a typical procedure, the solid zeolite, in its acid or ammonium form, and metal salt are ground making a physical mixture. The physical mixture is then put in a flow reactor and heated according to a temperature program to temperatures greater than 500 °C. The high temperature allows for the migration of metal salts with substantial vapor pressure (such as copper (I) chloride) into the zeolite pores along with the release of water.

2.3 Materials Characterization

In the following subsections, a description of methods used for catalyst characterization, the physical principles behind each method, the specific equipment used, and experimental protocol associated with each method is given.

2.3.1 Powder X-ray Diffraction (XRD)

Catalyst samples were characterized by X-ray powder diffraction (XRD) to identify the structure and position of atoms present within the crystalline material, identify the crystalline phases present, check for impurity phases, and quantify unit cell parameters. A stream of high energy electrons which are excited into higher

energy levels are used to generate X-rays. The X-ray beam passes through a filter to create a monochromatic beam, which is shinned onto the polycrystalline sample at an incident angle, θ , above the horizontal plane (Figure 2.1). A detector measures the X-ray intensity at an angle, θ , above the plane resulting from interactions between the X-ray radiation and the electrons from the material which reflect at an angle equal to the incidence angle. The measurement proceeds as the incident angle is slowly increased [6].

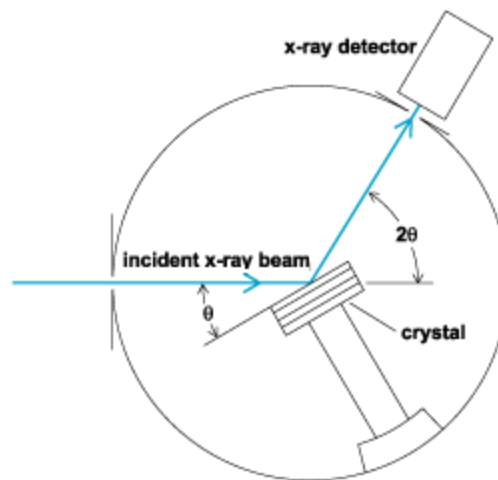


Figure 2.1 Schematic of a typical X-ray diffraction experiment.

XRD diffraction provides information about the atomic structure of the crystal, spacing between the crystal planes, and symmetry of the three dimensional lattice of the material. X-ray waves add constructively depending on the crystal spacing in a few specific directions as determined by Bragg's law, whose equation is:

$$n\lambda = 2d\sin \theta \quad (\text{Eqn. 2.1})$$

where d is the spacing for the planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam [7]. Constructive interference occurs from a set of consecutive parallel planes of the material. Peak positions provide information about the size of the unit cell, and the relative intensities provide information about the position of atoms within the unit cell. Neutron diffraction allows for the determination of the positions of extraframework cations and molecules in the intercrystalline pore system of the zeolite.

Powder XRD patterns depend on the geometry of the crystal and atomic composition of the material. Because of the dependence, XRD patterns provide a unique fingerprint for each distinct sample. In the case of zeolites, measured XRD patterns can be compared against those found in a crystal database to quickly identify any impurity phases and verify the success of synthesis [8]. The presence of amorphous material can be detected by an abnormal increase in the baseline with increasing incident angle of the X-ray beam. For small crystals (less than 150 nm in diameter) the size of crystalline domains can be calculated from the parameter β , the full width at half maximum (FWHM) of a diffraction peak, using the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (\text{Eqn. 2.2})$$

where K is a “shape factor”, β is the peak FWHM, λ is the wavelength of incident radiation (1.5418 Å for Cu K α radiation), θ is the angle of incident radiation, and τ is

the correlation length of sample. Small crystalline domains give rise to diffraction patterns with broader diffraction peaks [9].

XRD patterns reported in this thesis were typically collected from 5-50° 2 θ and recorded on a Phillips X'Pert X'ray diffractometer using Cu K α radiation ($\lambda = 1.54060$ Å for $\kappa\alpha_1$). Typical scans were taken using a step size of 0.02° with measurement lasting 2 s per step.

In addition to obtaining phase information and crystal size, XRD patterns may be used to determine the unit cell parameters of the tested samples using refinement. For these experiments, the samples were mixed with an internal silicon standard (NIST, 10~20 wt. %) prior to experiment to correct the peak positions before refinement. Refinement was carried out using the UnitCellWin program using a nonlinear least-square method [6].

2.3.2 N₂ Adsorption Isotherm Measurements

Following synthesis or ion exchange and thermal treatment, the catalyst sample can also be characterized by nitrogen physisorption to determine the pore volume, surface area, and pore size distributions of the sample. In a typical experiment, the sample is enclosed in a glass cell and evacuated and heated to temperatures between 100-400 °C, then cooled -196 °C in a container of liquid nitrogen. The partial pressure of N₂ is increased incrementally and the amount of N₂ adsorbed after equilibrium is recorded. The gas is deposited on the sample over a range pressures forms what is called an adsorption isotherm. Depending on the structure of the material, whether it

be non-porous, mesoporous, or microporous different adsorption isotherms are observed as shown in Figure 2.2 [10].

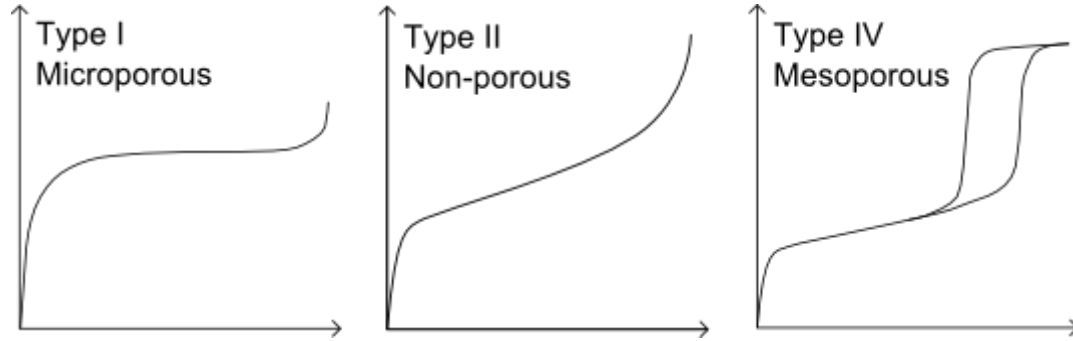


Figure 2.2 Examples of some adsorption isotherms for different classes of materials.

By measuring the number of molecules adsorbed at monolayer coverage one can calculate the internal surface area of the catalyst sample by using the adsorbing molecule's cross-sectional area. During experiment, coverage beyond one monolayer occurs at higher N₂ partial pressures with condensation of liquid N₂ in the pores. Surface areas of mesoporous materials and some oxides can be determined using Brunauer, Emmett, and Teller (BET) theory which allows one to relate the volume of N₂ adsorbed and volume of N₂ adsorbed at a monolayer. BET method extends the classical model of monolayer adsorption developed by Langmuir and quantifies surface area using the following equation:

$$\frac{1}{\left(\frac{p_0}{p}-1\right)} * \frac{1}{V} = \frac{c-1}{cV_{mono}} \left(\frac{p}{p_0}\right) + \frac{1}{cV_{mono}} \quad (\text{Eqn. 2.3})$$

where V_{mono} is the volume of gas that would constitute one monolayer, c is the BET constant, p/p_0 is the ratio of the pressure of the gas to the pressure at surface

saturation, and V is the volume of gas adsorbed at pressure p . A plot of $\frac{1}{\left(\frac{p_0}{p}-1\right)}$ vs. $\frac{p}{p_0}$ has a slope of $\frac{c-1}{cV_{mono}}$ and intercept $\frac{1}{cV_{mono}}$. The volume of a monolayer, V_{mono} , can be used to determine the BET surface area, S_{BET} , using the following equation:

$$S_{BET} = \frac{(V_{mono}N_A A)}{mV} \quad (\text{Eqn. 2.4})$$

where A is the cross-sectional area of the adsorbate ($16.2 \times 10^{-20} \text{ m}^2$ for N_2), N_A is Avogadro's number, and V is the molar volume of the adsorbate gas ($22400 \text{ cm}^3/\text{mol}$). The BET model assumes that all adsorption sites are equivalent and that an infinite number of layers of adsorbate may be formed under adsorption conditions. These assumptions mean that the model is not suitable for microporous materials and materials with a heterogeneous distribution of adsorption sites [11].

For microporous materials, the t -plot method is more appropriate. To determine the microporosity of the material the empirical equation developed by Harkins and Jura is used:

$$t_{HJ} = \left(\frac{13.99}{0.034 + \ln\left(\frac{p}{p_0}\right)} \right)^{0.5} \quad (\text{Eqn. 2.5})$$

This equation has been shown to describe the system in the low pressure regime where adsorption within micropores increases rapidly with adsorbate pressure as shown in Figure 2.2. The t -curve is compared with the experimental isotherm to form a t -plot. At each $\frac{p}{p_0}$ value, the experimental volume adsorbed is plotted versus the statistical

thickness, t_{HJ} . The linear range lies between monolayer and capillary condensation and the slope of the t-plot is equal to the area of the pores that are micropores [12].

N₂ adsorption isotherms in this thesis were measured using Micromeritics ASAP 2020 and 3Flex adsorption instruments. Prior to isotherm measurement, samples were degassed at 300 °C for 8 h under vacuum. Sample weights of the degassed samples were used in the data analysis. During sample measurement, samples were immersed in a liquid N₂ bath (- 196 °C). Data analysis was performed using Micromeritics software.

2.3.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

Scanning electron microscopy (SEM) was used to determine crystal morphology and size of individual crystallites of the catalyst samples. In a typical experiment, a sample is bombarded with a focused beam of electrons which excite the atoms of the sample and cause the release of secondary electrons coming off the sample. Secondary electrons are k-shell electrons that are ejected from the sample because of inelastic scattering interactions. These electrons are collected at the detector to form an image. Because the electron beam is very narrow, the images give the appearance of three-dimensional depth [13].

SEM experiments are run under vacuum. Prior to imaging, samples are mounted on a layer of conductive carbon tape and sputter coated using a Denton Vacuum Desk IV sputtering system. Scanning electron micrographs in this thesis were

recorded using a JEOL 7400 F Scanning Electron Microscope operated at 3 kV and a current setting of 10 mA.

Energy dispersive X-ray spectroscopy (EDS) experiments were conducted using a peripheral attachment to the SEM operated at the same current setting but at higher voltages (8-10 kV). The electron transfer process associated with EDS is typically a two-step process. An incident electron beam from the source ejects an electron from outer shell. This vacancy is compensated for with the ejection of an electron from the inner shell to the outer shell. To compensate for this, an electron of higher energy fills this vacancy releasing energy which is detected in the form of X-rays, which are characteristic of the element under investigation allowing for quantitative chemical information to be obtained [14].

2.3.4 Inductively Coupled Plasma Analysis (ICP)

To determine the elemental composition of the synthesized and ion exchanged zeolites ICP was used. This method is particularly important to characterize the elemental composition of the synthesized BEA zeolites as not all of the metal in the synthesis gel may be incorporated into the zeolite framework. In addition, this method may also be used to detect samples containing lighter elements such as Li, which are not detectable by other techniques such as EDS. In a typical procedure, catalyst samples were first dissolved and the resulting solution was sprayed into a high-temperature argon plasma at $\sim 10,000$ K where the sample is vaporized. Atoms within the vaporized sample are excited by collisions with argon atoms within the plasma. The subsequent relaxation of these atoms results in the emission of photons which are

characteristic of the element. The intensity of these photons can be used to quantify the concentration of certain elements [15]. Results from analysis of various elements may be used to determine the elemental composition of the sample. ICP in this thesis was performed by Galbraith Laboratories in their facility in Knoxville, TN.

2.3.5 Ultraviolet-Visible Spectroscopy (UV-Vis)

Ultraviolet-visible spectroscopy (UV-Vis) was used to study electronic transitions and vibrations of the tested catalysts in the ultraviolet-visible spectral region (200-800 nm wavelength) of the electromagnetic spectrum. These spectra can provide information regarding the catalyst active site structure. In a typical experiment, ultraviolet or visible light is used to excite π or non-bonding electrons in the ground state. The excitation is associated with a photon absorption and is measured as a function of wavelength. The wavelength of light absorbed depends on the atomic composition and molecular structure of the tested sample. The intensity of absorbance determines the concentration of the molecule or absorbing species. For powdered samples, a diffuse-reflective method is employed which is described by Kubelka-Munk theory since transmission of light through the powdered samples can be very low and limited due to light scattering. Kubelka-Munk theory assumes that radiation is composed to two oppositely directed radiation flux through a continuous medium. The Kubelka-Munk function is given by:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \quad (\text{Eqn. 2.6})$$

where K is an absorption coefficient, S is the scattering coefficient, and R is the ratio of the diffuse reflectance of the tested sample to a reference material (barium sulfate) [16].

A relationship exists relating the absorption-edge energy and the domain size of oxide materials. The absorption-edge energy can be calculated by fitting a straight line through a plot of $[F(R_{\infty})h\nu]^2$ vs $h\nu$, which is associated with the low energy rise. Absorption edge energy decreases with increasing particle size so clustering of metal oxides is observed as a shift in the absorption-edge energy [17].

2.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

Like UV-Vis spectroscopy, FTIR measures absorption of light as a function of wavelength and provides information on the catalyst active site structure and strength. In a typical experiment, the sample is shined with a beam containing many frequencies of light and the absorption of that beam is measured [18]. The process is repeated except with another beam of light which contains a different combination of frequencies. The absorption at each wavelength is inferred using a computer which takes all of the data and works backwards.

The beam of light is generated by shining a broadband light source containing the full spectrum of wavelengths of light to be measured into a Michelson interferometer. A Michelson interferometer contains a certain configuration of mirrors moved by a motor. The motor moves the mirrors, which periodically block or transmit

each wavelength of light. The wavelengths of light are modulated so that a different spectrum of light comes out of the interferometer.

FTIR experiments in this thesis were run by dosing catalyst samples with acetonitrile-*d*3. Throughout the experiment, the vibrational energy of the CN stretching vibration was monitored. Upon adduct formation with the Lewis acids tested, the absorption band associated with the CN stretching vibration shifts to higher frequencies as compared to neat CD₃CN. The frequency shift of the CN stretching vibration is proportional to the polarizing power of the Lewis acid. More blue-shifted absorptions (larger wavenumbers) belong to sites that are considered to be stronger Lewis acids.

FTIR spectra in this thesis were measured using a Mattson Galaxy FTIR instrument with a diffuse-reflectance attachment (Collector II) purchased from Spectra-Tech Inc. The tested samples were heated in flowing He to 500 °C to remove any water on the samples prior to FTIR experiments. After cooling to room temperature, samples were dosed with acetonitrile-*d*3 vapors and FTIR spectra were measured.

2.3.7 Temperature-Programmed Desorption Thermogravimetric Analysis (TPD-TGA)

Temperature-programmed desorption thermogravimetric analysis (TPD-TGA) was used to measure the nature, strength, and number of acid sites of the tested catalyst samples. In a typical experiment, gas molecules are dosed into a vacuum

chamber containing the sample and adsorb onto material due to interaction with the sample. The sample is then heated at a constant temperature ramp and the desorbing gas molecules are monitored. Molecules desorbing from the samples can be monitored by mass spectrometry and the mass of the sample and adsorbed molecules can be measured by TGA [19]. It is important to note that this method lacks specificity, with desorption of Lewis and Brønsted acid sites occurring over a wide temperature range. Results of TGA experiments may be used to calculate the number of active sites in a sample. In the case of the characterization of framework Lewis acid sites in high silica zeolites, it was observed that many adsorbates, such as diethylether, form stoichiometric complexes with acid sites present in the material [20].

TPD can be described based on the Arrhenius equation with desorption behaving as an activated process:

$$r(t) = -\frac{d\sigma}{dt} = v_n \sigma^n * e^{-\frac{E_{act}}{RT}} \quad (\text{Eqn. 2.7})$$

where E_{act} is the activation energy of desorption [kJ/mol], T is the temperature [K], R is the universal gas constant, n is the order of desorption, σ is the surface coverage, v_n is the pre-exponential factor [Hz], and $r(t)$ is the desorption rate [mol/cm² sec].

The activation energy of desorption, E_{act} , for a first order desorption process can be determined from the temperature maximum, T_m , using the Redhead equation:

$$\frac{E_{act}}{RT_m^2} = \frac{v_1}{\beta} * e^{-\frac{E_{act}}{RT}} \quad (\text{Eqn. 2.8})$$

where β , is the linear rate of temperature increase. The activation energy of desorption is a measure of the interaction between the active site of the catalyst and probe molecule. The larger the temperature maximum of desorption the stronger the interaction between the active site and the probe molecule. Care must be taken when applying the Redhead equation to microporous materials as multiple desorption-adsorption events may take place [21].

TPD-TGA experiments were run using a CAHN 1000 microbalance mounted on a high-vacuum chamber initially held at 1×10^{-8} Torr. Throughout the experiment, the mass of the sample was recorded using a microbalance and desorbing species were monitored using a UT1 quadrupole mass spectrometer. Prior to experiments, samples were heated to 500 °C prior to being exposed to 3 Torr of the probe molecule, diethyl ether, at room temperature. During desorption, the heating rate was increased at a rate of 10 °C/min.

2.3.8 Solid-State Nuclear Magnetic Resonance Spectroscopy (SSNMR)

SSNMR is based on much of the same principles as those for classical liquid-state NMR (see Chapter 1). A chemical bond gives rise to interaction between two atoms, effecting the behavior of nuclear spins, which interact with magnetic or electric fields. As compared to liquid-state NMR experiments, SSNMR experiments are characterized by the presence of anisotropic (directionally dependent) interactions [22]. For zeolite crystals whose atoms have little or no mobility, anisotropic interactions have substantial influence on the behavior of these spins. Peak positions

provide information related to the structure of the catalyst, including the coordination of metal active site. Furthermore, this method can be used to detect defects present in the crystal lattice.

For the characterization of the coordination environment of the silicon atoms in the synthesized zeolites, ^{29}Si magic-angle-spinning (MAS) and ^1H - ^{29}Si cross-polarization magic angle spinning (CP-MAS) NMR experiments were used. ^{29}Si is a low sensitivity nucleus with a spin of $\frac{1}{2}$. In magic angle spinning (MAS) experiments, the sample is spun at the magic angle θ_m (ca. 54.74°) with respect to the direction of the magnetic field, narrowing the peaks and increasing the resolution of the experiment. In CP-MAS experiments, cross polarization is used to enhance the signal of the ^{29}Si atoms by the transfer of magnetization from the abundant ^1H to the ^{29}Si nucleus. ^{29}Si MAS NMR provides information regarding the possible environment of a Si atom in a tetrahedral coordinated zeolite. In the case of aluminosilicate zeolite samples, the Si/Al ratio of the zeolite can also be calculated. For siliceous zeolites, the concentration of defects (Si-OH) can be calculated by dividing the peak area of chemical shifts around 100-105 ppm which belong to Si-OH or Q^3 groups by the peak area of chemical shifts around 105-120 ppm which belong to Q^4 groups.

^{29}Si NMR experiments were performed at a Bruker AVIII500 solid-state NMR spectrometer at a magnetic field of 11.7 T using a HX double resonance MAS probe in the NMR laboratory at the University of Delaware. The NMR spectra were collected

at room temperature and the MAS frequency was 10 kHz with a 90 ° pulse width of 2.65 μ sec at 145 W.

2.4 Reaction Product Characterization

This section details the techniques used to characterize the reaction products, the physical principle behind each technique, equipment used, and procedure followed. Detailed characterization of the reaction products and by-products allow one to determine the reaction network and gain mechanistic insight into the reaction.

2.4.1 Gas Chromatography (GC)

For gas chromatography (GC) experiments, a liquid product is vaporized and sent through a thin column using an inert carrier gas, separating the compounds in the mixture. Compounds with larger molecular weights tend to elute at longer residence times. The separated compounds can then possibly be detected using either a flame ionization detector (FID) or thermal conductivity detector (TCD). FIDs are usually more sensitive to hydrocarbons and TCDs are more frequently used for detecting hydrogen and inert gases. Products formed can be confirmed using injection of standards purchased from commercial vendors.

In a typical procedure used to analyze liquid product samples by GC, the product solution was diluted in a 1:3 volume: volume mixture of product to ethyl acetate (HPLC-grade, 99.9%, Sigma-Aldrich) and analyzed using an Agilent 6850 series GC.

2.4.2 Mass Spectroscopy (MS)

Mass spectroscopy (MS) is an analytical technique that sorts ions based on their mass. In a typical experiment, a molecule is ionized by bombarding it with electrons, causing some of the sample's molecules to break into charged fragments. The resulting charged fragments are separated according to their mass-to-charge ratio. The results are displayed as a spectrum which displays the relative abundance of detected ions as a function of the mass-to-charge ratio and is unique to the fragmented molecule. The unique spectra of each molecule allows for its identification which can be confirmed using a database. Mass spectroscopy experiments in this thesis were performed using a Shimadzu QP2010 Plus GC-MS.

2.4.3 High-Performance Liquid Chromatography (HPLC)

Like GC, high-performance liquid chromatography (HPLC) is used to separate and identify liquid products and by-products. This technique uses a liquid as the mobile phase at lower temperatures. The elution times of the compounds depend on their interaction with the column and solvent used. In general, compounds with larger molecular weights tend to elute at longer residence times. Various detectors can be used to detect products and by-products such as UV-Vis or photodiode. Products formed can be identified using injection of standards. HPLC may be used to elucidate a reaction network and to understand the effect of temperature on selectivity.

For a typical procedure, the liquid product was diluted 1:4 in water, and samples were filtered using a 0.2 μm filter. Analysis was performed on a Waters e2695

separations module equipped with a refractive index detector. A Biorad HPX87H (300 x 7.8) column was used at 65 °C with 0.005 M concentration of sulfuric acid in D.I. water at a flow rate of 0.65 mL/min of the mobile phase.

2.4.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

Much of the theory behind NMR can be found in Chapter 1 (see section 1.4). Experiments were run using the following methods. ¹H-quantitative nuclear magnetic resonance (¹H-qNMR) spectra were recorded at 25 °C with a Bruker AV400 NMR spectrometer operating at 400.13 MHz (¹H). The experiments were measured with the following parameters validated for qNMR: 30° pulse, preacquisition delay of 6 μs, 64 k data points (corresponding to an acquisition time of 5.8 s at a sweep width of 4807 Hz), and a relaxation delay of 10 s. Fourier transformation was done and exponential filtering of 0.3 Mz. Phase and baseline corrections were done manually. Integrations were taken over 64 times full width at half height (FWHH) when possible [22]. ¹³C NMR, 2D COSY, 2D HMBC, and 2D HMQC were run using standard parameters of the Bruker AV400 spectrometer.

2.4.5 Organic Elemental Analysis

Organic elemental compositions are typically determined using combustion analysis. This technique can be useful for characterizing polymeric by-products typically formed in biomass conversion reactions. In a typical experiment, the sample is burned in an excess of oxygen and various traps collect the combustion products. These include molecules such as carbon dioxide, water, and nitric oxide. Using the

mass of the combustion products, the composition of the unknown sample can be determined.

The carbon and hydrogen content of the isolated polymers were analyzed using a PerkinElmer 2400 Series II CHNS/O analyzer at Galbraith Laboratories facility in Knoxville, Tennessee. The oxygen content was determined using a Thermo Finnigan FlashTM Elemental Analyzer and the sulfur content was determined using a LECO SC-432DR.

2.4.6 Reaction Procedure

All reactions reported in chapters 3-6 were run in batch reactors. Diels-Alder and dehydration reaction experiments described in chapters 3 and 4 on renewable phthalic anhydride and benzoic acid synthesis were run at atmospheric pressure under nitrogen. Experiments reported in chapter 5 on renewable *p*-xylene synthesis were run under high pressure of ethylene in a 45 mL closed Parr reactor (series 4703-4714, General Purpose Pressure Vessels). Glucose isomerization and dehydration reaction experiments reported in chapter 6 were also run at atmospheric pressure under nitrogen in 15 mL thick-walled glass vials (Sigma-Aldrich). More details on the equipment used and protocol followed can be found in the respective chapters.

2.5 Summary

This chapter describes the experimental methods and techniques used in this dissertation. In the first section, details on the synthesis and post-synthesis modification of the catalysts used in this study are given followed by a section on

materials characterization. Important catalyst characterization techniques are described such as XRD, SEM, UV-Vis, FTIR, and TPD-TGA which are used to relate catalyst structure to observed activity. Finally, sections on reaction product analysis and the reaction protocols are given. These methods are used for the determination of reaction networks and the mechanism of the reaction.

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Chapter 3

RENEWABLE PRODUCTION OF PHTHALIC ANHYDRIDE FROM BIOMASS-DERIVED FURAN AND MALEIC ANHYDRIDE

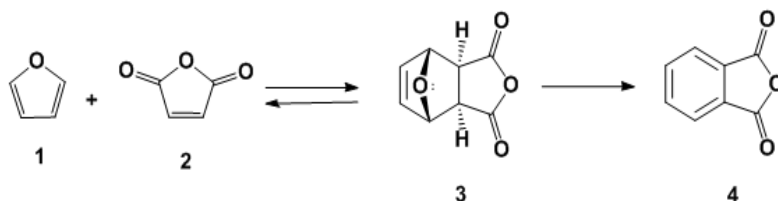
3.1 Introduction

The consumption of fossil fuels for the production of chemicals and fuels has led to increasing levels of CO₂ in the atmosphere and, in response, there has been an intense research effort towards the conversion of renewable biomass feedstocks into fuels and chemicals [1-6]. Lignocellulosic biomass, which is comprised of up to 70 wt. % of cellulose and hemicellulose, is one promising renewable biomass feedstock [7].

One important chemical intermediate that could be produced from biomass is phthalic anhydride. Phthalic anhydride is used for the manufacture of plasticizers, unsaturated polyesters, and alkyd resins [8]. In 2000, the worldwide production of phthalic anhydride was estimated to be 3,232,000 tonnes per year [9, 10]. Phthalic anhydride is currently produced from petroleum-derived feedstocks by the vapor phase oxidation of *o*-xylene or naphthalene via the Gibbs phthalic anhydride process [11]. Myriant has suggested the use of renewable bio-succinic acid as an alternative to phthalic anhydride [10]. Although this route may be promising, an alternative route to produce phthalic anhydride from the high-yield hemicellulose-derived molecule, furfural would also be interesting as this molecule has been commercially produced from biomass since the early 1900's.

Phthalic anhydride can be synthesized from the furfural-derived molecules, furan (**1**) and maleic anhydride (**2**) (Scheme 3.1). Furan is industrially manufactured

by the decarbonylation of furfural in yields of around 96% [12-14] and maleic anhydride can be obtained renewably by the oxidation of furfural using a $\text{VOx}/\text{Al}_2\text{O}_3$ catalyst [15] or by the oxidation of 5-(hydroxymethyl)furfural (HMF) in the liquid phase [16]. Maleic anhydride can be obtained from furfural by a gas phase process with 73% yield. To synthesize phthalic anhydride (**4**), furan and maleic anhydride can be converted in a two-process steps of Diels–Alder cycloaddition to produce the Diels–Alder product, **3**, followed by dehydration to aromatics. Another aromatic molecule that can be synthesized following this approach is *p*-xylene which can be prepared by the Diels–Alder and dehydration reactions of 2,5-dimethylfuran (DMF) and ethylene [17]. In the latter system, selectivity decreases with the removal of the α - and β -methyl groups on the furan ring. For the reaction of DMF and ethylene, an 80% selectivity to *p*-xylene has been achieved while in reactions run using furan and ethylene only an 18% selectivity to benzene is achieved [18]. This reduction in yield is due to the polymerization of furan, which occurs in the presence of Brønsted acids [19, 20]. To minimize the side reactions associated with furan, the Diels–Alder and dehydration reactions were carried out separately for higher yields of phthalic anhydride.



Scheme 3.1 Route to renewable phthalic anhydride (**4**) from biomass-derived furan (**1**) and maleic anhydride (**2**).

The Diels–Alder reaction of furan and maleic anhydride has been previously investigated [21-25]. Reaction were typically run at low temperatures due to thermodynamic equilibrium limitations and in organic solvents such as diethyl ether [21, 22, 26, 27], acetonitrile [23, 24], or tetrahydrofuran [28]. Yields of around 35% to **3** were measured after 24 h of reaction at room temperature [26]. To simplify process separation and to make the process more environmentally friendly, the reaction can be run without solvent or in a ‘green’ solvent. One such approach is the addition of water in a variation of the “on water” reaction procedure originally reported by Sharpless and coworkers for a series of Diels–Alder reactions [29, 30]. For some Diels–Alder reactions, it was observed that the presence of water increases the reaction rate, decreases the maximum reactor temperature, and results in the formation of a higher purity product.

Diels–Alder products decompose via retro-Diels–Alder reactions at higher temperatures to the starting reactants (Scheme 3.1) [31]. Molecule **3** has been

dehydrated using HBr in glacial acetic acid. However, few details regarding the yield of product and by-products were given [32]. The dehydration of the adduct of 2-methylfuran and maleic anhydride was run in 85% sulfuric acid at 0 °C to produce 3-methylphthalic acid in 25% selectivity [33]. It was shown that the retro-Diels–Alder reaction competes with the acid catalyzed dehydration. A 66% yield of 3-methylphthalic anhydride was obtained at -55 °C when binary mixtures of sulfolane and sulfuric acid were used as a solvent. The dehydration of the Diels-Alder product of 2-acetoxymethylfuran and maleic anhydride was carried out in acetic anhydride with catalytic amounts of sulfuric acid. For this dehydration reaction, only a 57% yield of the aromatic product was achieved [34]. Running the dehydration reaction at higher yields and at temperatures which increase the reactor temperature would decrease process cost [35]. Side reactions and by-products including polymeric ones have not yet been investigated for the dehydration of Diels-Alder products of furan (Scheme 3.1) [33].

In this chapter, the renewable production of phthalic anhydride is discussed. In the first reaction step, the solvent-free Diels–Alder reaction of furan and maleic anhydride is investigated and thermodynamic data is collected to assess the safety of the process in the case of thermal runaway. In addition, the “on water” effect is investigated and the criteria for its applicability is evaluated based on the solubility and reactivity of maleic anhydride in water. Secondly, an alternative method for the dehydration of **3** is described in which the reaction is initially run at ambient temperature. This method involves the use of binary mixtures of methanesulfonic acid

(MSA) and acetic anhydride as the dehydration medium. Acetic anhydride reacts with sulfonic acids to generate mixed sulfonic carboxylic anhydrides [36]. With these strong acylating agents [37], the Diels-Alder product may readily be cleaved at room temperature in the presence of anhydride to form a stable reaction intermediate which may be converted to phthalic anhydride by heating. A proposed mechanism of the dehydration the Diels-Alder product using mixed anhydrides is given.

3.2 Experimental Methods

3.2.1 Diels-Alder Reactions

Furan (99+%, Sigma-Aldrich), DMF (99%, Sigma-Aldrich), 2-methylfuran (99%, contained 0.024% BHT as a stabilizer, Sigma-Aldrich), and maleic anhydride (99.0+%, Sigma-Aldrich) were stored under an inert atmosphere and used as received. Reactions were performed in a 600 mL Parr reactor (Parr Instrument Company – model 452HC3) equipped with temperature and pressure sensors. In a typical reaction procedure, maleic anhydride was first placed into the 600 mL Parr reactor under a nitrogen atmosphere. If the reaction was run “on-water”, deionized water (D.I.) was added at this point. After this step, an equimolar amount of furan was added to the reactor. The reactor was then sealed, flushed three times with nitrogen, and pressurized to 1.70 bar. During reaction set-up, light exposure of the reactants was minimized. The mixture was allowed to react for 240 min, initially stirring at a rate of 650 rpm while the temperature and pressure of the reactor were monitored.

Immediately following reaction completion, the solid product was ground with a mortar and pestle, and analyzed by ^1H nuclear magnetic resonance (NMR) to determine its purity. The yield was calculated based on the weight of the solid and the ratio of **3** to the sum of the peak area of maleic anhydride [^1H NMR (400 MHz, DMSO) δ 7.48 (2H, s, $-\text{CHv}$)], maleic acid [^1H NMR (400 MHz, DMSO) δ 6.23 (2H, s, $-\text{CHv}$)] and oxanorbornene dicarboxylic anhydride (**3**) [38]:

$$\% \text{Yield} = \frac{\text{Oxanorbornene peak area at 5.35 ppm}}{\text{Oxanorbornene peak area at 5.35 ppm and maleic anhydride and acid peak areas}}$$

The product was analyzed by ^1H NMR and found to be *exo*-4,10-dioxatricyclo[5.2.1.0]dec-8-ene-3,5-dione. For reactions run “on-water”, water was first filtered off and the reported yield was calculated based on the weight of the dry Diels-Alder product after washing with diethyl ether (cooled to $-20\text{ }^{\circ}\text{C}$).

^1H NMR (400 MHz, DMSO) δ 6.58 (2H, s, $-\text{CH=}$), 5.35 (2H, s, $-\text{CH-O-}$), 3.33 (2H, s, $-\text{CH-}$) ppm; IR (neat) ν 575, 634, 675, 690, 733, 849, 877, 883, 920, 922, 1020, 1080, 1150, 1210, 1220, 1280, 1310, 1780 cm^{-1} .

Experiments investigating the thermodynamics of the solvent-free Diels-Alder reaction were also conducted in the 600 mL Parr reactor (Parr Instrument Company – model 452HC3) equipped temperature and pressure sensors. 0.10 moles of the Diels-Alder product (**3**) were loaded into the reactor which was then pressurized under 10 psig of nitrogen. The temperature of the reactor was increased stepwise and total reactor pressure was monitored. Experiments assessing the “on-water” effect were

similarly conducted except with the addition of 3.09 mL of water into the reactor before the addition of **3**.

exo-cis-1-Methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, the Diels-Alder product of 2-methylfuran and maleic anhydride, was prepared by reacting 0.0666 moles (6.53 g) of maleic anhydride and 0.0666 moles (5.47 g) of 2-methylfuran in a 45 mL closed Parr reactor (series 4703–4714, General Purpose Pressure Vessels) for 24 h at room temperature under a nitrogen atmosphere. Following the reaction, the solid was washed with diethyl ether (-20 °C) to give 10.068 g of a white product (84% yield). ¹H NMR (400 MHz, DMSO-d₆) δ 6.58 (dd, J = 5.5, 1.8 Hz, 7H), 6.41 (d, J = 5.6 Hz, 7H), 5.22 (d, J = 1.9 Hz, 7H), 3.44 (d, J = 6.6 Hz, 8H), 3.20 (d, J = 6.6 Hz, 7H), 1.62 (s, 22H); IR (neat) ν 579, 615, 661, 673, 735, 845, 876, 895, 922, 955, 982, 1070, 1090, 1140, 1230, 1320, 1390, 1770, 1840 cm⁻¹.

The adduct of DMF and maleic anhydride, 1,7-dimethyl-4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione, was similarly prepared by reacting 0.0618 moles (6.06 g) of maleic anhydride and 0.0618 moles (5.94 g) of DMF in a 45 mL closed Parr reactor for 24 h. The solid was washed with diethyl ether (cooled to -20 °C) to give 8.981 g of a white solid (75% yield).

¹H NMR (400 MHz, DMSO-d₆) δ 6.41 (s, 5H), 3.32 (s, 6H), 1.58 (s, 16H); IR (neat) ν 579, 625, 669, 744, 831, 862, 918, 976, 1040, 1080, 1210, 1240, 1320, 1390, 1440, 1760, 1850, 2990 cm⁻¹.

3.2.2 Dehydration Reaction

MSA (99.5%+, Sigma Aldrich), acetic anhydride (99.4%, Fisher Scientific), glacial acetic acid (99.9%, Fisher Scientific), methanesulfonic anhydride (97%, Sigma-Aldrich), maleic anhydride (99.0+%, Sigma-Aldrich) and sulfolane (99 +%, Sigma-Aldrich) were used as received and stored under dry inert atmospheres. In a 20 mL disposable scintillation vial, MSA was added in addition to 0.00301 moles (0.362 grams) of sulfolane (99%+, Sigma-Aldrich), which was used as an internal standard. Sulfolane is stable in the presence of strong acids and is stable at the highest temperatures used (~120 °C) [39]. For reactions performed using mixed-sulfonic carboxylic anhydrides, acetic anhydride, was then added to this mixture. The formation of the mixed-sulfonic carboxylic anhydride [^1H NMR (400 MHz, CDCl_3) δ 2.28 (3H, s, COCH_3), 3.33 (3H, s, SO_2CH_3)] occurs over 5 minutes at room temperature accompanied by an exotherm [36]. The reaction was then heated to the desired temperature and 0.00602 moles (1.0 g) of *exo*-4,10-Dioxa-tricyclo[5.2.1.0]dec-8-ene-3,5-dione (Sigma-Aldrich) was slowly added to the mixture while monitoring the temperature. The vial was then flushed with nitrogen. Reaction conversion and selectivity was calculated using the internal standard by quantitative nuclear magnetic resonance spectroscopy (qNMR). All the reactions were conducted such that the total solution volume was 5 mL.

Following reaction, the product solution was cooled to room temperature and organic products were extracted with anhydrous toluene (99.8%, Sigma-Aldrich) (10

mL, 3 times). The toluene fractions were combined and the solvent was removed in a rotary evaporator. The resulting solid was recrystallized from acetic anhydride and washed with cold hexane to give phthalic anhydride (white crystal). Yields calculated based on the weight of phthalic anhydride were consistent with those determined by qNMR.

^1H NMR (400 MHz, DMSO) δ 8.09 (2H, dd, $-\text{CHv}$), 8.01 (2H, dd, $-\text{CHv}$); IR (neat) ν 534, 642, 677, 710, 798, 839, 903, 1000, 1110, 1160, 1260, 1360, 1470, 1600, 1760, 1790, 1840 cm^{-1} ; m/z 148.

The stable intermediate formed during the dehydration of the Diels-Alder product, (rac) (3aS,4S,5S,7aS)-1,3-dioxo-1,3,3a,4,5,7a-hexahydroisobenzofuran-4,5-diyl diacetate, was isolated by running the reaction at conditions such that this reaction intermediate was formed (0.039 moles of MSA and 0.0264 moles of acetic anhydride, 24 h, 25 °C) without detectable amounts of any aromatic molecules. The intermediate was separated using a 2:1 mixture of hexanes (99.9%, Fisher Scientific) and ethyl acetate (99.9%, Fisher Scientific) by flash chromatography using Supelco® spherical flash silica (45–75 μm). To identify the structure of the intermediate, this molecule was analyzed by 2D NMR correlation spectroscopy (COSY), heteronuclear multiple bond correlation (HMBC), heteronuclear multiple quantum coherence (HMQC), and high resolution mass spectroscopy (HRMS) [40] (see Fig. A1 of Appendix A).

^1H NMR (400 MHz, Chloroform- d) δ 6.30 (dd, $J = 10.0, 3.8$ Hz, 1H), 6.22–6.12 (m, 1H), 5.47–5.40 (m, 1H), 5.23 (dd, $J = 5.4, 3.8$ Hz, 1H), 3.82 (ddd, $J = 9.3,$

3.8, 2.6 Hz, 1H), 3.73 (dd, $J = 9.3, 4.2$ Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H). HRMS (EI) m/z , calcd for $[C_{12}H_{12}O_7]$: 269.0661; found: 269.0661.

The yields of the aromatic products 3,6-dimethyl phthalic anhydride and 3-methyl phthalic anhydride were also calculated by qNMR. For the dehydration of the Diels-Alder product of DMF and maleic anhydride, the peaks at 7.68 (2H, s, $-CH=$) and 7.62 (2H, s, $-CH=$) corresponding to the molecules 3,6-dimethyl phthalic anhydride and 3,6 dimethyl phthalic acid were integrated. For the dehydration of the Diels-Alder products of 2-methylfuran and maleic anhydride, the yield was calculated by integrating the peaks found between 7.9 to 7.3 ppm corresponding to the three protons of 3-methyl phthalic anhydride and 3-methyl phthalic acid in the aromatics region of the NMR spectra.

3.2.3 Polymer Separation

To establish the complete reaction network, the polymers formed during reaction were characterized. The polymer of furan was prepared by adding 0.00602 moles (0.44 mL) of furan dropwise to MSA while stirring. The reaction was allowed to proceed for 3 h. The resulting solid was filtered, washed three times with deionized water, and dried for at 80 °C 48 h. This polymer was named polymer F. The polymer during the dehydration of the Diels-Alder product was prepared from reactions run at the same conditions in neat MSA as those used to prepare polymer F but with the Diels-Alder product as the reactant. The polymer was isolated by slowly pouring the reaction mixture onto ice packed onto a filtration column. The filtered solid was

washed with ice cold water three times and dried at 80 °C for 48 h. This polymer was named polymer O.

3.2.4 Analytical NMR Experiments

NMR spectra were recorded at 25 °C using a Bruker AV400 NMR spectrometer operating at 400.13 MHz (¹H). The experiments were measured with the following parameters for qNMR38: 30° pulse, preacquisition delay of 6 μs, 64 k data points (corresponding to an acquisition time of 3.96 s at a sweep width of 8278 Hz), relaxation delay of 1 s. Fourier transformation was done and exponential filtering of 0.3 Mz. Phase and baseline corrections were done manually. Integrations were taken over 64 times full width at half height (FWHH) when possible. ¹³C NMR, 2D COSY, 2D HMBC, and 2D HMQC were run using standard parameters of the Bruker AV400 spectrometer. A test of linearity for phthalic anhydride and oxanorbornene dicarboxylic anhydride (**3**) in dimethyl sulfoxide was performed using the qNMR parameters giving a correlation coefficient $R^2 > 98\%$ in both cases. A large correlation coefficient indicates that qNMR is an accurate technique to use to determine reaction conversion, yield, and selectivity.

3.2.5 Attenuated Total Reflectance (ATR) Infrared Spectroscopy

ATR-IR spectroscopy was used to identify the functional groups of the polymers formed during reaction. A Nicolet 8700 FTIR spectrometer equipped with a DTG detector and a Golden Gate single-reflection diamond ATR was used for all IR spectroscopy measurements. The instrument was equipped with a purge gas of de-

humidified air to remove water vapor. The resolution of the instrument was set at 4 cm^{-1} and the number of scans to 16.

3.2.6 Elemental Analysis

Elemental analysis was conducted at Galbraith Laboratories at their facility in Knoxville, Tennessee. The carbon and hydrogen content of the isolated polymers were analyzed using a PerkinElmer 2400 Series II CHNS/O analyzer at Galbraith Laboratories. The oxygen content was determined using a Thermo Finnigan FlashTM Elemental Analyzer and the sulfur content was determined using a LECO SC-432DR.

3.2.7 Karl-Fischer Titration

Karl-Fischer (KF) titration was performed to determine the water content of liquid samples using a Mettler Toledo V20 Volumetric KF titrator. For optimal execution of the KF titration, the sample was buffered with imidazole (Sigma-Aldrich, 99%) so that the pH of the solution was in the range between 4 and 8 in dry methanol (Hydranal[®]). MSA was found to have a water content of 1.80 wt. % water.

3.3 Results and Discussion

3.3.1 Diels-Alder Reaction of Furan and Maleic Anhydride

The Diels-Alder reaction of furan and maleic anhydride was run without solvent at room temperature in a 600 mL Parr reactor. After 4 h of reaction, the Diels-Alder product (**3**), furan (**1**), and maleic anhydride (**2**) were detected. No other side products were detected. A 96% yield to the Diels-Alder product of furan and maleic

anhydride (**3**) was obtained for reactions run using a 1.4 mol basis of furan and maleic anhydride. For reactions run using 1.4 mole basis of furan and maleic anhydride, the temperature of the reactor increased to 84 °C after 40 minutes of reaction (Figure A2) and the pressure of the reactor increased as well due to the evaporation of furan into the head space of the reactor (Figure A2).

Running the Diels–Alder reaction at three different scales (0.69 mol, 1.4 mol, 2.1 mol of each reactant) revealed that the reaction is resistant to thermal runaway due to the reduction of the equilibrium constant at high temperatures (Figures A2 and A3). This observation is contrary to the solvent-free normal Diels–Alder reaction which can thermally runaway and forms explosive mixtures [29]. Doubling and tripling the loading of both **1** and **2** did not lead to an increase in the peak reaction temperature (92 °C). In fact, as the reaction temperature approached 150 °C, the Diels–Alder product (**3**) was converted back to the starting reactants [41]. Separate experiments in which **3** was heated to different temperatures confirmed this observation with the Diels–Alder product converting to the starting reactants before melting. When the Parr reactor was equipped with an insulated jacket, the peak reactor temperature plateaued at ~92 °C (Figure A5). This suggests again that the intrinsic thermodynamics of the reaction govern the peak reactor temperature.

Guidelines have been described to classify a reaction as occurring “in-water” versus “on-water” based on the solubility of the reactants. Depending on the reactants and solvent used, substantial rate accelerations by Marcus trans-phase H-bonding are

possible [42]. A reaction occurs “in-water” if both reactants are soluble. For phthalic anhydride synthesis, the Diels–Alder reaction of furan and maleic anhydride was run in the presence of a small amount of water. It has been shown that running this reaction in the presence of water results in rate increases and serves to absorb some of the heat of the reaction at the risk of hydrolysis side reactions [29]. As a reference, maleic anhydride can be hydrolyzed to maleic acid at room temperature [43]. As shown in Table 3.1, adding 21 mL of water to the reaction mixture decreased selectivity from 81% to 66% after 1 h of reaction. Adding 35 mL of water to the reactor resulted in only a 35% yield of the Diels-Alder product. Adding 10 mL of water to the reactor resulted in an increase in the peak reactor temperature and in the hydrolysis of the anhydride functional group. Experiments probing the equilibrium of reaction indicate that the conversion of the Diels-Alder product, **3**, to the starting materials increases in the presence of water at similar temperatures and concentrations (Figure A6). No rate enhancements were observed for the Diels–Alder reaction between furan and maleic anhydride were observed in the presence of water. Maleic anhydride’s solubility in water places it in the transition between ‘on water’ and ‘in-water’ where opposing normal H-bonding effects on both reactants in water can also inhibit the ‘on-water’ effect, despite the physical appearance of the two-phase system [42].

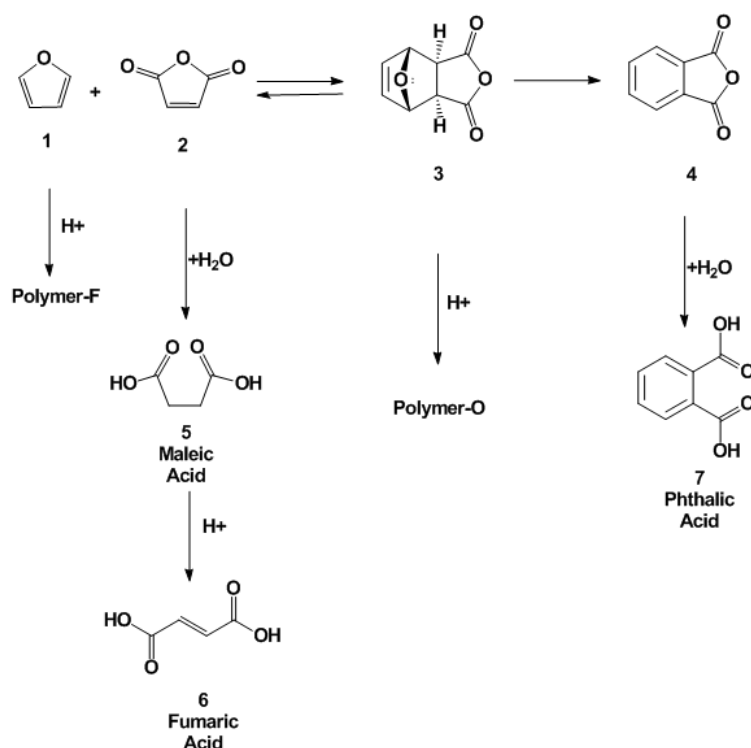
Table 3.1 Selectivity of Diels-Alder reaction of furan (0.69 moles) and maleic anhydride (0.69 moles) to oxanorbornene dicarboxylic anhydride after 1 h of reaction

Solvent and amount	Selectivity to oxanorbornene (3) (%)
heptane, 20 mL	74
Solvent-free	81
water, 10 mL	68
water, 21 mL	62
water, 35 mL	32

3.3.2 Dehydration of *exo*-4,10-dioxa-tricyclo[5.2.1.0]dec-8-ene-3,5-dione (**3**)

The dehydration of the Diels-Alder product, oxanorbornene dicarboxylic anhydride (*exo*-4,10-Dioxa-tricyclo[5.2.1.0]dec-8-ene-3,5-dione, **3**), was investigated in neat MSA at three different temperatures (25, 80, and 120 °C). MSA was selected as the reaction promoter because it is a nonoxidizing, biodegradable alternative to sulfuric acid with high thermal stability [44, 45]. Within 5 minutes of reaction a brownish, black tar-like residue appeared at the three temperatures investigated. After reaction completion, phthalic anhydride (**4**), phthalic acid (**7**), maleic anhydride (**2**), maleic acid (**5**), and fumaric acid (**6**) were all detected by proton NMR (Scheme 3.2). No furan was detected in the NMR spectra.

The formation of by-products was assigned to two major pathways. Decomposition of oxanorbornene dicarboxylic anhydride (**3**) by the retro Diels-Alder reaction to maleic anhydride (**2**) and furan (**1**) resulted in the polymerization of furan which readily occurs in acid [19] and the polymerization of the Diels-Alder product (Scheme 3.2) [19]. As a control experiment, the dehydration of the Diels–Alder product of DMF and maleic anhydride, 1,7-dimethyl-4,10-dioxa-tricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione, and the Diels–Alder adduct of 2-methylfuran and maleic anhydride, *exo-cis*-1-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride were conducted in neat MSA at 25 °C (Table 3.2).



Scheme 3.2 Reaction channels for the formation of phthalic anhydride (**4**) and by-products by the conversion of furan (**1**) and maleic anhydride (**2**).

Table 3.2 Selectivity of the dehydration of substituted oxanorbornenes in neat MSA at 25 °C after 3 h.

Substitution of Diels-Alder Product	Aromatics Selectivity (%)
R ₁ =CH ₃ , R ₂ =CH ₃	66
R ₁ =CH ₃ , R ₂ =CH ₃	48
R ₁ =CH ₃ , R ₂ =CH ₃	14

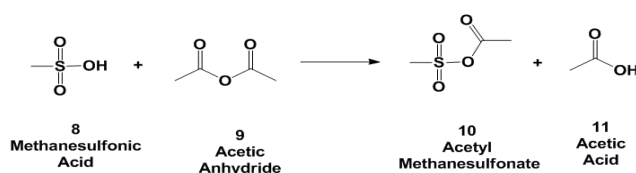
For the dehydration reaction of the Diels-Alder product of furan and maleic anhydride, the aromatic product yield increases with increasing substitution of the Diels-Alder product, suggesting that the methyl groups act as protecting groups for polymerization. For these reactions run in neat MSA at 25 °C after 3 h, minimal amounts of maleic anhydride (<5% yield) were detected. Control experiments confirm that maleic anhydride, maleic acid, and fumaric acid are stable at 25 °C in MSA. Because of the stability of maleic anhydride in this reaction environment, the yield of maleic anhydride was used as a measure of the extent of the retro-Diels–Alder reaction. To confirm that there are two side reaction channels, the reaction was run in neat MSA at 25 °C for 3 h and the resulting solid product was isolated and analyzed by ATR-IR spectroscopy and by elemental analysis. The ATR-IR spectrum of the isolated polymer (polymer O) and polymer formed by the polymerization of neat furan in MSA (polymer F) at the same conditions have distinctly different absorption bands

(Figure A7). In the region characteristic of carbonyl stretching frequencies (1670–1820 cm^{-1}), the oxanorbornene polymer has several absorption bands while the furan polymer does not. The IR spectrum of furan was consistent with characteristic vibrations of the furyl group in polyfuran previously found [19]. The elemental composition of the two polymers are different (Polymer F – 64.08, 5.66, 29.31% C, H, O and Polymer O – 55.92, 4.74, 37.10%, C, H, O), supporting the idea that there are two decomposition pathways. ^1H NMR samples taken of the isolated polymers revealed that the samples are free of residual phthalic acid and furan.

As observed by others for similar Diels-Alder products [33], the retro-Diels–Alder reaction competes with the acid promoted dehydration for the Diels-Alder product of furan and maleic anhydride. Running at lower reaction temperatures decreased the losses associated with the retro-Diels–Alder reaction to 24%. The optimal results in neat MSA were obtained at 25 °C where a 14% yield of phthalic anhydride was achieved after 3 days of reaction (23% yield of phthalic anhydride plus phthalic acid). This yield is similar to results reported for other oxanorbornene dicarboxylic anhydride systems in neat acids [33, 35]. However, 62% of the oxanorbornene dicarboxylic anhydride was converted directly to unidentified by-products.

3.3.2.1 Mixed-Sulfonic Carboxylic Anhydrides

Because of the poor yields obtained using neat MSA, dehydration of the oxanorbornene dicarboxylic anhydride was also conducted using mixed sulfonic carboxylic anhydrides. Mixed sulfonic carboxylic anhydrides are strong acylating agents that have been shown to rapidly cleave the ether rings with high selectivity to their ring-opened products [37]. Mixtures of acetic anhydride and methanesulfonic acid formed acetyl methanesulfonate (**10**) at room temperature after 5 minutes of reaction (Scheme 3.3). The formation of acetyl methanesulfonate (**10**) was tracked with varying ratios of MSA and acetic anhydride in the mixture (Figure A8).



Scheme 3.3 Formation of mixed sulfonic-carboxylic anhydride from MSA and acetic anhydride.

The dehydration of **3** was further studied using binary mixtures of MSA and acetic anhydride at 25 °C to cleave the ether ring. In this reaction the mixed anhydride is consumed, generating MSA and acetic acid and the oxanorbornene is dehydrated to phthalic anhydride. Unlike the reaction run in pure MSA, the reaction medium was yellow until 2 h of reaction. The reaction products and by-products were monitored by qNMR and it was found that the oxanorbornene dicarboxylic anhydride signal disappeared after two hours of reaction with the appearance of phthalic anhydride (**4**)

as well as another unidentified compound (this compound is the diacetate (**12**), see below). The reaction temperature was then increased to 80 °C for 4 h and the disappearance of the unidentified compound was correlated to the appearance of phthalic anhydride, indicating that this compound is an intermediate. After 4 hours, phthalic anhydride, maleic anhydride, and acetic acid peaks due to the formation of the mixed anhydride were detected by proton NMR (Appendix A9). No maleic acid or fumaric acid was detected indicating that the reaction medium was nearly water-free, and no furan was detected by NMR as well. In addition, only 5% of the oxanorbornene dicarboxylic anhydride was converted to maleic anhydride by the retro-Diels–Alder reaction. Running the reaction to completion, an 80% selectivity to phthalic anhydride and an 87% selectivity to aromatics (phthalic anhydride and acid) was obtained.

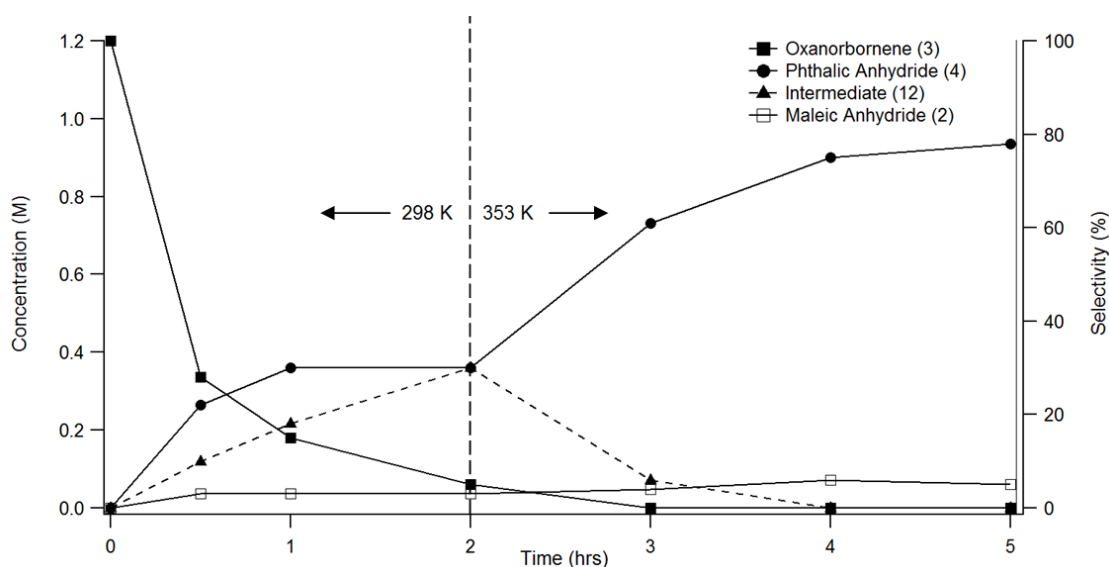


Figure 3.1 Time evolution of phthalic anhydride (**4**) and intermediate (**12**) selectivity. The reaction was run at 298 K for 2 h followed by a 4 h period at 353 K in 62 mmol of MSA and 11 mmol of acetic anhydride.

As a control experiment, the dehydration reaction was run using the same composition of MSA and oxanorbornene dicarboxylic anhydride, but replacing acetic anhydride with maleic anhydride, acetic acid, or methanesulfonic anhydride (Table 3.3). As in the neat MSA experiments, using maleic anhydride the reaction mixture turned blackish brown after a few minutes of reaction. A 14% yield to phthalic anhydride was obtained at 25 °C for 2 h and then at 80 °C for 4 h. This shows that despite maleic anhydride's ability to uptake water to form maleic acid in the presence of MSA, the increase in yield of the reaction is not due to the absence of water. A separate experiment was conducted using the same composition of MSA and oxanorbornene dicarboxylic anhydride, but using an equivalent molar ratio of acetic acid as maleic anhydride and acetic anhydride. Once again, the mixture turned blackish-brown after a few minutes of reaction and a 6 % yield to phthalic anhydride was at 25 °C for 2 h then 80 °C for 4 h. A separate experiment was conducted using the same composition of MSA and oxanorbornene dicarboxylic anhydride, but using an equivalent molar ratio of methanesulfonic anhydride as maleic anhydride and acetic anhydride. The mixture also turned blackish-brown after a few minutes of reaction and a 4% yield of phthalic anhydride was obtained following 2 h of reaction at 25 °C and then 4 h at 80 °C. Finally, an experiment was conducted using the same composition

of MSA and oxanorbornene dicarboxylic anhydride, but using an equivalent molar ratio of methanesulfonic anhydride as maleic anhydride and acetic anhydride. The mixture turned blackish-brown after a few minutes of reaction and a 23% yield of phthalic anhydride was obtained at 25 °C for 2 h and then at 80 °C for 4 h. Although methanesulfonic anhydride has a similar structure as acetic anhydride, its effect on the reaction is drastically different, indicating the favorable properties of acetic anhydride.

Table 3.3 Selectivity to phthalic anhydride. These reactions were run at 25 °C for 2 h followed by a 4 h period at 80 °C.

Solvent Composition:	Selectivity to Phthalic Anhydride (%)
78 mmol MSA	11
62 mmol MSA, 11 mmol Acetic Acid	6
62 mmol MSA:11 mmol Maleic Anhydride	15
62 mmol MSA: 11 mmol Acetic Anhydride	80
62 mmol MSA: 11 mmol Methanesulfonic anhydride	23

The observation of the diacetate (**12**) by NMR suggests a plausible reaction mechanism (Figure 3.2) for this dehydration. The mixed sulfonic-carboxylic anhydride (**10**) is attacked by the bridging oxygen of the oxanorbornene leading to a ring-opened product. The added acetal group then leans over the resonance stabilized product and

is subsequently attacked by acetic acid to form the diacetate observed (**12**). In the presence of acid and heat the diacetate is converted to phthalic anhydride (**4**).

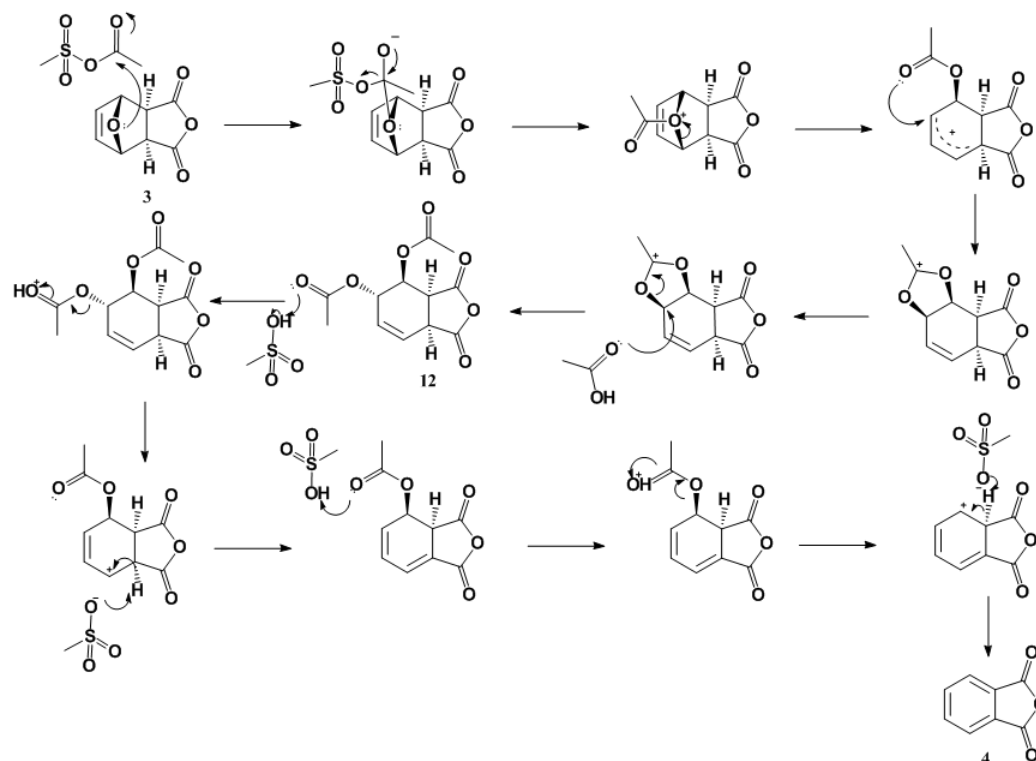


Figure 3.2 Proposed reaction mechanism for the dehydration of the Diels-Alder product.

Running the reaction at different molar ratios of MSA (**8**) to acetic anhydride (**9**) provides further insights into the mechanism for the conversion of the oxanorbornene dicarboxylic anhydride to phthalic anhydride. For these experiments, the total volume of the reactor was held constant and the reactor temperature was maintained at 25 °C for 1 day. Conversion of the oxanorbornene increased with increasing ratios of MSA (**8**) to acetic anhydride (**9**) (Figure 3.2). This is because some acidity is required to open the oxanorbornene ring. The selectivity of phthalic

anhydride is maximized in the presence of excess acid supporting the proposed reaction mechanism. At intermediate molar ratios, selectivity to the diacetate intermediate increased, going through a maximum. At larger molar ratios of MSA (8) to acetic anhydride (9) the carbon balance did not completely close, suggesting some selectivity losses associated with the polymerization of the oxanorbornene dicarboxylic anhydride. Thus, the acid promoted dehydration competes with ring-opening using mixed-sulfonic carboxylic anhydrides. With decreasing ratios of MSA to acetic anhydride, more maleic anhydride appeared suggesting that the rate of ring opening decreases with decreasing acidity as indicated by the drop in conversion.

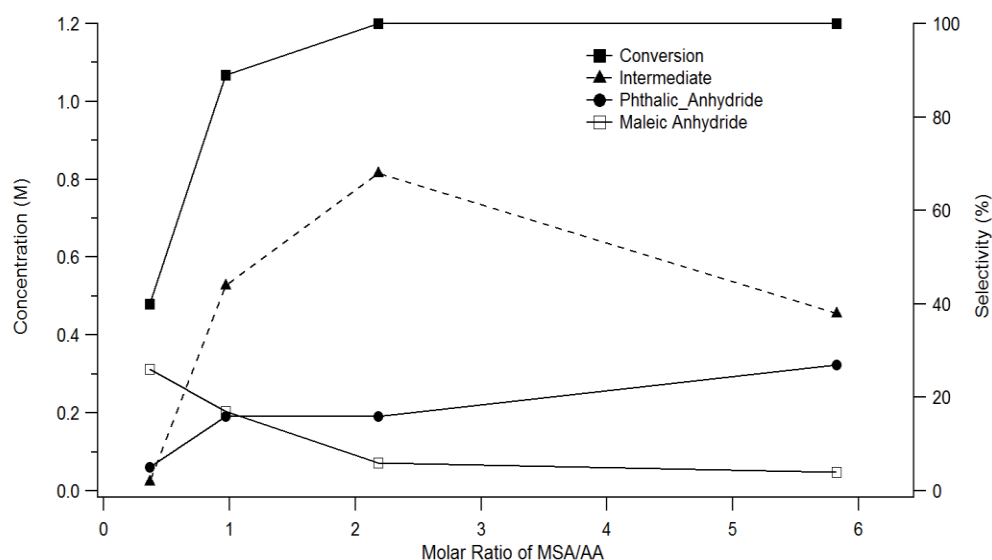


Figure 3.3 Yield of phthalic anhydride as a function of the molar ratio acetic anhydride and MSA. Reactions were performed for 24 h at 25 °C using a 1.2 M concentration of oxanorbornene dicarboxylic anhydride.

Selective dehydration of oxanorbornene compounds is inherently difficult. Oxanorbornene dicarboxylic anhydride (**3**) is heat sensitive and undergoes the retro-Diels–Alder reaction leading to the formation of furan and maleic anhydride. In the acidic environment required by dehydration reactions, furan readily polymerizes, leading to low selectivity. These limitations can be avoided by running the reaction in binary mixtures of MSA (**8**) and acetic anhydride (**9**) in two stages: in the first stage, the oxanorbornene ring is cleaved at 25 °C leading to the formation of a stable intermediate (**12**), and in the second stage, the reaction temperature is increased to 80 °C to drive the reaction to completion leading to a selectivity as high as 80% to phthalic anhydride. At industrial scales, phthalic anhydride may be extracted or separated from the reaction mixture by chromatography or by precipitation. Acetic acid and residual anhydride may be distilled from the reaction mixture and the acetic anhydride regenerated via ketene [46]. MSA may also be reused recycling all of the key reactants.

3.4 Conclusions

In this chapter, the development of a renewable route for the production of phthalic anhydride is described. The process consists of two steps: Diels–Alder cycloaddition of furan and maleic anhydride followed by dehydration of the oxanorbornene dicarboxylic anhydride to produce phthalic anhydride. High yields (96%) for the Diels–Alder cycloaddition of furan and maleic anhydride were obtained under solvent-free conditions. We demonstrate that the Diels–Alder reaction of furan

and maleic anhydride is kinetically self-limiting for thermodynamic reasons. By using binary mixtures of MSA and acetic anhydride to ring-open the oxanorbornene, the selectivity of phthalic anhydride can be increased from 11% in neat MSA to 80% using mixed sulfonic-carboxylic anhydrides under the same conditions. This ring-opening strategy may find use for the dehydration of other oxanorbornene dicarboxylic anhydrides and for the conversion of furans to aromatics.

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Chapter 4

DIELS-ALDER AND DEHYDRATION REACTIONS OF BIOMASS-DERIVED FURAN AND ACRYLIC ACID FOR THE SYNTHESIS OF BENZOIC ACID

4.1 Introduction

The shale gas revolution has created opportunities for the development of efficient processes for the production of aromatic commodity chemicals from biomass. This is due to the shift in cracker feedstock to natural gas which reduces the availability of benzene, toluene and xylenes (BTX), the aromatic building blocks of the chemical industry [1]. One route for the synthesis of aromatics is the Diels-Alder reaction of biomass-derived furans with a dienophile followed by dehydration of the Diels-Alder product to form aromatic chemicals. The selection of furan and dienophile may allow routes for renewable aromatics production that may be commercially viable. Two biomass-derived furans obtained from biomass are furfural and 5-(hydroxymethyl)furfural (HMF). The global market of furfural was estimated to have been around 300,000 tons in 2013 [2]. Furfural yields of up to 96% can be obtained from corn-stover [3]. Thus, finding efficient routes to aromatics from furfural is of interest.

Sequential Diels-Alder-dehydration routes to aromatics from furfural and HMF have been investigated, and typically, reactions of furfural-derived furans are more unselective. 2,5-Disubstituted furans, such as oxidized derivatives of HMF and 2,5-

dimethylfuran (DMF), have been reacted by sequential Diels-Alder-dehydration reactions with ethylene to produce terephthalic acid intermediates and *p*-xylene with high selectivity (> 81% under the best conditions and HMF derivative) using Lewis and Brønsted acid-containing solid catalysts [4]. The reaction of DMF and ethylene is particularly selective with yields as high as 90%. The high selectivity observed is presumably due to protecting methyl groups at the α - and β - carbon positions of the furan ring. In the case of hemicellulose-derived furans, such as 2-methylfuran and furan, selectivity to the aromatic products, toluene and benzene, decreases to 46 and 35%, respectively, at 90% conversion because of polymerization side-reactions of the unsubstituted furan [5]. Although routes for the conversion of unsubstituted furans to aromatics exist, side reactions associated with the polymerization of furan and the use of high-pressure ethylene at high temperatures make these routes more challenging to commercially implement. Therefore, the discovery of routes to toluene and particularly benzene-derived monomers for consumer products and goods from abundant, non-edible biomass feedstocks that are selective could be useful.

Benzene is an important commodity chemical used for the synthesis of Nylon-6, polycarbonates, phenolic resins, and epoxy resins. These polymers are used for the manufacture of everyday consumer goods such as DVDs and toothbrushes. The yearly production of benzene is about 47 million tons, a portion of which is alkylated to isopropylbenzene (cumene) and oxidized to produce acetone and phenol (11 million tons produced annually) [6]. Benzene is also hydrogenated to cyclohexane which is

converted to caprolactam for Nylon 6 synthesis. Biomass-derived benzoic acid can serve as a drop-in replacement to produce many of the consumer products and polymers typically produced by benzene (Figure 4.1). Using known industrial processes, benzoic acid can be transformed, into high-volume commodity chemicals such as phenol, caprolactam, glycol dibenzoates and sodium and potassium benzoate, key intermediates in the synthesis of consumer products and polymers [7].

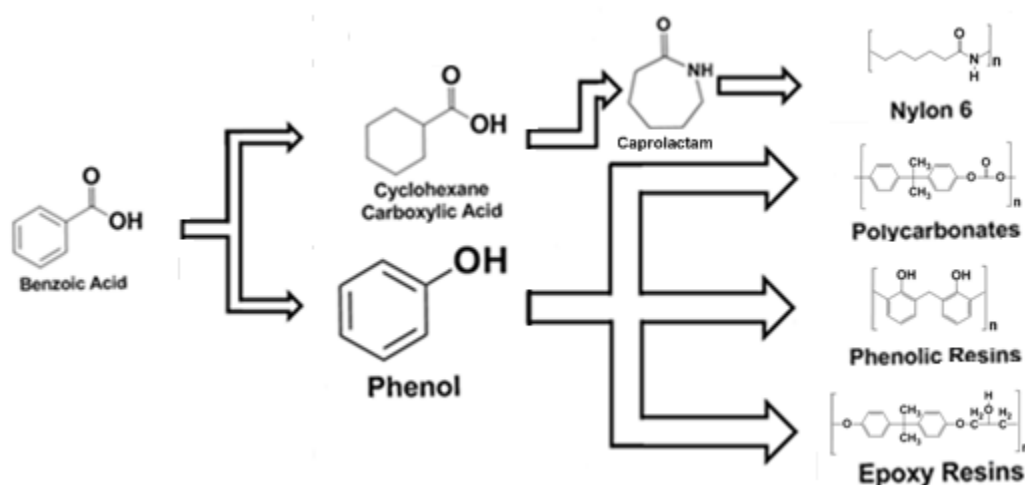
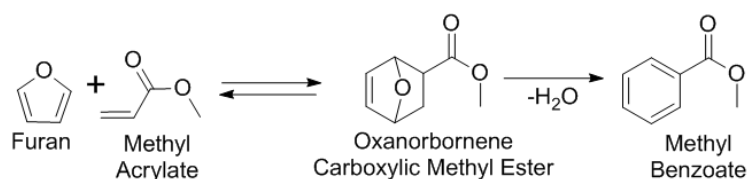


Figure 4.1 Conversion of benzoic acid to nylon 6, polycarbonates, phenolic resins, and epoxy resins.

In this chapter, Diels-Alder and dehydration reactions to selectively produce benzoic acid from biomass beginning with the furfural-derived molecule, furan are investigated. Furan and methyl acrylate (or acrylic acid) are shown to react in a two-step Diels-Alder and dehydration reaction protocol to produce methyl benzoate or benzoic acid (Scheme 4.1). Furan is industrially manufactured from biomass by the

decarbonylation of furfural in 99% yield [8]. Acrylic acid could be produced renewably from biodiesel (glycerol) by catalytic routes or from cellulose by chemocatalytic and biological routes [9]. For example, acrylic acid can be produced from glucose by retro-aldol condensation to form lactic acid followed by dehydration [10]. Biologically, glucose can be converted to acrylic acid in 92% yield using *E. coli* and there are current efforts aimed at commercializing the production of renewable acrylic acid [11].

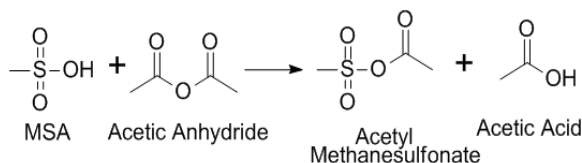


Scheme 4.1 Reaction sequence for the conversion of furan to methyl benzoate.

A biomass-based route to benzoic acid that has previously been considered is the formic acid-mediated deoxygenation of the glucose-derived materials quinic acid and shikimic acid [12]. Quinic acid was converted to benzoic acid in a one-step process achieving ~90% yield. Quinic acid can be isolated from natural sources such as cinchona bark, coffee beans, tobacco or by fermentative production from glucose. Here, we report a route to benzoic acid from biomass-derived furfural, which is commercially produced using improvements to the Quaker Oats batch process originally commercialized in the 1920s.

We explored a number of different catalytic materials and conditions for the selective synthesis of benzoic acid and found that a two-step Diels-Alder and dehydration reaction procedure is best at this time. Running the reaction in a two-step procedure is of particular importance to avoid unwanted side reactions of furan and methyl acrylate (or acrylic acid) in the presence of Lewis and Brønsted acids required for these Diels-Alder and dehydration reactions. Molecular sieves having the zeolite BEA topology containing Lewis acidic centers in the +4 oxidation state are excellent catalysts for Diels-Alder reactions of furan [13]. The absence of strong Brønsted acidity in these materials is important to avoid unwanted side reactions of furan. The activity of Hf-, Zr-, and Sn-BEA Lewis acidic zeolites as compared to other Lewis and Brønsted acid homogeneous and heterogeneous catalysts for Diels-Alder reactions of furan has not been reported. We also explored a number of different catalytic and non-catalytic strategies for the dehydration of the Diels-Alder adduct (oxanorbornene carboxylic methyl ester or acid) and found that dehydration in binary mixtures of methanesulfonic acid (MSA) and acetic anhydride containing the mixed anhydride, acetyl methanesulfonate is most selective. Acetyl methanesulfonate is formed by the reaction of MSA and acetic anhydride (Scheme 4.2). This compound is known to behave as a strong acylating agent in a variety of other reactions, such as for ether bond cleavage and esterification [14]. The effect of oxanorbornene concentration, stereochemistry and functional group on the dehydration of these compounds using mixed anhydrides has not been reported. Taken together, these findings suggest that a two-step Diels-Alder and dehydration reaction protocol using Lewis acidic-zeolites

and mixed anhydrides could be applied to the synthesis of other valuable aromatic chemicals such as benzophenone and benzaldehyde from furfural or its derivatives in high selectivity.



Scheme 4.2 Formation of mixed sulfonic-carboxylic anhydride from MSA and acetic anhydride.

4.2 Experimental Methods

4.2.1 Materials Synthesis

Hf-, Zr-, Sn- and Si-BEA were prepared by a hydrothermal synthesis method. 15 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, 99%) was added drop wise to a solution 16.032 g of tetraethylammonium hydroxide (TEAOH, 35 wt%, Sachem) with constant stirring. After mixing for 90 min, either HfCl₂O·8H₂O (Alfa Aesar, 98+%), ZrCl₂O·8H₂O (Sigma Aldrich, 98 %) or SnCl₄·5·H₂O (Sigma Aldrich, 98%) in 1.943 g of DI water were added. The mixture was aged at room temperature until the solution decreased in weight by 13 g due to ethanol evaporation; additional 1.15 g of water. To the resulting solution, 1.59 g of HF (Acros, 48 wt %) was added causing the formation of a thick paste. The final gel composition was as follows: 1.0 SiO₂: 0.005 MO₂: 0.54 TEAOH: 7.5 H₂O: 0.54 HF (M=Hf, Zr, and Sn). Si/M~100 samples were

similarly prepared except with the addition of 0.18 g (4 wt. %) dealuminated BEA seed crystals after HF addition [32]. The crystallization was carried out in rotating (40 rpm) Teflon-lined stainless steel autoclaves (Parr) at 140 °C for 14 days. The product was collected by filtration and washed thoroughly with DI water. The zeolites were calcined in air in a two-step process first at 120 °C for 2 h and then at 550 °C for 3 h using a ramping rate of 3 °C/min. Spent Hf-BEA catalyst was regenerated at identical conditions as calcination. Si-BEA was prepared following an identical procedure except without the addition of a metal source and dealuminated Beta seed crystals.

To determine the effect of Lewis acid metal addition to the zeolite sample, a sample was prepared by simple impregnation of M (M=Hf, Zr, Sn) into Si-BEA (EF-M-BEA) to compare to samples where Lewis acid metal addition was done during hydrothermal synthesis. The appropriate amount of $\text{HfCl}_2\text{O} \cdot 8 \text{H}_2\text{O}$, $\text{ZrCl}_2\text{O} \cdot 8 \text{H}_2\text{O}$ or $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were added to 0.3 g of water. The solution was added dropwise to 0.3 g of Si-BEA with continuous mixing. The powder was stirred for 4 h at room temperature then put into a convection oven at 100 °C overnight. The sample was then calcined in air using a ramping rate of 5 °C/min up to a temperature of 580 °C and held at this temperature for 4 h.

Sn-MCM-41 with a Si/Sn ratio of 50 was prepared following a previously reported hydrothermal synthesis procedure [18]. HfO_2 (Sigma Aldrich, 98%), ZnCl_2 (Sigma Aldrich), and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, 99%) were used as purchased. H-

BEA (Guild associates) contained 17.5% clay binder by weight and a SiO₂/Al₂O₃ ratio of 34 (including binder).

4.2.2 Analytical Methods

X-ray powder diffraction (XRD) patterns were recorded on a Phillips X'Pert X-ray diffractometer using Cu K α radiation. The micropore volumes of samples were determined using nitrogen adsorption isotherms at -196 °C measured using a Micromeritics 3-Flex instrument. All samples were degassed for 8 h under vacuum at 300 °C before adsorption measurements. The micropore volumes and surface areas of BEA zeolites were determined using the t-plot method. Scanning electron microscopy (SEM) images were taken using a JOEL JSM-7400 F high resolution scanning electron microscope.

4.2.3 Diels-Alder Reactions

Furan (Sigma-Aldrich, 99+ %), methyl acrylate (Sigma-Aldrich, 99 %, contains ≤ 100 ppm monomethyl ether hydroquinone as inhibitor), and acrylic acid (99.0+%, Sigma-Aldrich) were stored under an inert atmosphere and used as received. Diels-Alder reactions were performed in 20 mL thick-walled glass vials (Sigma-Aldrich). Reactions were run under solvent free conditions at 25 °C for 24 h. 6.9 mmols of furan, 1.79 mmols of acrylic acid and 0.10 g of zeolite BEA catalyst or the appropriate amount of homogeneous Lewis acid catalyst were loaded into the reactor. For reactions run using Si-BEA catalyst, an identical mass of catalyst was used as for

the Lewis acid metal-containing zeolites. Reactions run using methyl acrylate were run using 1.36 mmoles of methyl acrylate. For all reactions, 0.166 mmoles of *p*-xylene ($\geq 99\%$, Sigma-Aldrich) was used as an internal standard, which was added before addition of the catalyst. The reactor was flushed with N₂ gas before reaction, sealed and transferred to an optimchem digital balance stirrer temperature controlled at 25 °C for reaction.

Yield and selectivity were determined by using the internal standard (*p*-xylene) and the peaks corresponding to the endo and exo isomers of the cycloadduct (3.18 and 2.49 ppm for oxanorbornene carboxylic acid, 3.76 and 3.67 ppm for the ester and 2.9 and 2.57 ppm for the Diels-Alder adduct of 2,5-dimethylfuran and acrylic acid). For the Diels-Alder reaction of 2-methylfuran and acrylic acid, the moles of acrylic acid converted were used to calculate yield and selectivity since it was known that the mass balance is closed under these conditions of reaction. NMR spectra were recorded at 25 °C with a Bruker AVIII600 NMR spectrometer operating at 600.13 MHz (¹H). A test of linearity for acrylic acid using the qNMR parameters gave a correlation coefficient $R^2 > 98\%$ indicating the accuracy of this technique. ¹³C NMR, 2D COSY, 2D HMBC, and 2D HMQC were run using standard parameters of the Bruker AV400 spectrometer.

The Diels-Alder products (oxanorbornenes) were isolated by flash chromatography. The solution was filtered with a 0.2 micron filter (Corning) and rotavapped for 1 h at 25 °C to remove furan. The remaining solution was run through

a flash chromatography column containing Versa Flash spherical flash silica (45-75 μm) using a 2:1 solution of hexane (99.9%, Fisher Chemical) to ethyl acetate (99.9%, Fisher Chemical) as the mobile phase.

Oxanorbornene carboxylic methyl ester (endo- and exo-2-carbomethoxy-7-oxabicyclo[2.2.1]hept-5-ene) [33]:

^1H NMR (600 MHz, Chloroform-*d*) δ 6.44 (dd, $J = 5.9, 1.7$ Hz, 1H_{endo}), 6.39 (dd, $J = 5.9, 1.6$ Hz, 1H_{exo}), 6.35 (dd, $J = 5.8, 1.7$ Hz, 1H_{exo}), 6.23 (dd, $J = 5.8, 1.5$ Hz, 1H_{endo}), 5.21 – 5.18 (m, 1H_{exo}), 5.18 – 5.14 (m, 1H_{endo}), 5.10 – 5.06 (m, 1H_{exo}), 5.05 – 5.00 (m, 1H_{endo}), 3.73 (s, 3H_{exo}), 3.65 (s, 3H_{endo}), 3.12 (dt, $J = 9.0, 4.2$ Hz, 1H_{endo}), 2.44 (dd, $J = 8.6, 3.9$ Hz, 1H_{exo}), 2.17 (dt, $J = 11.6, 4.3$ Hz, 1H_{exo}), 2.11 (ddd, $J = 11.4, 9.3, 4.7$ Hz, 1H_{endo}), 1.62 – 1.57 (m, 1H_{endo} , 1H_{exo}).

Oxanorbornene carboxylic acid (endo- and exo-2-carboxylic-7-oxabicyclo[2.2.1]hept-5-ene):

^1H NMR (600 MHz, Chloroform-*d*) δ 6.45 (dd, $J = 5.8, 1.7$ Hz, 1H_{endo}), 6.41 (dd, $J = 5.8, 1.6$ Hz, 1H_{exo}), 6.36 (dd, $J = 5.8, 1.7$ Hz, 1H_{exo}), 6.30 (dd, $J = 5.8, 1.6$ Hz, 1H_{endo}), 5.22 (d, $J = 1.8$ Hz, 1H_{endo}), 5.21 – 5.17 (m, 1H_{exo}), 5.12 – 5.08 (m, 1H_{exo}), 5.04 (dd, $J = 4.9, 1.7$ Hz, 1H_{endo}), 3.17 (ddd, $J = 9.0, 4.8, 3.8$ Hz, 1H_{endo}), 2.47 (dd, $J = 8.5, 3.8$ Hz, 1H_{exo}), 2.20 – 2.07 (m, 1H_{endo} and 1H_{exo}), 1.62 – 1.54 (m, 1H_{endo} and 1H_{exo}).

4.2.4 Dehydration Reactions

Methanesulfonic acid (99.5 %+, Sigma Aldrich) and acetic anhydride (99.4%, Fisher Scientific) were used as received and stored under N₂. 31 mmoles of MSA and 7.7 mmoles of MSA or 5.3 mmoles of acetic anhydride in addition to 0.208 mmol (0.025 grams) of sulfolane (99 %+, Sigma-Aldrich) which was used as an internal standard were added to a 20 mL disposable scintillation vial. Sulfolane was selected as internal standard because of its high stability against strong acids as well as good thermal stability. The mixture was then stirred for 5 minutes at room temperature. In the case of acetic anhydride, MSA and acetic anhydride reacted to form acetyl methanesulfonate [¹H NMR (400 MHz, CDCl₃) δ 2.28 (3H, s, COCH₃), 3.33 (3H, s, SO₂CH₃)] [34]. The oxanorbornene was slowly added while stirring. The vial was then flushed with nitrogen. Conversion and selectivity were calculated using the internal standard by qNMR.

The intermediate was isolated using a flash chromatography column containing Versa Flash spherical flash silica (45-75 μm) using a 3:1 solution of hexane (99.9%, Fisher Chemical) to ethyl acetate (99.9%, Fisher Chemical) as the mobile phase.

4,5-diacetoxycyclohex-2-enecarboxylic acid (Note, the methyl group attached to the carboxylic acid group of 5-(methoxycarbonyl)cyclohex-3-ene-1,2-diyl diacetate is hydrolyzed during flash chromatography as was observed for methyl benzoate):

^1H NMR (600 MHz, Chloroform-*d*) δ 6.31 (ddt, J = 8.7, 6.8, 1.7 Hz, 1H), 5.71 (dt, J = 9.6, 2.3 Hz, 1H), 5.51 (q, J = 2.5 Hz, 1H), 5.00 (dt, J = 5.6, 2.4 Hz, 1H), 3.01 (dd, J = 6.8, 4.7 Hz, 1H), 2.57 (dt, J = 11.4, 5.4 Hz, 1H), 2.24 (d, J = 11.8 Hz, 1H), 2.17 (s, 4H), 2.14 (s, 3H). HRMS (EI) m/z , calcd for $[\text{C}_9\text{H}_{12}\text{O}_5]$: 201.0763; found: 201.

See Figures B14 and B15 for 2D NMR COSY and HMQC spectra of this compound.

4.2.5 TPD-TGA

TPD-TGA experiments were carried out using a CAHN 1000 microbalance mounted within a high vacuum chamber, as described elsewhere. The base pressure of the system was 1×10^{-8} Torr. During TPD-TGA measurements, the sample weight could be recorded continuously using the microbalance and the desorbing species monitored using a UTI quadrupole mass spectrometer. The peaks intensities at selected m/e from the mass spectra are reported here in arbitrary units (a.u.). The sample temperature was measured with a thermocouple placed near the sample, and the heating rate during desorption was maintained at 10 $^{\circ}\text{C}/\text{min}$ by a temperature controller. Unless otherwise noted, the samples were heated in vacuo to 500 $^{\circ}\text{C}$, then cooled in vacuo, prior to exposing them to the vapors of the adsorbate of interest. The solid samples were exposed to diethyl ether at room temperature using 3 Torr of vapor until there was no further uptake. The system was then evacuated for 1 h before beginning the TPD-TGA experiment.

4.2.6 UV-Vis Spectroscopy

UV-Vis spectroscopy experiments in this chapter were run using a UV-Vis spectrometer (Jasco V-550) equipped with a diffuse-reflectance cell with BaSO₄ as the reference material.

4.2.7 FTIR Spectroscopy

FTIR spectra were collected on a Mattson Galaxy FTIR with a diffuse-reflectance attachment (Collector II) purchased from Spectra-Tech Inc. Spectra were collected at 2 cm⁻¹ resolution. The samples were initially heated to 500 °C in flowing He to remove any water. After cooling the samples to room temperature, acetonitrile-d₃ vapors were exposed to the sample, with the excess acetonitrile then flushed from the solid using flowing He at 1 cm³/s.

4.2.8 Elemental Analysis

Chemical analyses of zeolite samples were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) measured by Galbraith Laboratories at their facility in Knoxville, Tennessee.

4.2.9 ²⁹Si NMR Spectroscopy

The powdered sample was packed into a 4 mm Bruker rotor, and all the ²⁹Si NMR experiments were performed at a Bruker AVIII500 solid NMR spectrometer with a magnetic field of 11.7 T using a HX double resonance MAS

probe. The NMR spectra were collected at room temperature and the MAS frequency was 10 kHz with a 90 ° pulse width of 2.65 μ sec at 145 W. The number of scans was set to 2048 with a delay time of 30 seconds. $^1\text{H} \rightarrow ^{29}\text{Si}$ CP-MAS NMR spectra were acquired with a 90 ° pulse length of 2.65 μ sec at 145 W and a recycle delay of 5 s with the number of scans set to 2048.

4.3 RESULTS AND DISCUSSION

4.3.1 Materials Characterization

X-ray diffraction, nitrogen adsorption and SEM were used to characterize the microporous and mesoporous catalysts tested. Samples of Hf-, Zr- and Sn-BEA with a Si/M ratios~100 and 200 (M=Hf, Zr or Sn containing 3.38, 2.01 and 2.45 or 1.57, 1.08 and 1.08 wt% HfO₂, ZrO₂, and SnO₂ respectively) were prepared based on existing protocols (see experimental section for details) [15]. As a control, samples containing extraframework (EF) Hf-, Zr-, and Sn- oxides, prepared by impregnation over a sample of all-silica zeolite BEA, were also investigated. The X-ray diffraction patterns of the calcined samples are consistent with the structure of zeolite Beta, with no evidence of impurities and undetectable amounts of amorphous material (Figure B1). Micropore volumes measured using nitrogen adsorption isotherms show that Hf-, Zr-, Sn- and Si-BEA all have the high microporous volumes (~ 0.20 cm³/g) characteristic of zeolite BEA samples of good quality (Table B1) [16]. Nitrogen adsorption experiments of the EF-M-BEA (M=Hf, Zr, and Sn) indicate that the metal is

impregnated on the external surface of the zeolite particles forming metal oxide (MO_2) nanoparticles, as was previously observed [17]. The X-ray diffraction pattern of Sn-MCM-41 (Si/Sn=50) was well defined and displayed the characteristic (100), (110) and (200) reflections corresponding to hexagonal array channels (Figure B2) [18]. The nitrogen-adsorption isotherm of Sn-MCM-41 displayed the type IV profile characteristic of mesoporous MCM-41 materials (Figure B3) with the expected high single point BET surface area of $720 \text{ m}^2\text{g}^{-1}$ (determined at $P/P_0=0.302$) [18]. SEM images of the synthesized zeolites show the typical morphology of zeolite BEA prepared in fluoride media [19] having a truncated square bipyramidal particle shape [20] and a size between 2-5 micrometers (Figure 4.2a).

Spectroscopic investigations of the synthesized zeolite Beta catalysts were performed to verify the effect of metal precursor addition before zeolite crystallization on the catalyst. ^{29}Si MAS NMR spectroscopy shows resolved signals at ca. 116, 115, 113, 112, and 111 ppm and very few framework defects (tetrahedral-atom vacancies) in all cases, but broader signals for Hf-, Sn-, and Zr-BEA as compared to Si-BEA (Figure B4). This broadening, which increases as metal content increases, greatly reduces the resolution of the experiments. For zeolites with Si/M ratios of around 100, only three broad resonances are apparent at ca. -115, -113, and -111 ppm. This was previously observed in the case of Ti and Zr-heteroatom incorporation in zeolite BEA [21]. UV-Vis spectra shows a progression in the energy of the absorption edge in the order $\text{HfO}_2 < \text{EF-Hf-BEA} < \text{Hf-BEA}$, which has been previously reported for the Sn

analogue for this series [22]. An increase in the absorption edge energy is correlated with a decrease in the metal cluster size, suggesting smaller clusters of HfO_2 in Hf-BEA than in EF-Hf-BEA. For the different metals tested, a progression in the energy of absorption edge was observed for the different metals tested in the order of EF-Sn-BEA < EF-Zr-BEA < EF-Hf-BEA (Figure B5).

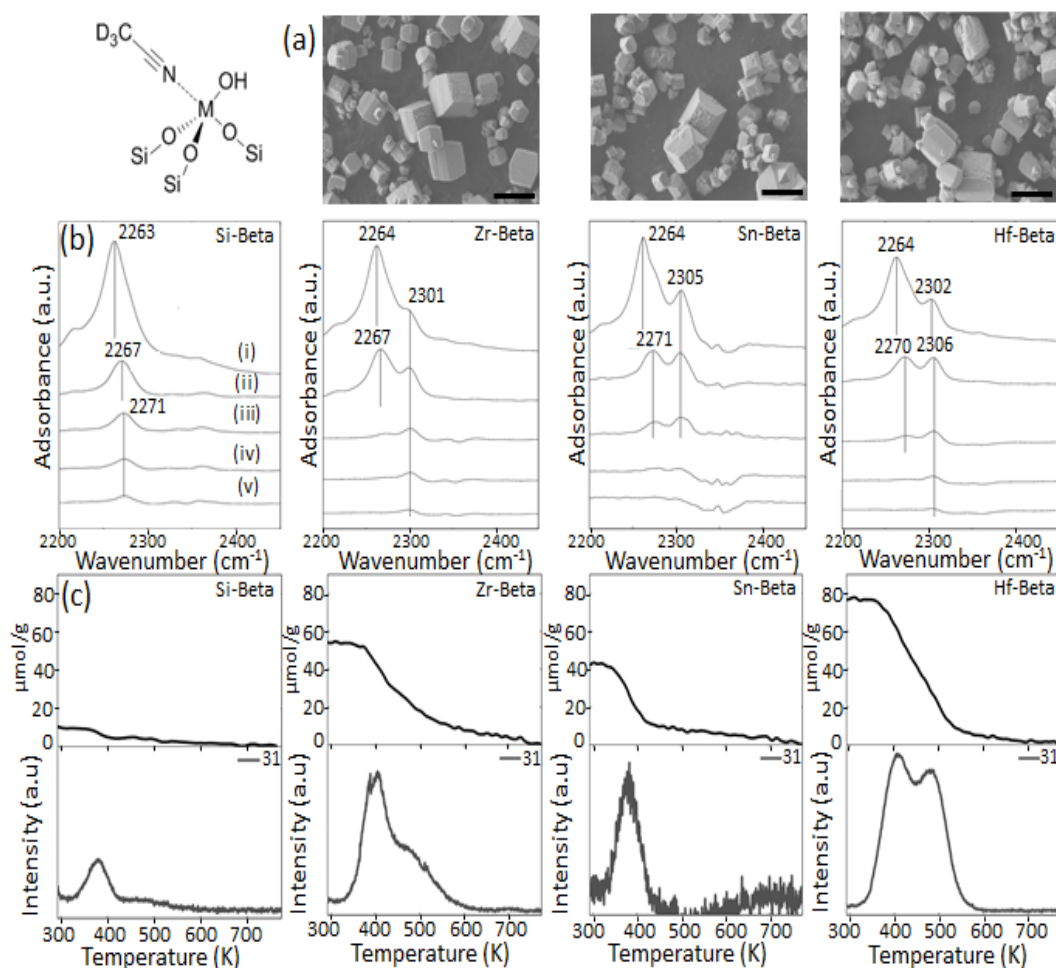


Figure 4.2 Characterization of zeolite BEA samples by (a) SEM, (b) FTIR and (c) TPD-TGA. (a) SEM images of the synthesized zeolites. Scale bar 6 μm. (b) FTIR spectra of M-BEA (i) in pure He flow at RT immediately after removing CD₃CN vapor; in He flow after heating to 60 °C for (ii) 1 min; (iii) 2 min; (iv) 3 min; (v) 5 min. (c) TPD (lower curves) and TGA (upper curves) traces of diethyl ether dosed onto M-BEA (M=Hf-, Sn-, Zr-, or Si). Diethyl ether was monitored in the mass spec

by its $m/e=31$ peak. The Si/M ratios of the zeolites are Si/Hf=219, Si/Sn=230, and Si/Zr=325 respectively.

Fourier-transform infrared (FTIR) spectra of acetonitrile- d_3 adsorbed in M-BEA, Si-BEA, and EF-M-BEA (Figure 4.2b) confirm the presence of acetonitrile- d_3 interaction with Lewis acid sites in M-BEA zeolites. Spectra of Hf-BEA at room temperature after acetonitrile- d_3 exposure show two ν (C-N) stretches, centered at 2264 cm^{-1} corresponding to a bulk acetonitrile- d_3 stretch and a higher frequency 2302 cm^{-1} peak, corresponding to acetonitrile- d_3 (C-N) stretch associated with acetonitrile- d_3 interaction with the Lewis acid site. As acetonitrile- d_3 is removed from the sample by mild heating and continued flushing with He, the 2264 cm^{-1} feature decreases, while the feature at 2302 cm^{-1} narrows and shifts to 2306 cm^{-1} . The Zr- and Sn-BEA samples show similar behavior with the final higher frequency peak shifts being 2301 and 2305 cm^{-1} , respectively. The Si-BEA sample does not show any features at the higher frequency after evacuation temperatures confirming the absence of adsorption sites for acetonitrile- d_3 . FTIR spectra of acetonitrile- d_3 on EF-M-BEA, prepared by impregnation of the metal precursor after zeolite crystallization, were identical to those for Si-BEA, a result that is consistent with no Lewis acids present which interact with the acetonitrile- d_3 in these samples (Figure B6). Reaction results for Diels-Alder reaction of furan and acrylic acid of EF-M- and M-BEA zeolites are consistent with FTIR experiments (see Table 4.1).

M-BEA and EF-M-BEA zeolites were also characterized by temperature programmed desorption (TPD) thermogravimetric analysis (TGA) to probe whether the Lewis acids exist as isolated active sites. It has been shown that diethyl ether forms one-to-one complexes with framework sites in Sn-BEA by TPD-TGA [22]. Similar probe-molecule studies using diethyl ether were conducted to characterize these samples. Hf-BEA (Hf/Si=219) adsorbs 80 $\mu\text{mol/g}$ of diethyl ether, an amount that is very close to the Hf concentration of 72 $\mu\text{mol/g}$ as determined by ICP-OES (Figure 4.2c). Similarly, Zr- and Sn-BEA samples adsorb 55 and 43 $\mu\text{mol/g}$ of diethyl ether. On the other hand, Si-BEA only adsorbed 10 $\mu\text{mol/g}$. The TPD traces show a +10 $^{\circ}\text{C}$ peak temperature shift when comparing metal-containing to Si-BEA zeolites with shoulder peaks shifted + 80 $^{\circ}\text{C}$ or greater for Hf and Zr-BEA zeolites (Figure 4.2c). The difference in peak temperature and shape when comparing Si to M-BEA zeolites suggests that there are different adsorption sites for these two classes of materials. However, because desorption from porous materials is coupled with diffusion and readsorption, caution must be used in the interpretation of this peak. The calculated activation energies of desorption of these shoulder peaks for Hf- and Zr-BEA assuming monomolecular adsorption of diethyl ether and a pre-exponential factor of 10^{13} s^{-1} are 136 and 133 kJ/mol respectively. Correspondingly, the activation energy of desorption of diethyl ether from Sn-BEA is 111 kJ/mol. Increasing the metal concentration in Hf- and Zr-BEA zeolites led to an increase in diethyl ether adsorption to 150 and 120 $\mu\text{mol/g}$ for Si/Hf=127 and Si/Zr=149, which is in excess of the theoretical adsorption amounts for these materials of 130 and 110 $\mu\text{mol/g}$ as

determined by ICP-OES. These results are consistent with previous TPD-TGA studies on Sn-BEA zeolite (Si/Sn=118) showing that while some of the excess diethyl ether is associated with silanol groups in the zeolite—or unspecific adsorption—the diethyl ether coverage approximately corresponds to the calculated concentration of M-BEA zeolite, suggesting the formation of 1:1 complexes of diethyl ether and the Lewis acid sites [22]. TPD-TGA of diethyl ether dosed on EF-M-BEA samples, which were prepared by metal impregnation of Si-BEA zeolite (see experimental methods section), were similar to that of Si-BEA dosed with diethylether (Figure B7). The TPD-TGA results indicate that the Hf-, Zr- and Sn- metal cations are present as isolated metal sites in uniformly dispersed in M-BEA samples as supported by UV-Vis spectroscopy, N₂ adsorption and ²⁹Si MAS NMR experiments. TPD-TGA results also indicate that metal cations in EF-M-BEA samples exist as metal clusters on the external surface of the zeolite particles as supported by UV-Vis and N₂ adsorption experiments.

4.3.2 Sequential Diels-Alder-Dehydration Reaction of Furan and Methyl Acrylate

Furan and methyl acrylate were reacted in *n*-heptane to screen for activity in the one-step sequential Diels-Alder-dehydration reaction to methyl benzoate (Scheme 4.1) using heterogeneous Brønsted (H-BEA) and Lewis acidic (Hf-, Zr- and Sn-BEA) zeolite catalysts. In all cases for the heterogeneous catalysts tested for the Diels-Alder-dehydration reaction (200 °C for 7 h with 40 psi of nitrogen) no aromatic product was detected. This was accompanied by fouling of the catalysts as indicated by the

darkening (coking) of the solids. The darkening of the catalyst, which occurred at low conversions (<3%) of methyl acrylate, suggests that these catalysts are deactivated by deposition of byproducts. It was found that doubling the catalyst amount of Hf-Beta leads to an increased conversion (11%) of methyl acrylate but still no aromatics production (150 °C for 7 h with 40 psi nitrogen under solvent-free conditions). The sequential Diels-Alder-dehydration reaction has been run successfully using 2,5-dimethylfuran and ethylene (>99% conversion 90% selectivity to aromatics) at high temperature because those two reactants are much more stable in the presence of acids than furan and methyl acrylate [4-5, 23]. Aromatics production by Diels-Alder-dehydration reactions of 2,5-disubstituted furans and methyl acrylate conversion to unknown (by ^1H NMR) side products illustrate two of the major challenges for this Diels-Alder-dehydration reaction: the sensitivity of furan to the Brønsted and Lewis acids used and the polymerization of methyl acrylate at these conditions. To overcome these two challenges, the Diels-Alder and dehydration reactions were run in two separate steps.

4.3.3 Diels-Alder Reaction

The Diels-Alder reaction of furan and methyl acrylate was run without solvent to minimize potential costs and the environmental impact of the process. Without a catalyst no reaction was observed over 24 h at 25 °C. To assess the role of thermodynamic equilibrium on yield, the equilibrium constant was determined for a range of temperatures (see Appendix B and Figure B8 for experimental details), and

using Van't Hoff's relation the equilibrium conversion as a function of temperature was obtained (See Figure B9). These data indicate that the reaction is kinetically limited at temperatures below 27 °C and equilibrium limited at temperatures above 57 °C. Therefore a highly active catalyst is needed to achieve high conversion at low temperatures (57 °C or below).

Fraile et al. [24] investigated the reaction of methyl acrylate and furan (25 °C, 24 h) using titanium chloride and zinc chloride supported on silica. At 75% conversion, the turnover frequency was only 0.025 h⁻¹ for TiCl₄/SiO₂, the most active catalyst. Furthermore, the reacting mixture contained 67% wt./wt. catalyst. We investigated Hf-, Zr- and Sn-containing zeolite Beta catalysts due to their demonstrated ability to catalyze the Baeyer-Villager [25] and MPV [16] reactions by coordination to the carbonyl groups of the reactants. For example, using *in situ* IR spectroscopy Sn-Beta has been shown to activate the carbonyl group of cyclohexanone for the Baeyer-Villiger oxidation [25]. The three materials are very effective catalysts for the Diels-Alder reaction of furan. Hf-Beta, in particular, catalyzes this reaction at a turnover frequency of 1.9 h⁻¹ at 25 °C (average over 24 h under solvent-free conditions). A turnover frequency of 3.7 h⁻¹ is achieved at 35 °C after 3 h. A 25% yield of the oxanorbornene was achieved after 24 h of reaction at 25 °C using Hf-Beta (Si/Hf=219), at a corresponding turnover frequency of 1.9 h⁻¹ (Table B2). Turnover frequencies of 2.4 h⁻¹ and 2.0 h⁻¹ were achieved using Zr- (Si/Zr=325) and Sn-Beta (Si/Sn=230) zeolites after 24 h of reaction at 25 °C. The turnover frequencies for Hf-,

Zr-, and Sn-Beta zeolites are approximately one hundred times higher than those observed for $\text{TiCl}_4/\text{SiO}_2$ at 25 °C [24]. For the Si/M~200 materials which were prepared by an unseeded synthesis method, catalyst amount was directly proportional to product yield (Figure B10). However, Si/M~100 catalysts, prepared using a seeded synthesis method, have lower turnover frequencies (Table B2) and for these samples there is no 1:1 correlation between catalyst amount and moles of product produced, with a lower product production rate than expected (114.74 vs. the 180.72 $\mu\text{mol product gcat}^{-1}\text{h}^{-1}$ calculated based on turnover rates for the ~200 materials). This may be caused by the increasing abundance of silanol groups in the Si/M~100 materials as compared to the unseeded Si/M~200 zeolites (see Figure B11 for ^1H - ^{29}Si CP-MAS NMR spectra) which leads to the increasing hydrophilic character of the zeolite and possibly catalyst poisoning [21a].

Hf-Beta (Si/Hf=127) which had nearly twice the amount of silanols, as determined by CP-MAS as compared to Zr-Beta (Si/Zr=149), possessed roughly half the turnover frequency of its counterpart (Table B2). Because the amount of product formed and catalyst amount were not proportional for these materials, the Si/M~100 zeolite catalysts were not investigated further. Running the Diels-Alder reaction of furan and methyl acrylate using H-Beta—that is, a catalyst with Brønsted acid sites—resulted in a much lower turnover frequency of the metal site (0.19 h^{-1}) as compared to the Lewis acid metal-containing catalysts at 31% yield of the oxanorbornene product.

It also led to a variety of byproducts due to the reactivity of furans with Brønsted acids.

Investigations of the Diels-Alder reaction of furan and acrylic acid, the more reactive dienophile, for a series of heterogeneous and homogeneous catalysts showed that Hf-, Zr- and Sn-Beta have nearly the same reactivity with an turnover frequency of $\sim 5 \text{ h}^{-1}$ at roughly 50% yield of the oxanorbornene (Table 4.1). Si-Beta (no other metal heteroatoms present) provided a 13% yield to the Diels-Alder product showing that confinement of furan and acrylic acid alone is sufficient to catalyze the formation of this Diels-Alder adduct, although at much lower rates. Hafnium, zirconium, and tin impregnated Si-Beta zeolite catalysts (EF-Hf, EF-Zr, and EF-Sn-Beta respectively), that is, materials with similar composition that do not contain Hf, Zr, or Sn present in the synthesis gel, show almost no reactivity achieving only 13% conversion. Bulk HfO_2 , tested independently, shows reaction rates that are more than ten times slower (0.092 h^{-1}) than Hf-Beta. When using the Brønsted acid zeolite, H-Beta, as a catalyst for the Diels-Alder reaction of furan and acrylic acid, a much lower turnover frequency of 0.35 h^{-1} at a 44% yield of the oxanorbornene was detected by ^1H NMR. This was accompanied by darkening of the catalyst. The mesoporous tin-silicate Sn-MCM-41 provided a 15% yield to the corresponding oxanorbornene and a turnover frequency of the tin site of 1.4 h^{-1} after 24 h of reaction. The lower turnover frequency and yields when comparing Sn-MCM-41 and Sn-Beta materials suggest that confinement effects in the zeolite Beta framework play a role in reactivity. Also, based

on adsorption shifts from deuterated acetonitrile studies, the more blue-shifted hydrolyzed site of Sn-Beta zeolite (2317 cm^{-1}) is a stronger Lewis acid than the tin site present in Sn-MCM-41 (2312 cm^{-1}), suggesting that the stronger acidity corresponds to a higher activity [26]. Hf-, Sn-, and Zr-Beta zeolites compared to bulk metal oxides and metal-impregnated Si-Beta zeolite.

Table 4.1 Yield and Turnover Frequency of the Diels-Alder Reaction of Furan and Acrylic Acid Catalyzed by Lewis Acidic Zeolite Beta and other Materials^a

Catalyst	Metal:Hf Molar Ratio ^b	Yield (%) ^c	Turnover Frequency [h ⁻¹] ^d
Hf-Beta	1.0	51	5.1 (3.8)
Sn-Beta	1.0	48	5.0 (3.6)
Zr-Beta	0.68	31	4.5 (2.6)
Si-Beta	-	13	-
EF-Hf-Beta	1.1	12	1.1 (~0.00)
EF-Sn-Beta	1.1	16	1.5 (0.27)
EF-Zr-Beta	1.1	14	1.3 (0.090)
H- Beta	12	44	0.35
HfO ₂	11	10	0.092
Sn-MCM-41	1.1	15	1.4
ZnCl ₂	4.9	18	0.36
AlCl ₃	11	8	0.076

Reactions were run under solvent free conditions at 298 K for 24 h. 6.9 mmols of furan and 1.79 mmols of acrylic acid and 0.10 g of zeolite Beta catalyst corresponding to 0.0075 mmol loading

of Hf or 0.42 mol% Hf with respect to acrylic acid (Si/Hf=219). Metal contents of the zeolites in bold were determined by ICP-OES. All reactions were ~100% selective to the oxanorbornene with respect to the acrylic acid. An identical mass of Si-Beta catalyst was used compared to the amount of metal containing zeolite catalysts.

^aReactions run without a catalyst gave no yield of oxanorbornene under these reaction conditions.

^bThe molar ratio is defined as the moles of metal, where the metal can be Hf, Zr, Sn, Al, or Zn in catalyst divided by the moles of Hf in Hf-Beta (0.0075 mmoles).

^cYield was calculated with respect to acrylic acid conversion.

^dTurnover frequency calculated by moles of oxanorbornene produced divided by moles of metal in catalyst. Values in parenthesis are turnover frequencies calculated after subtracting the yield of product associated with Si-Beta.

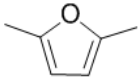
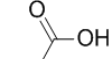
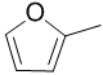
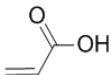
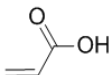
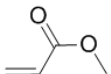
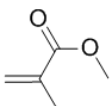
Because the Diels-Alder reaction of furan and methyl acrylate (or acrylic acid) is an exothermic reversible reaction, an optimal temperature profile was devised to maximize the yield at shorter times using a combination of kinetics (Figure B12), thermodynamics, and approximate kinetic rate expressions (see Equations B2 and B3). Equation B3 was used to find a (optimal) temperature profile using MATLAB. Using the temperature of 4 h at 35 °C and 20 h at 25 °C, a 30% yield of the oxanorbornene

was achieved while minimizing side reactions. Higher temperatures were also applied for the Diels-Alder reaction of furan and methyl acrylate. For example, running the reaction at 35 °C for 24 h provided a 46% yield of the Diels-Alder product of methyl acrylate and furan. However, 16% of the limiting reactant, methyl acrylate, was converted to undetectable side-products (by ^1H NMR spectroscopy). Using another temperature program of 3 h at 40 °C, 5 h at 35 °C, and 24 h at 25 °C, a 67% yield of the Diels-Alder adduct of acrylic acid and furan was obtained.

Hf-Beta zeolite was also shown to be recyclable and maintained similar reactivity over three runs for the Diels-Alder reaction of furan and acrylic acid. In between each reaction the catalyst was washed with methanol and dried at 120 °C overnight. Regeneration of the catalyst by calcination did not lead to a significant drop in activity (Figure B13). TGA studies of the regenerated catalyst indicated that there was no significant leaching of Hf after each reaction cycle as evidenced by the adsorption of $\sim 90\text{ }\mu\text{mol/g}$ of diethyl ether for the spent catalyst (experimental error of TGA $\sim 20\text{ }\mu\text{mol/g}$). FTIR spectra also show a 2310 cm^{-1} adsorption shift associated with CD_3CN interaction with Hf in Hf-Beta. XRD patterns of the regenerated catalyst indicated no significant degradation of the catalyst structure. Hf-Beta zeolite was able to catalyze the reaction of furans and various alpha-Beta unsaturated ketones and acids (Table 4.2). Turnover frequencies of 2.80 and 3.88 h^{-1} for the reaction of 2-methyl and 2,5-dimethylfuran with acrylic acid were similar to those observed for the Diels-Alder reaction of furan and acrylic acid of 5.08 h^{-1} . The reaction of furan and methyl acrylate

possessed a turnover frequency of 2.50 h^{-1} . For all reactions, endo:exo ratios greater than one were observed, indicating that the kinetically favored product was made in a larger proportion. Running the Diels-Alder reaction of furan and methyl acrylate at 25°C for five days led to a decrease in the endo:exo ratio from 1.9 to 1.7 suggesting a greater extent of retro-Diels-Alder reaction at longer reaction times as previously seen for the Diels-Alder reaction of cyclopentadiene and *p*-benzoquinone catalyzed by Lewis acidic ITQ-2 [27].

Table 4.2. Yield and Turnover Frequency of the Diels-Alder Reaction of Various Furans and Acrylates Catalyzed by Hf-Beta Zeolite

Diene	Dienophile	Yield (%) ^a	Turnover Frequency [h ⁻¹] ^b
		39	3.9
		28	2.8
		51	5.1
		25	1.9
		0	NA

^aYields reported are for the oxanorbornene products

^bTurnover frequency calculated by moles of oxanorbornene produced divided by moles of Hf metal in Hf-Beta.

Reactions were run under solvent free conditions at 298 K for 24 h using 0.50 mL of diene and 0.12 mL of dienophile.

Correspondingly, 4.6 mmol of 2,5-dimethylfuran, 5.6 mmol of 2-methylfuran, or 6.9 mmol of furan and 1.79 mmol of acrylic acid or 1.36 mmol of methyl

acrylate were added and 0.0075 mmol
loading of Hf (Si/M=219).

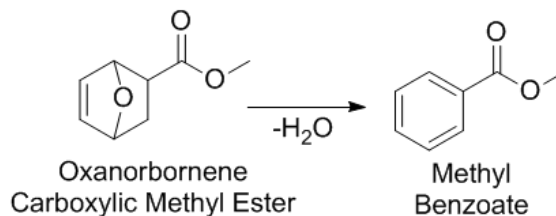
4.3.4 Dehydration of the Diels-Alder Product of Furan and Methyl Acrylate

The dehydration of Diels-Alder products of furan is difficult to accomplish with high selectivity because these molecules are sensitive to heat and they can polymerize in the presence of acids [28]. Retro-Diels-Alder, polymerization, and dehydration reactions are all competing channels for the transformation of the Diels-Alder products and are the principal factors determining product selectivity [28b, 29]. Dehydration of oxanorbornene carboxylic methyl ester catalyzed by the Brønsted acid catalyst, H-Beta zeolite, yielded methyl benzoate in less than 1% selectivity at 100% conversion after 7 h of reaction at 150, 200, and 250 °C. The selectivity to methyl acrylate decreased with increasing temperature from 35% at 150 °C to 33 and 29% at 200 and 250 °C, presumably due to decomposition side-reactions. Furan was also detected following reaction though in much lower selectivity (5.2, 4.1 and 4%) as compared to methyl acrylate at the temperatures investigated. The catalyst fouled as indicated by the change in color possibly due to the formation of organic byproducts from the decomposition of furan, methyl acrylate and/or the oxanorbornene (Figure B9).

To suppress the retro-Diels-Alder reaction, which accounts for at least 35% of the decomposition of the oxanorbornene intermediate at 150 °C, the dehydration

reaction was run homogeneously at lower temperatures in the Brønsted acid, MSA. MSA is a non-oxidizing, biodegradable and a thermally stable alternative to sulfuric acid [30]. Running the reaction in neat MSA (at a temperature of 25 °C for 2 h followed by a temperature increase to 80 °C for 1 h) produced methyl benzoate with a 1.7% selectivity (Table 4.3). The reaction medium was modified to increase selectivity to methyl benzoate by using acetyl methanesulfonate, a mixed anhydride easily formed from MSA and acetic anhydride, to open the ether bond of the oxanorbornene. Under the same reaction conditions, the acetyl methanesulfonate system produced methyl benzoate in 96% selectivity at 100% conversion. Running the reaction using oxanorbornene carboxylic acid, the Diels-Alder product of furan and acrylic acid as the reactant, led to a drop in the selectivity of aromatics from 96% to 43% at 100% conversion under identical conditions of temperature program, concentration and time. Because of the significantly lower selectivity, dehydration of the oxanorbornene ester is the preferred route for aromatics synthesis from oxanorbornene carboxylates as compared to the acid.

Table 4.3. Selectivity of the Dehydration of Oxanorbornene Carboxylic Methyl Ester in Binary Mixtures of MSA and Acetic Anhydride^a



Reactant Concentration (M)	Endo:Exo Ratio	Selectivity (%) ^b
0.13	0.43	96
0.65	0.43	83
0.65	1.89	89

Reactions were run in 31 mmoles of MSA and 5.3 mmoles of acetic anhydride at 25 °C for 2 h followed by temperature increase to 80 °C for 1 h.

^aReactions run in neat MSA resulted in a 1.7% selectivity to the product at 100% conversion (0.13 M concentration, 0.43 endo:exo ratio of oxanorbornene carboxylic methyl ester).

^bSelectivity at 100% conversion

In the case of Brønsted acid (MSA) promoted dehydration, no reaction intermediate was detected. In the case of acyl group promoted dehydration (acetyl methanesulfonate), a stable reaction intermediate was detected. The observation of a

ring-opened acetate intermediate suggests the reaction mechanism depicted in Figure 4.3. The acyl group is an electrophile and attacks the resonance-stabilized cation formed from ring-opening of the bridging oxygen of the oxanorbornene leading to the more stable ring-opened product, 5-(methoxycarbonyl)cyclohex-3-ene-1,2-diyl diacetate. An optimal temperature reaction profile for the dehydration of this oxanorbornene was devised by first running at 25 °C for 2 h to minimize the retro-Diels-Alder reaction and to form a stable intermediate. The temperature is then increased to 80 °C for 1 h to convert the intermediate to methyl benzoate.

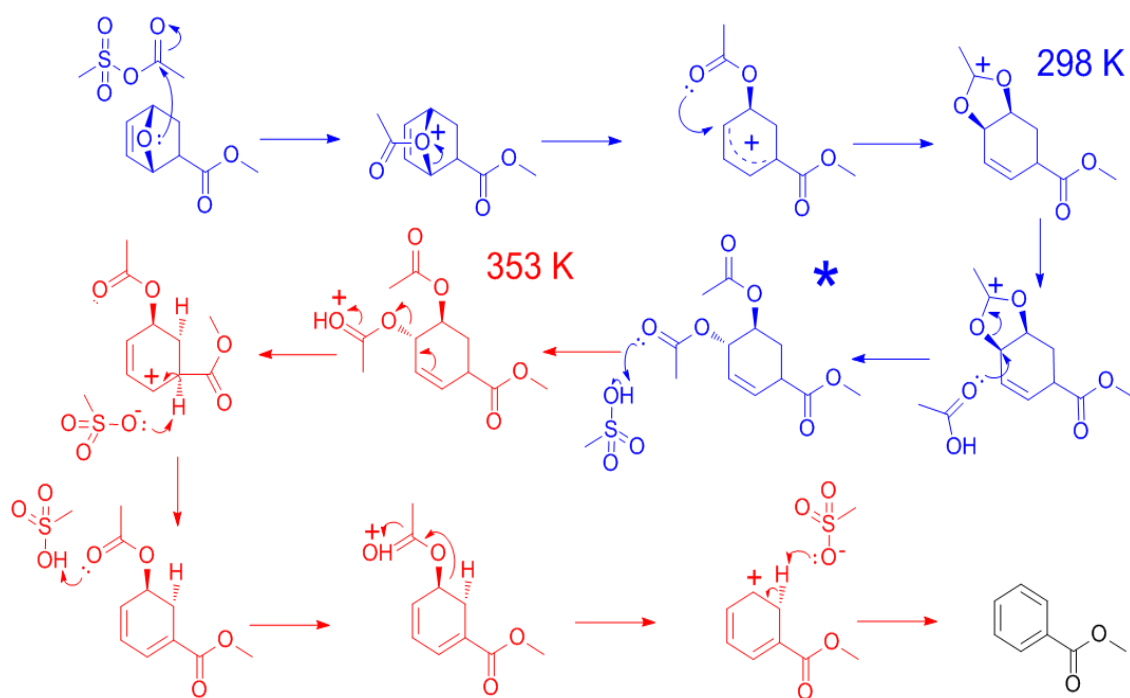


Figure 4.3. Proposed reaction mechanism for the dehydration of oxanorbornene carboxylic methyl ester. The intermediate (5-(methoxycarbonyl)cyclohex-3-ene-1,2-diyl diacetate) is marked with an asterisk. The reaction was run at 25 °C for 2 h (blue

chemical structures) to form a stable intermediate then at 80 ° for 1 h (red chemical structures) to drive the reaction to completion.

The dehydration reaction was also run at different concentrations of oxanorbornene, endo:exo ratios to test the robustness of this dehydration approach (Table 4.3). Increasing the concentration five-fold led to lower (but still acceptable) selectivity of 83% at full conversion. Running the reaction at the same concentration, a change in the endo:exo ratio of the oxanorbornene from 0.43 to 1.89 led only to a slight increase in the selectivity from 83 to 89% at 100% conversion. The selectivity for the dehydration of oxanorbornene carboxylic acid decreased slightly from 43 to 41% selectivity at 100% conversion when running at a higher concentration (0.36 M) at an identical endo:exo ratio and identical reaction conditions. Although this dehydration process consumes one mole of acetic anhydride for each mole of benzoic acid produced, the acetic acid produced can be recycled into acetic anhydride using well-known process chemistry [31]. These results indicate that high concentrations of oxanorbornene can be dehydrated selectively within the stoichiometry of the dehydration reaction with the mixed anhydride.

4.4 Conclusions

We report the discovery of routes to toluene and benzene-derived monomers for consumer products and goods from a high-yield hemicellulose derived furan that are selective. Benzoic acid is a potential platform to prepare a number of commodity

chemicals as it can be transformed to precursors to nylon 6, polycarbonates, phenolic resins, and epoxy resins, polymers which make up four of the six major polymers supplied by fossil-fuel-derived benzene (Figure 3.1). We explored a number of different catalytic materials and conditions for the selective synthesis of benzoic acid and found that a two-step Diels-Alder and dehydration reaction procedure is best at this time (Scheme 4.1). Running the reaction in a two-step procedure is of particular importance to avoid unwanted side reactions of furan and methyl acrylate (or acrylic acid) in the presence of Lewis and Brønsted acids required for these Diels-Alder and dehydration reactions. It has been shown that Hf-, Zr-, and Sn-Beta zeolites selectively catalyze the thermodynamically limited Diels-Alder reactions of furans with acrylates with very high activity as compared to other homogenous and other heterogeneous Lewis acid catalyst with no side reactions observed. It was also shown that mixtures of MSA and acetic anhydride selectively dehydrate Diels-Alder adduct with yields of up to 96%, with little effect of the stereochemistry of the Diels-Alder adduct and concentration on the observed selectivity to the aromatic product. Overall, furan can be selectively transformed into benzoic acid in a 96% combined selectivity of the Diels-Alder and dehydration reactions. These findings suggest that a two-step Diels-Alder and dehydration reaction protocol using Lewis acidic-zeolites and mixed anhydrides could be applied to the synthesis of other valuable aromatic chemicals such as benzophenone and benzaldehyde from biomass-derived furfural or its derivatives in high selectivity.

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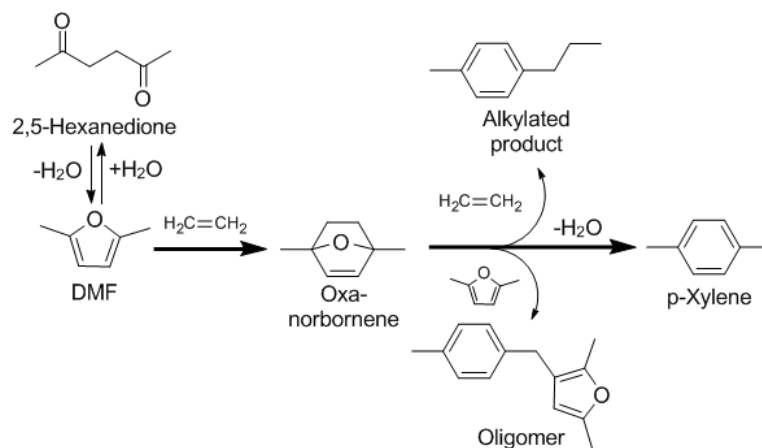
Chapter 5

THE SOLVENT-FREE SYNTHESIS OF *p*-XYLENE FROM 2,5-DIMETHYLFURAN AND ETHYLENE CATALYZED BY METAL-EXCHANGED FAUJASITE ZEOLITES

5.1 Introduction

p-Xylene is an important commodity chemical used for the production of terephthalic acid and polyethylene terephthalate (PET). PET is currently produced from petroleum at a rate of over 31 million tons per year for plastic bottle and textile manufacture [1]. As an alternative to the conventional petrochemical route, a biomass-based route to *p*-xylene was recently demonstrated *via* the Diels-Alder cycloaddition of 2,5-dimethylfuran (DMF) and ethylene to form 1,4-dimethyl-7-oxabicyclo[2.2.1]hept-2-ene (Diels-Alder product) and subsequent dehydration to *p*-xylene over solid acid catalysts (Scheme 5.1) [2]. DMF and ethylene can be obtained from cellulosic biomass. Cellulose, which comprises 40-50% of lignocellulosic biomass such as corn-stover, sugar cane, and bagasse, can be efficiently hydrolyzed to glucose with yields of nearly 100% [3]. Glucose can be subsequently isomerization to fructose, dehydrated to 5-(hydroxymethyl)furfural (HMF), and hydrodeoxygenated to DMF [4]. Ethylene is industrially manufactured from biomass-derived ethanol. For the reaction of DMF and ethylene, three side reactions decrease *p*-xylene selectivity: hydrolysis of DMF to 2,5-hexanedione, alkylation of reaction intermediates by ethylene, and Friedel-Crafts-type reactions of dehydration intermediates resulting in oligomer formation. The rates of the latter two reactions, which are irreversible, may

be decreased by tuning the acidity of the catalyst, increasing the overall selectivity to the desired product [5].



Scheme 5.1 Synthesis of *p*-xylene from DMF and ethylene.

Reaction selectivity and solvent affect the economics and environmental impact of the renewable *p*-xylene production process [6]. Sensitivity analysis was used to show that a 15% decrease in *p*-xylene selectivity increases minimum *p*-xylene cost by 21.7%. The use of *n*-heptane as a solvent for the process adds additional process steps and ~4% of the estimated *p*-xylene cost. Life cycle analysis (LCA) indicates that release of *n*-heptane from the process contributes to marine and freshwater ecotoxicity, water depletion, and fossil fuel depletion [7]. A selective, solvent-free process for the conversion of DMF and ethylene to *p*-xylene could reduce or eliminate these economic and environmental drawbacks. This process would satisfy many of the twelve principles of green chemistry such as having a high atom economy, using renewable feedstocks, being catalytic, and solvent-free [8]. From a green engineering

perspective, a solvent-free process would prevent waste and be designed for separation [9].

To catalyze the conversion of DMF and ethylene to *p*-xylene, zeolites with the framework topologies BEA (zeolite beta) and FAU (faujasite) have been used [2b, 10, 11]. These materials have large-pore three-dimensional architectures whose compositions can be changed by adjusting the silicon to aluminum ratio (Si/Al) of the synthesis gel, post-synthesis cation ion exchange, and other methods. The faujasite structure consists of six-membered double 6-rings (d6R) and sodalite cages (Figure 5.1). The introduction of Al^{3+} into the aluminosilicate structure introduces a charge imbalance compensated by cations: which occupy site I' in the six ring of the d6R, then site II, in the 6-ring of the sodalite cage, facing the supercage, followed by the more exposed site III with decreasing silicon to aluminum ratios [12]. For a given cation, acid strength decreases with decreasing silicon to aluminum ratio of the zeolite framework [13].

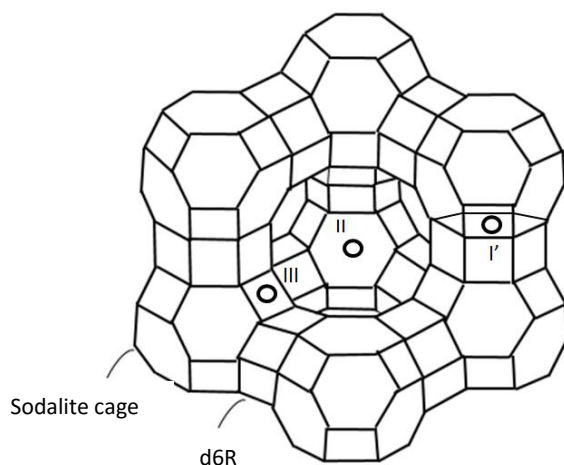


Figure 5.1 Structure of faujasite zeolite, which consists of six-membered double rings (d6R) and sodalite cages. The pore diameter defined by a 12 membered oxygen ring is 7.4 Å. Extraframework cations occupy sites I', II, and III marked in the figure.

The solvent-free conversion of DMF and ethylene to *p*-xylene is not selective when catalyzed by Brønsted acidic zeolites. At 300 °C, HY (FAU, Si/Al=2.6), catalyzes this reaction at 52% *p*-xylene selectivity at 11% DMF conversion, which is better than the selectivity of H-BEA [2b]. In *n*-heptane solvent, H-BEA is more selective for *p*-xylene synthesis than HY [10]. Varying the DMF concentration from 0.44 to 2.56 mM (0.36 wt.% DMF) at 200 °C *n*-heptane decreases *p*-xylene selectivity from 80% to 55% and increases the production of dimers and trimers from 18 to over 50% for reactions catalyzed by HY [11d]. At 250 °C and a 1.0 M concentration (14 wt. %) in *n*-heptane, DMF was converted to *p*-xylene in 90% selectivity at greater than 99% DMF conversion after 24 h for reactions catalyzed by H-BEA. For both HY and H-BEA catalysts, two kinetic regimes governing the rate of *p*-xylene formation have

been identified: a Diels-Alder and dehydration reaction limiting regime [10d,10b]. In the dehydration limiting regime, the rate of *p*-xylene synthesis increases with increasing acid site concentration, and then plateaus in the Diels-Alder cycloaddition limited regime, where the reaction rate is no longer controlled by the dehydration rate [2b].

Metal-exchanged faujasites are solid Lewis acids that can catalyze both Diels-Alder and dehydration reactions. Infrared studies utilizing small probe molecules suggest that Lewis acidity, as opposed to framework basicity, dominates in zeolites ion exchanged with small cations such as the alkali-metals, Li^+ and Na^+ [14]. This property allows these materials to catalyze Diels-Alder and dehydration reactions. For example, NaY catalyzes the Diels-Alder reaction of acrolein and furan [15]. Alkali metal exchanged zeolites X and Y also promote the dehydration of short alcohols [16]. DFT studies suggest that the Lewis acid catalyzed dehydration of oxanorbornene reaction intermediate proceeds through a different mechanism whereby side products, such as alkylated products and oligomers, may not be as readily produced (Scheme 5.1) [17].

In this chapter, the investigation and use of metal-exchanged faujasites as selective catalysts for the solvent-free conversion of DMF and ethylene to *p*-xylene is reported. NaX catalyzes *p*-xylene synthesis with 96% selectivity at 10% DMF conversion at 250 °C. High selectivity to *p*-xylene (> 90%) is maintained at conversions greater than 30%. This result is a major improvement over the 35%

selectivity to *p*-xylene obtained for HY zeolite. These catalysts are more selective for *p*-xylene synthesis than zeolites containing framework molecular sieves, Sn- and Zr-BEA, which yield a ~75% selectivity to *p*-xylene at 30% DMF conversion using *n*-heptane as solvent [11c]. The experimental results indicate that the increase in *p*-xylene selectivity associated with Lewis acidic faujasite catalyst is due to a combination of the effects of Lewis acid type, strength, and extraframework position in the faujasite framework.

5.2 Experimental Methods

5.2.1 Catalyst Preparation and Characterization

Metal-containing faujasites were prepared by ion exchange with chloride or nitrate salts of calcined, commercial faujasites with silicon to aluminum ratios of 40, 2.55, and 1.25 (Zeolyst International) following previously published protocols [18]. Prior to ion exchange or reaction, the sodium faujasites were calcined according to the following temperature program: ramp from room temperature to 80 °C at 2.5 °C/min and held at that temperature for 1 h, ramp at 2.0 °C/min to 120 °C and held at that temperature for 2 h followed by a ramp at 2.0 °C/min to 550 °C and held at this temperature for 8 h in air. In a typical aqueous ion-exchange procedure for preparing potassium X and Y zeolites, 5 g of calcined sodium faujasite was added to 200 mL of a 2.0 M solution of KCl ($\geq 99\%$, Sigma-Aldrich) in deionized water which was stirred at 25 °C for 24 h. After filtration, the sample was ion exchanged twice for 24 h in 200 mL of 1.0 M KCl. Ammonium faujasites were prepared by ion exchange of sodium

faujasites with two exchanges with 1.0 M and one with 2.0 M solutions of ammonium nitrate for at least 6 h at room temperature (Fisher Scientific, 99%). Silver faujasites were prepared by ion-exchange of ammonium faujasites with silver nitrate (J.T. Baker Chemical Company, 99.8%) [19]. Following the final filtration, the sample was washed three times with deionized water and dried overnight at 80 °C. CuY (Si/Al=2.55) was prepared by solid state ion-exchange (SSEI) of HY faujasite (Zeolyst International) with CuCl (Sigma Aldrich, $\geq 99\%$) [20]. Samples treated with bicarbonate salts were washed at 25 °C with 0.05 M solutions for 30 min prior to calcination.

X-ray powder diffraction (XRD) patterns of the zeolite catalysts were measured using a Phillips X'Pert X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The micropore volumes of the zeolites were calculated using the t-plot method from nitrogen adsorption isotherms measured using a Micromeritics 3-Flex instrument at -196 °C. Prior to nitrogen adsorption isotherm measurement, the samples were degassed for 8 h under vacuum at 300 °C. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed using a JOEL JSM-7400 F high resolution scanning electron microscope. Elemental compositions are reported from inductively coupled plasma-atomic emissions spectroscopy (ICP-AES) analysis obtained from Galbraith Laboratories facility in Knoxville, TN.

5.2.2 Reaction Experiments

0.10 g of zeolite or 0.02 g of HY (Si/Al=2.55), 7.22 g of freshly distilled DMF (99%, Sigma-Aldrich), and 0.365 g of *n*-decane (internal standard, 99%, Sigma-Aldrich) were initially charged into a 45 mL closed Parr reactor (series 4703-4714, General Purpose Pressure Vessels). The container was then purged with nitrogen gas, pressurized with ethylene (99.5%, Air Liquide) to 47 bar at room temperature, and heated using a Chemglass oil-bath unit. Reactions run at greater than 10% conversions, were run following the procedure described above except with half the amount of DMF. Experiments examining the hydrolysis of DMF reaction were run using 5.34 g of DMF, 0.5 g of deionized water, and 0.365 g of *n*-decane pressurized to 2.8 bar of nitrogen at room temperature. Mixing inside the reactor was accomplished by using a magnetic stirrer. Following reaction, the Parr reactor was cooled in an ice bath and the product solution was then filtered using a 0.2 μ m Nalgene syringe-filter. Product solutions analyzed by gas chromatography (GC) were diluted in ethyl acetate (HPLC-grade, 99.9%, Sigma-Aldrich) and analyzed using an Agilent 6850 series GC and 5973 MS detector. Products were confirmed by injection of standards. For product solutions analyzed by ^1H NMR spectroscopy: 0.005 mL of the product solution was diluted in 0.5 mL of deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) containing 0.03 vol. % tetramethylsilane (TMS) used as an internal standard (99.8%, Fisher). TOFs (turnover frequencies) were calculated by dividing the moles of *p*-xylene formed by the moles of

extraframework cations in the zeolite, which was determined by elemental analysis (ICP-AES).

5.2.3 Statistical Analysis of Reaction Results: ANOVA

Analysis of variance (ANOVA) was used to test the significance of the ion-exchanged cation element and Si/Al ratio of the faujasite zeolites on the rate of *p*-xylene production [21]. A two-factor factorial design was designed for a signal-to-noise ratio of 2.0, where the signal-to-noise ratio (ρ_{SN}) is defined as:

$$\rho_{SN} = \frac{\delta^*}{\sigma} \quad [\text{Eqn. 5.1}]$$

where δ^* and σ represent the smallest magnitude of the effect desired to be detected and standard deviation. Based on previous data, an estimate of 0.10 was used for the standard deviation expected from experimental results [2b]. A sample size of 12 was chosen based on equation 6 relating the signal-to-noise ratio to the appropriate sample size range.

$$\left(\frac{7}{\rho_{SN}}\right)^2 < n < \left(\frac{8}{\rho_{SN}}\right)^2$$

[Eqn. 5.2]

The experiments were performed systematically, randomly, and analyzed using Minitab software through the *Stat>DOE>Factorial>Analyze Factorial Design* option.

5.3 Results and Discussion

XRD patterns confirm that the faujasite samples retained their crystallinity and were free of impurities and amorphous material following aqueous ion exchange (Figure 5.2). SEM images show that the zeolite catalyst particles have an estimated individual crystallite sizes ranging ~ 0.2 - $2\ \mu\text{m}$ in diameter, having octahedral crystal habits (Figure 5.). The zeolite catalysts have the expected micropore volumes (~ 0.2 - $0.3\ \text{cm}^3/\text{g}$) of these molecular sieves following ion exchange of as determined by nitrogen adsorption experiments. The micropore volumes of these samples generally decrease with increasing molecular weight of the exchanged cation with AgX at the lower end (Table 5.1).

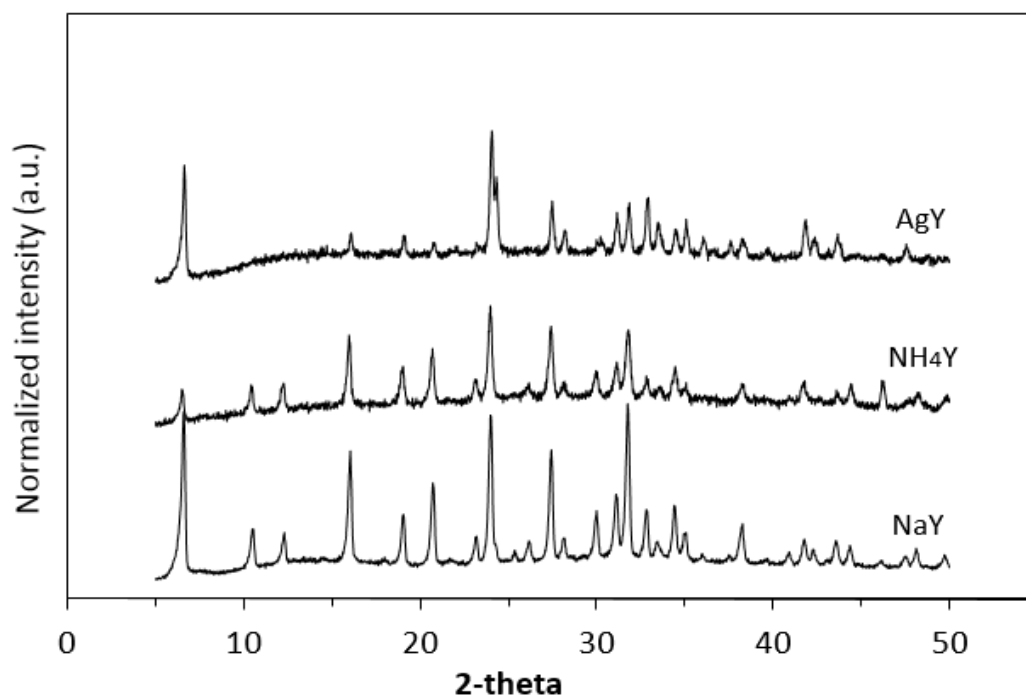


Figure 5.2. Powder XRD patterns of hydrated commercial or ion exchanged faujasite catalysts with silicon to aluminum ratios of 2.55.

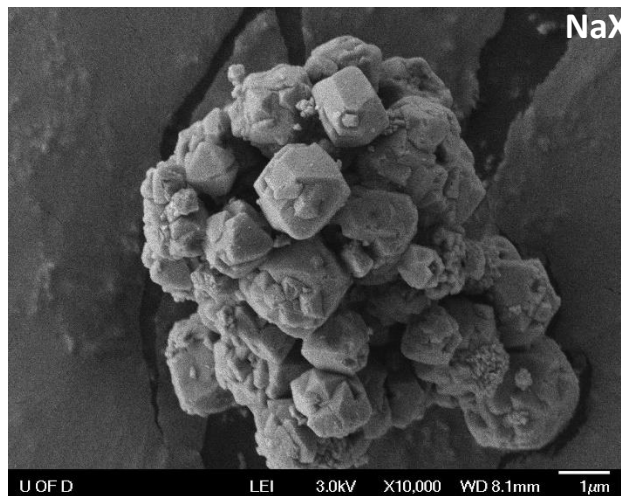
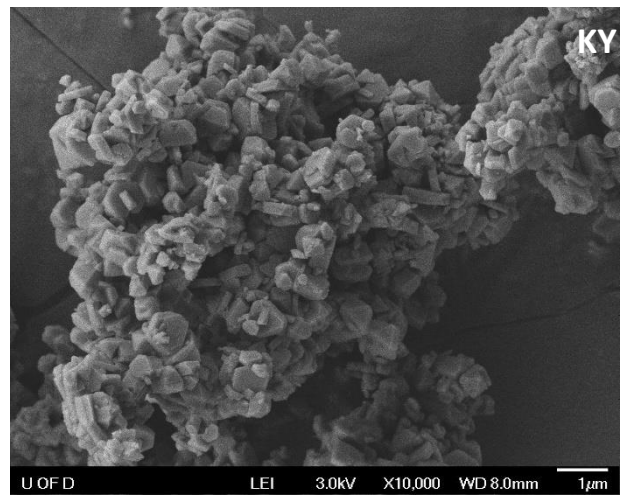
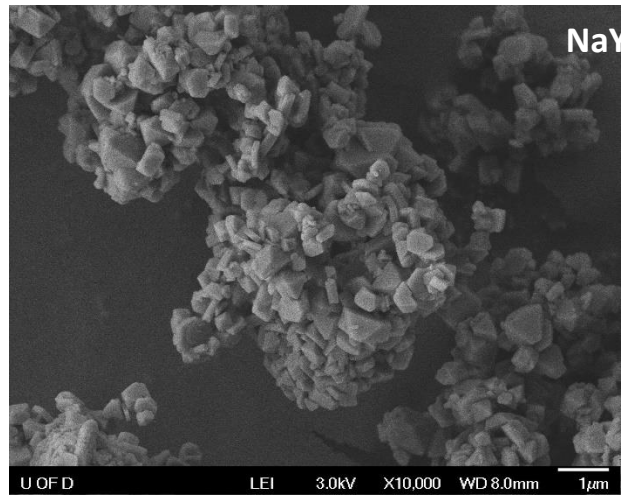


Figure 5.3 SEM images of faujasite zeolites.

Table 5.1 Chemical compositions and pore volumes of faujasite catalysts.

Catalyst (Si/Al Ratio)	Micropore volume (cm ³ g ⁻¹)
HY (44.9)	0.30
LiY (2.55)	0.24
LiX (1.25)	0.28
NaY (40)	0.24
NaY (2.62)	0.32
NaX (1.25)	0.27
KY (2.55)	0.28
KX (1.25)	0.25
AgY (2.55)	0.20
AgX (1.25)	0.19
CuY (2.55)	0.17

In control experiments probing for residual Brønsted acidity, it was found that washing of the metal-exchanged faujasites (Si/Al=2.55 and 1.25) with dilute solutions of bicarbonate salts containing the ion-exchanged metal at 25 °C did not significantly

affect DMF conversion or *p*-xylene yield (Figure 5.4). Because basic bicarbonate solutions react with acid sites, it is concluded that the observed reactivity of the alkali metal and silver exchanged zeolites is due to Lewis acid sites and not to any residual Brønsted acids sites that remain after ion exchange [18a].

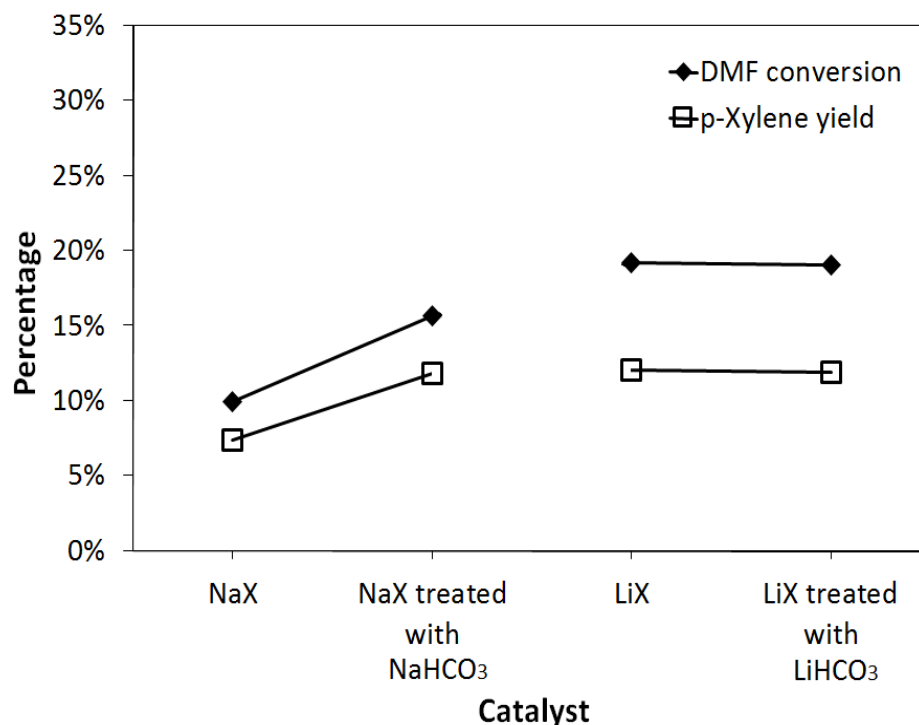


Figure 5.4. Effect of carbonate treatment on DMF conversion and *p*-xylene yield for the solvent-free reaction of DMF and ethylene catalyzed by NaX and LiX zeolites (Si/Al=1.25) at 47 bar of ethylene at 25 °C and 250 °C in the dehydration limited regime.

DMF conversion, *p*-xylene selectivity, and *p*-xylene TOFs can be found in Table 5.2. The metal exchanged faujasite catalysts with Si/Al ratios less than 40 are,

on average, nearly twice as selective as Brønsted acidic HY zeolite for the synthesis of *p*-xylene under the solvent-free conditions used here. *p*-Xylene selectivity increases with decreasing silicon to aluminum ratio of the metal-exchanged zeolites. The optimal Lewis acid catalyst tested at 220 °C, NaX zeolite, catalyzed the conversion of DMF and ethylene to *p*-xylene with 75% selectivity. At the same reaction conditions, HY zeolite catalyzes the reaction with 33% selectivity to *p*-xylene at similar conversions. At 250 °C, NaX catalyzes the reaction with 96% selectivity to *p*-xylene at 10% DMF conversion (see Table 5.2).

Table 5.2 DMF conversion and *p*-xylene selectivity of metal-exchanged faujasites and HY zeolite for the solvent-free reaction of DMF with ethylene run at 220 °C for 6 h pressurized to 47 bar of ethylene at 25 °C.

	DMF	<i>p</i> -Xylene	2,5-	1-Methyl-4-	<i>p</i> -Xylene TOF
Catalyst	Conversion	Selectivity	Hexanedione	propylbenzene	(site ⁻¹ h ⁻¹)
(Si/Al Ratio)	(%)	(%)	Selectivity	Selectivity	
			(%)	(%)	
HY (40)	7.5	33	-	-	4.1
LiY (40)	2.2	9.1	0.0	14	0.48
LiY (2.55)	9.5	32	5.3	31	0.84
LiX (1.25)	6.8	51	3.0	19	0.60
NaY (40)	2.3	8.7	0.0	14	0.49
NaY (2.55)	8.4	50	6.6	30	1.23
NaX (1.25)	5.2	75	5.3	3.0	0.99

KY (2.55)	10	56	22	20	1.8
KX (1.25)	4.0	48	0.0	0.0	0.40
AgY (2.55)	9.6	43	27	26	1.6
AgX (1.25)	9.5	48	13	28	1.8
CuY (2.55)	4.5	48	6.7	27	0.57

ANOVA was used to test the significance of cation type, framework composition, and the interaction between cation and framework composition on the TOF of *p*-xylene synthesis. P-values less than 0.05 were found for cation type, framework composition, and the interaction of these factors (Table C1 for experimental values and run orders). Based on the statistical significance of these factors, catalyst structure activity and selectivity trends can be confidently rationalized.

The selectivity to two by-products formed during reaction, 1-methyl-4-propylbenzene and 2,5-hexanedione are also shown in Table 5.2. Interestingly, selectivity to the alkylated product increases from metal-exchanged faujasites with silicon to aluminum ratios of 40 to 2.55 and decreases from metal-exchanged faujasites with silicon to aluminum ratios of 2.55 to 1.25. This may be due to a combination of effects. Cations only occupy the less accessible site I', located in double six-membered ring for materials with silicon to aluminum ratios of 40 [12]. With decreasing silicon to aluminum ratios (2.55 and 1.25), extraframework cations begin to occupy the more exposed sites II and III which become less acidic with decreasing silicon to aluminum ratio of the framework [13]. Therefore, it is postulated that the combination of the effects of Lewis acid strength, accessibility, and extraframework position contribute to the observed selectivity trends to by-products.

The rate of DMF hydrolysis to 2,5-hexanedione decreases when using the Lewis acidic NaY (Si/Al=40) catalyst as compared to Brønsted acidic HY (Si/Al=40) zeolite (DMF conversion: 1.6% vs. 9.8%, 2,5-hexanedione selectivity: 75% vs. 94% after 6 h of reaction at 250 °C). Dimers and trimers were produced in less than 10% selectivity when the reaction was catalyzed by NaX. On the other hand, HY catalyzed the solvent-free conversion of DMF and ethylene with greater than 30% selectivity to the alkylated product, 1-methyl-4-propylbenzene, and oligomers at 220 °C, again demonstrating how active site type (Brønsted vs. Lewis) influences the rate of by-product formation by perhaps altering the reaction mechanism as predicted by density functional theory [18a].

The TOFs of Lewis acidic extraframework cations for *p*-xylene synthesis depend on their type and position in the faujasite framework. Decreasing Si/Al ratios, which correspond to greater site densities, increase the rate of *p*-xylene synthesis per gram of catalyst (Figure 5.5). Average TOFs for *p*-xylene synthesis are shown in Figure 5.6. In the sodium and lithium series of alkali-metal faujasites, the TOF for *p*-xylene synthesis increases from samples with silicon to aluminum ratios of 40 to samples where the ratio is 2.55, and then decreases again for samples with Si/Al ratios of 1.25. The observed trend is postulated to be due to the combination of effects of extraframework cation type and position in the faujasite catalyst. As a general trend, potassium cations are more active than sodium cations, which are more active than lithium cations for *p*-xylene synthesis [21]. In comparison, the average TOF of HY is

4.1 cation⁻¹ h⁻¹, a TOF value more than twice that of the TOFs of metal-exchanged faujasites, but at the expense of 42% in selectivity as compared to NaX.

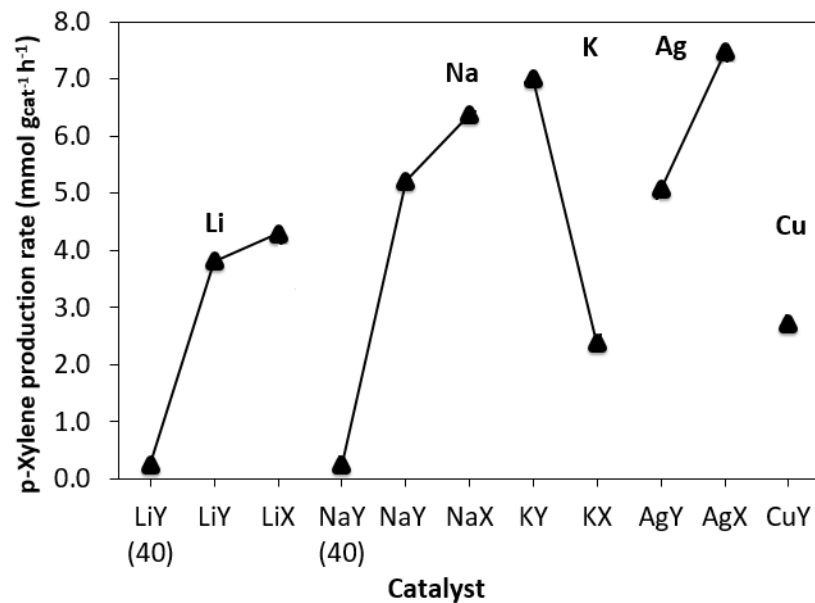


Figure 5.5 Effect of the silicon to aluminum ratio of Na⁺, Li⁺, K⁺, Ag⁺, and Cu⁺ ion exchanged faujasites vs. the rate of *p*-xylene synthesis for the reaction of DMF with ethylene run at 220 °C for 6 h. Reactions were run at <15% conversion of DMF under conditions in which the overall rate of *p*-xylene synthesis was limited by the rate of the dehydration of the Diel-Alder adduct.

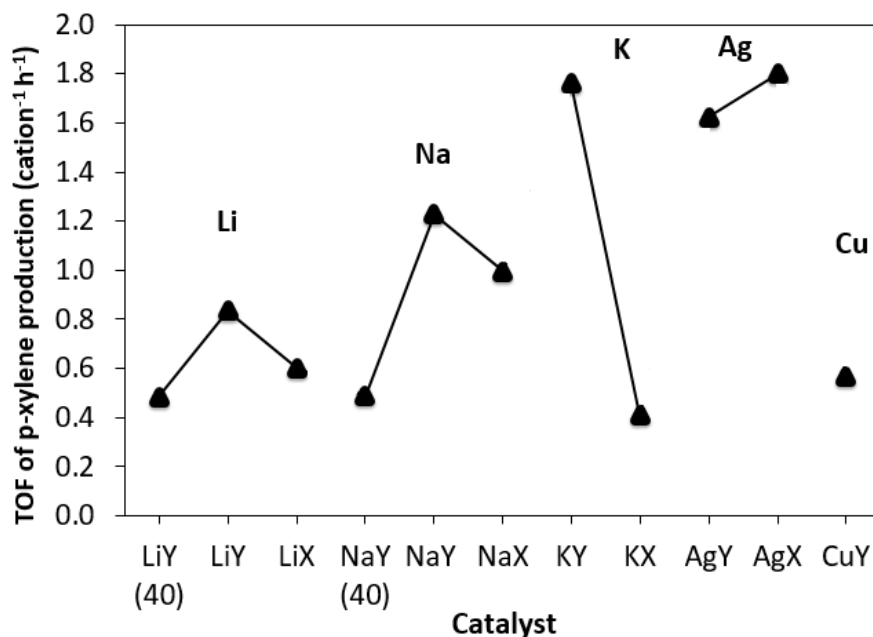


Figure 5.6 TOFs for *p*-xylene production versus Na⁺, Li⁺, K⁺, Ag⁺, and Cu⁺ ion-exchanged faujasites for the reaction of DMF with ethylene run at 220 °C for 6 h. TOFs were calculated at <15% conversion of DMF under conditions in which the overall rate of *p*-xylene production was limited by the rate of the dehydration of the Diel-Alder adduct.

At greater conversions (>30%), *p*-xylene selectivity greater than 90% can be maintained under solvent-free conditions with NaX zeolite. This is significantly better than the ~25% selectivity to *p*-xylene obtained on HY zeolite (65% selectivity to *p*-xylene), of H-BEA in *n*-heptane [7], and the 60 and 80% selectivity to *p*-xylene found for Sn- and Zr-BEA catalysts in *n*-heptane solvent at iso-conversion (Table 5.4) [11c]. Rates of irreversible Friedel-Crafts side reactions, such as alkylation and oligomer formation, are very small at higher conversions with NaX. NaX is reusable with DMF

conversion and *p*-xylene selectivity maintained for two reaction cycles at 250 °C, with less than a 5% drop in either conversion or selectivity. The results of this study illustrate how tuning the acidity of the active site in molecular sieves affects the experimentally observed reactivity and selectivity trends. These observations are supported by density functional theory (DFT) and ONIOM calculations [11b, 22]. The greater selectivity of NaX for the solvent-free conversion, decreases projected process cost and environmental impact.

Table 5.3 Selectivity and conversion for the solvent free Diels-Alder cycloaddition and dehydration reactions of DMF and ethylene run at 250 °C for 24 h.

Catalyst	Mass of catalyst (g)	DMF conversion (%)	<i>p</i> -Xylene selectivity (%)
NaX (Si/Al=1.25)	2.0	30	91
HY (Si/Al=2.25)	0.2	31	25

5.4 Conclusions

Metal-exchanged faujasites were found to be selective catalysts (96% selectivity to desired product at 10% conversion) for the solvent-free Diels-Alder cycloaddition and dehydration reactions of DMF and ethylene to *p*-xylene. Faujasites

Y and X containing extraframework Lewis-acids were more selective than faujasite zeolite containing strong Brønsted acid sites (>75 vs. 35% selectivity). Experiments run using Na^+ , Li^+ , and Ag^+ -exchanged faujasites of varying Si/Al ratios suggest that the increased selectivity of alkali metal exchanged zeolite X may be due to its decreased acidity and extraframework cation position. High selectivity (>90%) is maintained for the solvent-free conversion of DMF and ethylene to *p*-xylene at conversions greater than 30% when using NaX zeolite.

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Chapter 6

FURANS SYNTHESIS FROM GLUCOSE IN ALCOHOLIC SOLVENTS CATALYZED BY LEWIS ACIDIC BETA ZEOLITES AND BRØNSTED ACIDIC RESINS

6.1 Introduction

Only 3% of the 170 billion tons of lignocellulosic biomass generated annually are used by mankind [1]. The utilization of this non-edible feedstock for chemicals and fuels production could improve the sustainability of the chemical industry [2]. Cellulose, which comprises 40-50% of lignocellulosic biomass, can be hydrolyzed to glucose with 100% yield [3]. Glucose can be converted to 5-(hydroxymethyl)furfural (HMF), a platform chemical intermediate used in biorefineries for chemicals and fuels production. Both one- and two- step conversion processes of glucose to HMF have been demonstrated [4]. A one-step conversion could minimize the overall energy and solvent consumption of the process as compared to a two-step process of glucose isomerization to fructose in one reactor followed by dehydration to HMF in a second.

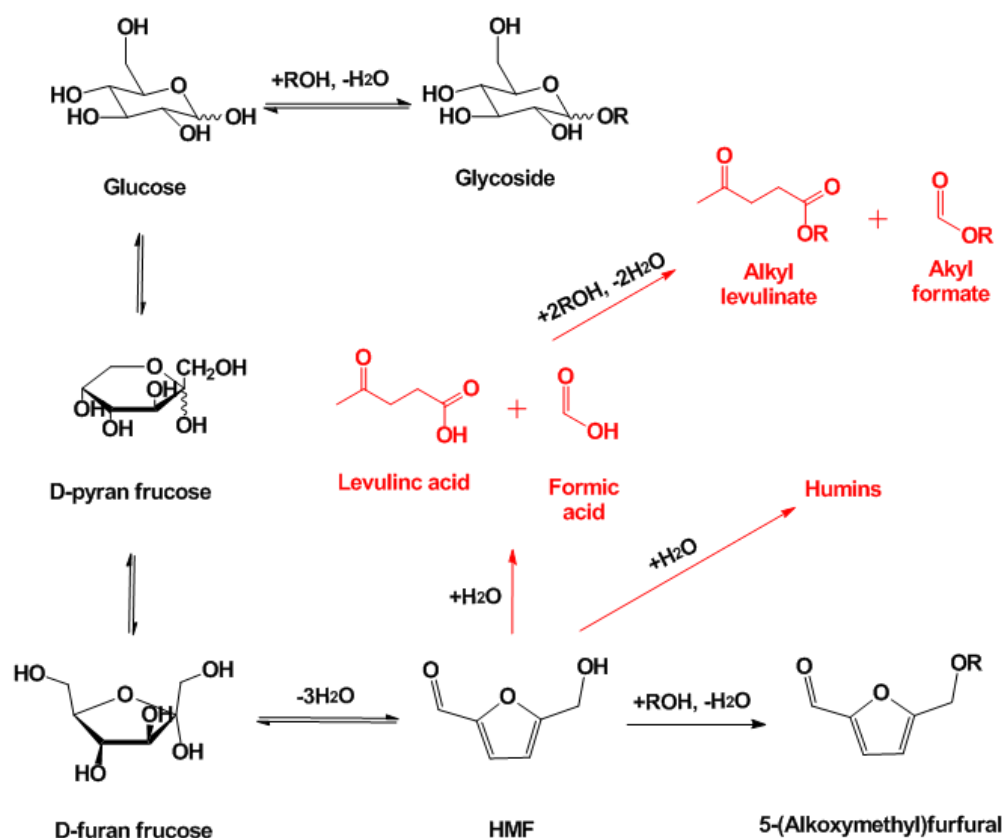
Both biphasic and monophasic, one-step conversion protocols have been investigated [5]. Biphasic systems consist of aqueous and organic phases. Reactions take place in the denser, aqueous phase and the product, HMF, is continuously extracted into the organic phase. Efficient extraction helps to minimize hydrolysis and decomposition side reactions of HMF. In the biphasic system consisting of an aqueous phase with 50 wt.% dimethyl sulfoxide (DMSO) and an organic phase with 7:3 (w/w) methylisbutylketone:2-butanol as an extracting solvent, glucose was isomerized and dehydrated to HMF with a 47% selectivity at 50% conversion [6]. In a similar biphasic

process using a heterogeneous catalyst, glucose was converted to HMF with a 72% selectivity at 79% sugar conversion using the Lewis acid, Sn-BEA zeolite, and HCl as catalysts in a biphasic (H₂O/tetrahydrofuran) system [7]. In the example above, the feed was a 10 wt.% glucose feed solution.

Monophasic systems consisting of ionic liquids as solvents have also been studied for HMF synthesis. For example, glucose was converted in 1-ethyl-3-methyl-imidazolium chloride and Cr(II) catalyst to HMF in 74% selectivity at 95% conversion [8]. The selectivity to HMF increases to 81% at nearly 100% glucose conversion when using an N-heterocyclic carbene complex as a catalyst and chromium-containing ionic liquid system [9]. The investigations of biphasic and monophasic ionic liquid based systems were conducted using feed solution containing 10 wt. % glucose. Additional studies were conducted using gamma γ -valerolactone (GVL) and tetrahydrofuran (THF) and 10 wt. % water. In THF containing 10 wt. % water, 2 wt. % glucose aqueous solutions were converted to HMF in 70% selectivity at 90% conversion [10]. The ionic-liquid based monophasic systems minimize byproduct formation, including humins, levulinic acid, and formic acid production from HMF. However, one drawback of ionic liquid based systems is their high boiling points, which makes separation more difficult.

Running the cascade reaction in a low boiling point (<100 °C) monophasic system using heterogeneous catalysts could offer advantages in process design and furan separation. To this end, glucose was converted to 5-(ethoxymethyl)furfural (EMF) in ethanol with 31% selectivity at 100% conversion using heterogeneous Lewis and a

Brønsted acid combinations [11]. EMF has an energy density of 30.3 MJ/L which is similar to that of gasoline (31.1 MJ/L) and performs well in engine tests when blended in commercial diesel as the fuel [12, 13]. In ethanol the Lewis acid Sn-BEA zeolite catalyzes the isomerization of glucose to fructose and the solid Brønsted acid, Amberlyst 131, catalyzes the dehydration of fructose to HMF and the subsequent etherification to EMF (Scheme 6.1). The overall reaction can be separated into individual components in order to establish why the mass balance is not closed. In this cascade reaction, nearly 100% of the fructose produced by isomerization is rapidly converted to EMF, implying that a process that efficiently isomerizes glucose would lead to the more selective synthesis of furans. HMF is also a problem because it is reactive and its conversion to is a suitable alternative as EMF is a more stable molecule. In a one-phase system utilizing a homogenous Lewis acid, glucose was converted to EMF in 38% selectivity at 100% conversion by AlCl_3 [14]. In an alternative one-reactor, two-step reaction protocol with the successive addition of dealuminated H-BEA zeolite followed by Amberlyst-15, glucose was converted to EMF with a 53% selectivity at 87% glucose conversion in ethanol [15]. The low selectivity of the glucose isomerization reaction is a major drawback for fructose for high-fructose corn syrup (HFCS) production or furans synthesis, which may be addressed by a combination of catalyst design and solvent effects which reduce by-product formation through consecutive reactions.



Scheme 6.1 Simplified reaction scheme for the conversion of glucose to HMF and 5-(alkoxymethyl)furfural in alcohols.

Structure activity and selectivity relationships have been developed for the use of porous stannosilicates- Sn-BEA, Sn-MCM-41, and Sn-MFI, as catalysts for glucose isomerization [16]. Sn-BEA zeolite, which consists of a three dimensional network of 12-ring pores 6.68 Å wide, has isolated Sn(IV) Lewis acid centers incorporated in the zeolite BEA framework through direct synthesis or post-synthesis techniques [17]. The ordered mesoporous material, Sn-MCM-41, possesses Sn(IV) atoms in the silica walls of MCM-41, which consists of a regular arrangement of 1D cylindrical

mesopores, 2 to 6.5 nm, that form a one-dimensional pore system [18]. The turnover frequency of glucose isomerization per tin atom of Sn-BEA is greater than that of the mesoporous Sn-MCM-41 and than that of microporous Sn-MFI (a zeolite with pores of about 5.4-5.6 Å, which severely restricts glucose diffusion into the crystal interior of this group). The rate of by-product formation is greatest for Sn-BEA catalyst with 55% of glucose molecules converted to by-products after 4 h of reaction [16a]. The rate of by-product formation is small for the glucose isomerization reaction to fructose and mannose catalyzed by Sn-MCM-41 in methanol. For Sn-BEA zeolite, it has been found that framework and extraframework tin sites in zeolite BEA react glucose differently, that the open tin site is the active site of the isomerization reaction, and that the rate of glucose isomerization and by-product formation is greater in methanol than in water with the reaction proceeding *via* a 1,2-hydride shift mechanism [16c, 19]. On the other hand, Sn-MCM-41 does not catalyze glucose isomerization in water [16a].

In this report, we investigate water's co-solvent effect on the selectivity of the glucose isomerization reaction in alcohols catalyzed by heterogeneous Lewis acidic catalysts for furan synthesis. Several studies have pointed out the special advantages of monophasic semiaqueous mixtures, including improved HMF yield and specificity, both by increasing the active furanose tautomers of fructose and by suppressing the further transformation of HMF in aqueous solution [20]. In the work presented in this chapter, the use of water as a co-solvent increases glucose solubility, converts alkyl glycosides to glucose, and may help to prevent side product formation during the

glucose isomerization reaction. The cascade reaction can be run in either ethanol or isopropanol using any of the materials: Sn-MCM-41, Sn-BEA, Hf-BEA, Zr-BEA, Amberlyst 15 and 70 (polymeric Brønsted acid catalysts). It was found that glucose can be converted to furans (HMF and IMF) with a selectivity of 88% at 60% glucose conversion using mixtures of Sn-BEA zeolite (Lewis acid) and Amberlyst 15 (Brønsted acid) catalysts in isopropanol. An effect of Lewis acid type of the catalyst on the isomerization activity is demonstrated. The effect of the temperature of reaction and the Brønsted acid on reaction selectivity was also investigated.

6.2 Experimental Methods

6.2.1 Catalyst Synthesis

Sn-, Zr-, and Hf-BEA zeolites were prepared by hydrothermal synthesis [17a, 21]. For the synthesis of these materials, 15 g of tetraethylorthosilicate (99%, TEOS, Sigma-Aldrich) was added dropwise to a solution of 16.03 g of tetraethylammonium hydroxide (TEAOH, 35 wt.%, Sachem) while stirring constantly. After the solution had been mixed for 90 min, $\text{HfCl}_2\text{O} \cdot 8\text{H}_2\text{O}$ (Alfa Aesar, 98+ %), $\text{ZrCl}_2\text{O} \cdot 8\text{H}_2\text{O}$ (98%, Sigma-Aldrich) or $\text{SnCl}_4 \cdot 5 \cdot \text{H}_2\text{O}$ (98%, Sigma-Aldrich) were added to 1.94 g of DI water. The mixture was aged at room temperature until the solution's weight decreased by 13 g due to ethanol evaporation. To the resulting solution, 1.59 g of HF (48 wt.%, Acros) was added causing the formation of a thick paste. The final gel composition was as follows: 1.0 SiO_2 : 0.005 MO_2 : 0.54 TEAOH: 7.5 H_2O : 0.54 HF (M=Hf, Zr, and Sn). Si/M~100 samples were prepared in a similar way except for the addition of 0.18

g (4 wt.%) dealuminated BEA seed crystals after HF addition [22]. The crystallization was carried out in rotating (40 rpm) Teflon-lined stainless steel autoclaves (Parr) at 140 °C for 14 days. After cooling the autoclaves in water, the product was collected by filtration and washed thoroughly with DI water. The zeolites were calcined in air in a two-step process; first at 120 °C for 2 h and then at by 580 °C for 3 h using a ramping rate of 3 °C /min to remove the structure-directing agent.

Sn-MCM-41 was prepared following a reported procedure [23]. 13.0 g of hexadecyltrimethylammonium bromide (CTAB) was dissolved in 38.0 g of deionized (DI) water. To this, 26.4 g of tetramethylammonium silicate (15-20 wt.%, TMA) was added slowly and the mixture was stirred for 50 min. 0.709 grams of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 2.1 g of water as then slowly added to this solution. The mixture was stirred for 2.5 h to give a gel with an approximate composition of 1 Si: 0.02 Sn: 0.44 CTAB: 0.27 TMA: 0.08 Cl⁻: 46 H₂O. The gel was transferred to a 45 mL Teflon-lined autoclave and heated to 140 °C for 15 h. After the synthesis, the autoclaves were cooled in running water. The synthesized material was filtered, washed with DI water and dried at 80 °C in air for overnight and then calcined at 550 °C for 6 h with a ramp rate of 1°C /min. Amberlyst 15-proton (dry, Sigma-Aldrich) was used as purchased and Amberlyst 70 (Rohm and Haas) was dried in air at 80 °C for several days beforehand.

6.2.2 Catalyst Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Phillips X'Pert X-ray diffractometer using Cu K α radiation. The micropore volumes of samples were

determined using nitrogen adsorption isotherms at -196 °C measured using a Micromeritics ASAP 2020 instrument. All samples were degassed for 8 h under vacuum at 300 °C before adsorption measurements. The micropore volumes and surface areas of BEA zeolites were determined using the t-plot method. The surface area of Sn-MCM-41 was calculated using the BET method. Scanning electron microscopy (SEM) images of diffraction patterns were measured using a JOEL JSM-7400 F high resolution scanning electron microscope. Chemical analyses of zeolite samples were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) measured by Galbraith Laboratories at their facility in Knoxville, Tennessee.

6.2.3 Reaction Experiments

Catalytic reactions were performed in a 15 mL thick-walled glass vials (Sigma-Aldrich). Glucose ($\geq 99.5\%$, Sigma-Aldrich) and saccharin ($\geq 99\%$, Sigma-Aldrich), which was used as an internal standard, were added to 5 mL solutions of known compositions containing ethanol (200 proof, Decon Laboratories), isopropanol (Anhydrous, 99.5%, Sigma-Aldrich), and/or water at 0.159 M and 0.017 M concentration of glucose and saccharin respectively. Sn-BEA, Zr-BEA, Hf-BEA, and Sn-MCM-41 were then added at 150:1 molar ratios of glucose/M (where M=Sn, Zr, or Hf). In reactions where Brønsted acid catalysis was required, 0.02 g of Amberlyst 15 (Sigma-Aldrich) or Amberlyst 70 (Rohm and Haas) were added. The reactor was then sealed using a 20 mm aluminum seal cap and placed in a Chemglass Optichem digital

hotplate stirrer and stirred at a rate of 500 rpm with a magnetic stirrer at the noted temperatures. Following completion of the reaction, the reactor was cooled in an ice bath, the contents were diluted in water using a 1:3 volume ratio of product solution to water, and samples were filtered using a 0.2 μm Nalgene syringe filter for high performance liquid chromatography (HPLC) analysis. HPLC was run using a Waters e2695 separations module equipped with a refractive index detector. A Biorad HPX87H (300 x 7.8) column was used at 65 °C with 0.005 mol/L sulfuric acid at a flow rate of 0.65 mL/min as the mobile phase. Elution times were determined using commercial standards of the compounds of interest. The ratio of Lewis to Brønsted acid catalyst was chosen based the observed rates of reaction of isomerization and dehydration in the presence of just one catalyst. The carbon balance is defined as the total yield of molecules detected by HPLC. This does not include humins and other undetectable by-products.

6.3 Results and Discussion

The structural and textural properties of the synthesized materials were characterized by powder X-ray diffraction, nitrogen adsorption, and SEM. Sn-, Zr-, and Hf-BEA with Si/M ratios of ~ 200 (M=Sn, Zr, or Hf containing 1.57, 1.08, and 1.08 wt.% of SnO₂, ZrO₂, or HfO₂) were prepared as described in the experimental methods section. The X-ray diffraction patterns of the calcined samples are consistent with the structure of zeolite BEA, with no evidence of impurities or detectable amounts of amorphous material (Figure 6.1). Micropore volumes measured using nitrogen adsorption isotherms show that Sn-, Zr-, and Hf-BEA have large microporous

volumes ($\sim 0.20 \text{ cm}^3/\text{g}$) characteristic of zeolite BEA samples of good quality (Table 6.1). The XRD pattern of Sn-MCM-41 is well defined and displays the (100), (110) and (200) reflections corresponding to a hexagonal array of channels (Figure 6.2) [24]. The N_2 adsorption-desorption isotherms of calcined Sn-MCM-41 display a type IV profile characteristic of mesoporous MCM-41 materials with a BET surface area of $794 \text{ m}^2\text{g}^{-1}$. SEM images of the synthesized BEA zeolites show the typical truncated square by-pyramidal morphology of these materials with $\sim 2\text{-}5 \text{ }\mu\text{m}$ particle size (Figure 6.3) [25].

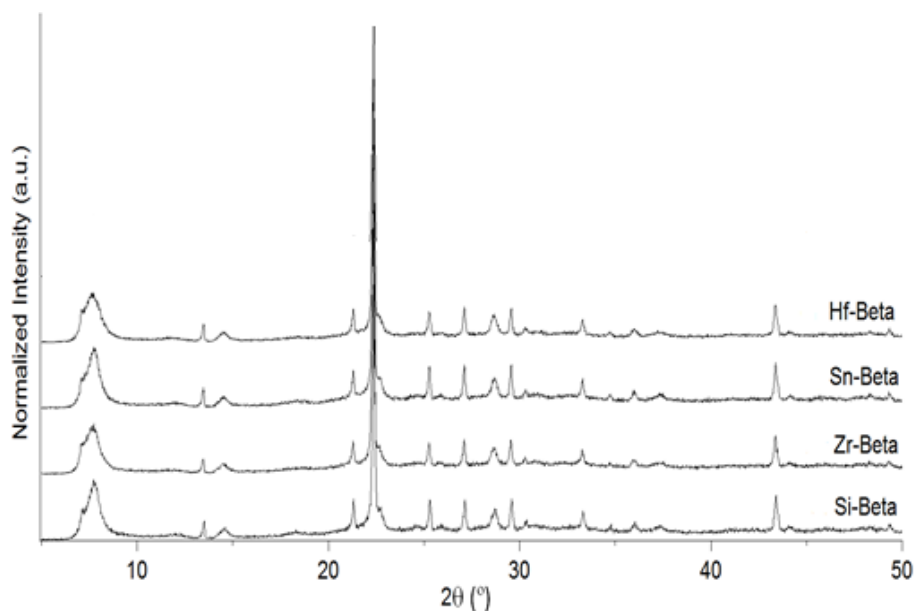


Figure 6.1. Powder X-ray diffraction patterns of Si-BEA, Zr-BEA (Si/Zr=325), Sn-BEA (Si/Sn=230), and Hf-BEA (Si/Hf=219) zeolites.

Table 6.1. Textural Properties of Zeolite BEA Samples.

Sample	microporous volume (cm ³ g ⁻¹) ^a	external surface area (m ² g ⁻¹) ^a
Hf-BEA (Si/Hf=219)	0.18	67.75
Zr-BEA (Si/Zr=325)	0.19	69.69
Sn-BEA (Si/Sn=230)	0.19	93.15
Si-BEA	0.20	58.32

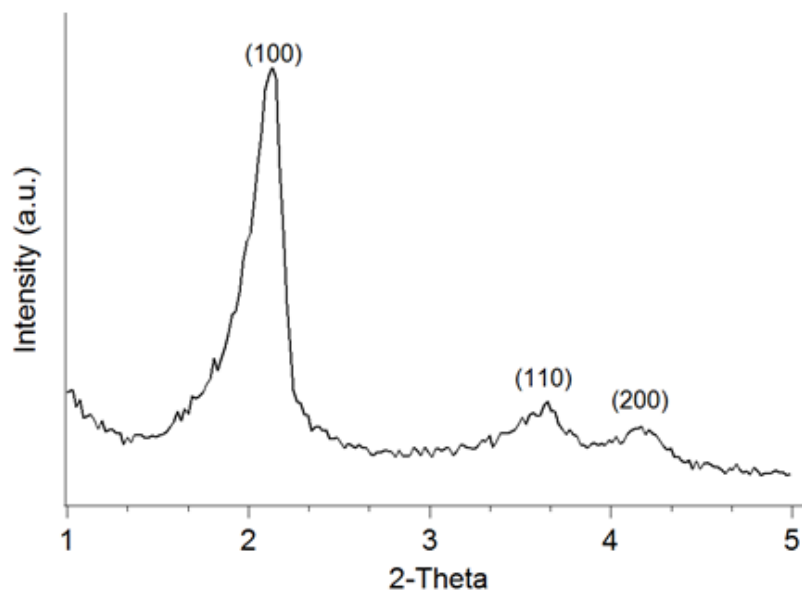


Figure 6.2 Powder X-ray diffraction pattern of Sn-MCM-41 (Si/Sn=50).

isomerization is not selective when catalyzed by Sn-BEA zeolite so experiments investigating furans synthesis using this catalyst were done using water as a co-solvent.

Running the cascade reaction for the conversion of glucose to furans using as combination Sn-MCM-41 and Amberlyst 15 catalysts at 90 °C in neat ethanol produces EMF in 26% selectivity after 24 h of reaction (see Figure D1 for reaction profile). The increased carbon balance (75 vs. 31%) is accompanied by the formation of ethyl α -D-glucopyranoside, the ethyl ether of glucose, which was not detected when using Sn-BEA and Amberlyst 131 as catalysts in neat ethanol [11]. At 70 °C, a 14% EMF selectivity was detected with the carbon balance remaining at 96%, even after 72 h of reaction time (Figure D3). Running the reaction by adding Sn-MCM-41 and Amberlyst 15 in sequence—with the Brønsted acid added after 4 h of reaction—provides a 33% yield to EMF after 18 h of reaction at 90 °C and a carbon balance of 82%. When using Sn-MCM-41 alone, a 60% carbon balance remains after 24 h of reaction time with no furan molecules detected. Although Sn-MCM-41 does not catalyze a significant amount of byproduct formation during glucose to fructose isomerization, the rate of glucose isomerization is slow as compared to the rate of glycoside formation, decreasing sugar conversion (Scheme 6.1).

The water's effect in alcoholic solvents is to increase the selectivity of the glucose isomerization reaction when catalyzed by Sn-BEA. For instance, running the reaction in a 2.5 weight % water in ethanol improves the carbon balance of the detected products as compared to reactions in neat ethanol [11] to 65% at a conversion of 68%

(Figure 6.2). At this conversion, the selectivity to HMF and EMF is 49% with 80% ratio of EMF/(EMF+HMF). Addition of a larger amounts of water decreases sugar conversion and decreases the formation of etherification products. In a 56 wt. % solution of water in ethanol, the carbon balance increases to 91% at 31% glucose conversion. At this conversion, the selectivity to HMF is 73% with no EMF detected. When catalyzed by Sn-MCM-41 as opposed to Sn-BEA which possesses isolated tin sites, and Amberlyst 15 as catalysts, the glucose isomerization reaction in ethanol is inhibited when run with over 5 wt.% water.

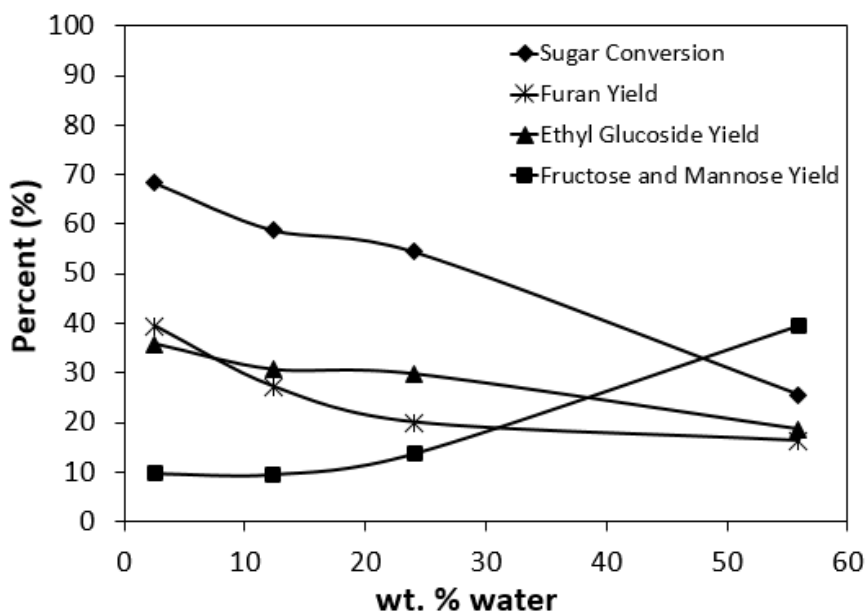


Figure 6.4 Conversion of glucose to HMF or EMF in ethanol at different weight fractions of water. Reactions were run at 90 °C for 18 h using a 0.159 M concentration of glucose and Sn-BEA (Si/Sn=100) and Amberlyst 15 catalysts.

Water's effect on the glucose isomerization reaction catalyzed by Sn-BEA on ethanol is similar to what is observed with isopropanol. An 88% furan selectivity at 60% sugar conversion was measured in isopropanol at 110 °C using a combination of Sn-BEA and Amberlyst 15 catalysts after only 6 h of reaction (Figure 6.3). With 7.5 wt. % water, the carbon balance following reaction is 93% with 80 mol% of the furanic molecules being HMF and the other 20% forming 5-(isopropoxymethyl)furfural (IMF). At 97% conversion, the selectivity to the furans, HMF and IMF, decreases to 39% due to humin formation.

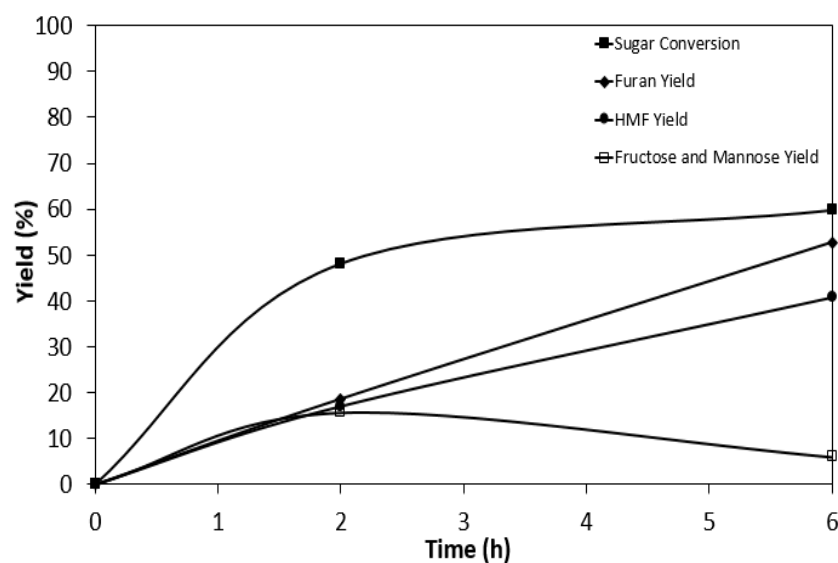


Figure 6.5 Conversion of glucose to HMF or IMF in isopropanol using 7.5 wt.% water as a co-solvent as a function of time. Reactions were run at 110 °C using a 0.159 M concentration of glucose using Sn-BEA (Si/Sn=100) and Amberlyst 15 catalysts.

Increasing the temperature of reaction from 120 to 140 °C in a solution of 7.5 wt.% water in isopropanol increases glucose conversion from 52 to 63% and decreases

the total carbon balance from 70 to 57% after 2 h of reaction. The furans' selectivity also decreases from 43 to 32% when the reaction is catalyzed by Sn-BEA and Amberlyst 70.

Mixtures of Lewis acidic molecular sieves Zr- or Hf-BEA and Amberlyst 70 also catalyze the cascade reaction with lower glucose conversion in solutions of 7.5 wt.% water in isopropanol as compared to reactions run with Sn-Beta and Amberlyst 70 (Table 6.1). At a 150:1 glucose to Lewis acid molar ratio, Zr-BEA catalyzed 10% sugar conversion at a selectivity of 44% after 8 h of reaction at 110 °C. Hf-BEA and Amberlyst 70 catalyzed the cascade reaction with 24% sugar conversion at 55% furans selectivity at identical conditions. Sugar conversion and furan selectivity were greater when using Sn-BEA as the Lewis acid catalyst and Amberlyst 70 as the Brønsted acid.

Table 6.2 Glucose, mannose, fructose, and glycoside conversion vs. HMF and IMF selectivity. Reactions were run at 110 °C with 0.02 g of Amberlyst 70 at a 150:1 molar ratio of glucose to Lewis acid in a 7.5 wt.% solution of water in isopropanol.

Lewis Acid Catalyst	Sugar	HMF and IMF
	Conversion (%)	Selectivity (%)
Zr-BEA	10	44
Hf-BEA	24	55

The Brønsted acid catalyst used affects the rate of isopropyl glycoside, by-product formation, and furanics selectivity (Table 6.2). The macroporous polymeric catalyst, Amberlyst 70, is more active than the styrene-divinylbenzene macroreticular catalyst, Amberlyst 15, and yields 53% glycoside as compared to the 32% of glycoside molecules yield at the same reaction conditions. The furanic molecule selectivity is also greater for Amberlyst 15 than Amberlyst 70.

Table 6.3 Glucose, mannose, fructose, and glycoside conversion vs. HMF and IMF selectivity at 110 °C with 0.02 g of Brønsted acid catalyst and Sn-BEA catalyst (150:1 molar ratio of glucose to Sn) in a 7.5 wt.% solution of water in isopropanol.

Brønsted Acid Catalyst	Acid Site Concentration (eq/kg)	BET Surface Area (m ² /g)	Sugar Conversion (%)	HMF and IMF Selectivity (%)
Amberlyst 15	4.7	53	60	88
Amberlyst 70	2.55	36	31	64

The results presented here are a significant improvement for the conversion of glucose to furans in alcoholic solvents with respect to reported results on glucose conversion in ethanol. When the cascade reaction is run in ethanol-water solvent catalyzed by the homogeneous catalyst, AlCl₃, in microwave reactors, nearly identical

yields to furans were measured, but at 20% greater conversion [26]. This protocol simplifies the reaction procedure and is more selective than alternative one-reactor, two-step reaction protocol for EMF synthesis with the sequential addition of dealuminated BEA zeolite followed by Amberlyst-15, which achieves a 53 % furans selectivity at 87% glucose conversion in ethanol [15]. The use of a heterogeneous catalyst free of strong Brønsted acids decreases oligomerization side reactions in the pores of the zeolite. Finally, the outcome is significantly better than the 31% selectivity of EMF at 100% glucose conversion found when the reaction is catalyzed by Sn-BEA and Amberlyst 131 catalysts in neat ethanol, demonstrating the unique co-solvent effect of water in preserving the carbon balance [11]. Reaction conditions were optimized across temperatures and catalyst composition.

6.4 Conclusions

The cascade reaction of glucose to furans was investigated in a one-phase alcoholic system using heterogeneous Lewis and Brønsted acid as catalysts. The side-reactions associated with glucose isomerization over Sn-BEA as a catalyst were reduced by the addition of <10 wt.% water to the alcohols. Glucose was converted to furans with an 88% selectivity at 60% sugar conversion in isopropanol in a low boiling-point monophasic system. It was also demonstrated that Sn-Beta is a better catalyst than Sn-MCM-41, Hf-BEA, and Zr-BEA for the glucose isomerization reaction run in semi-aqueous solutions of alcohols. Running the cascade reaction in a low boiling point (<100 °C) monophasic system using heterogeneous catalysts could offer advantages in process design and furan separation.

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Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Overview

Chemicals provide most of the material and energy for mankind. A majority of chemicals are produced from petroleum and the field of biomass conversion seeks to develop sustainable and economically competitive production routes to chemicals from renewable resources. The commercialization of these routes improves the sustainability of the chemical industry and decreases price fluctuations [1]. In addition, the use of biomass-derived feedstocks for chemicals and fuels production could decrease global annual CO₂ emissions [2]. This thesis presents processes for the production of two classes of chemicals: aromatics and furans.

The economics, practicality, feedstock availability, feedstock abundance, and environmental impact of the process were considered in the lab-scale design to convert the biomass-derived molecules to chemicals [3]. For the work presented in this thesis, an iterative design methodology was used that begins with a low level of detail and progressively creates more and more detail [4]. During design development, the economic viability of a large-scale process was considered. Lignocellulosic biomass was the chosen feedstock for chemicals production because of its abundance, its high rate of production, and because it is not consumed as a food supply.

The synthesis of aromatics and furans presented in this thesis often depended on catalysts to convert biomass-derived molecules to the desired products. Catalysts

materials used affected the rate of chemical reaction without being consumed by the reaction [5]. Catalysts were chosen to maximize the rate of desired as compared to undesired reactions. To accomplish this, the major side reactions were identified and the effect of catalyst structure and composition on product selectivity and rate of reaction was made. In this thesis, zeolites are the class of materials most often used to catalyze these reactions. Catalyst acid type (Brønsted vs. Lewis acid) was found to have a major effect on the selectivity and rate of reaction. Both framework and extraframework Lewis acid sites in zeolites BEA and FAU were tested as catalysts for these reactions at the lab-scale. In some cases, reactions were performed homogeneously without a catalyst.

Diels-Alder, dehydration, and isomerization reactions are discussed in chapters 2-6. The rate of these reactions increases with the activation of the oxygen-containing functional group in the reacting molecules. These are most often carbonyl groups which are activated by Lewis acid sites. The activation of the carbonyl groups decreases the activation energy of the reaction and increases the rate of reaction.

This thesis reports the development of selective routes for the conversion of biomass to aromatic and furan molecules. The lab-scale synthesis of the aromatic chemicals: phthalic anhydride, benzoic acid, and *p*-xylene is summarized as well as the synthesis of HMF and derivatives in alcoholic solvents. This concluding chapter provides a summary of the major findings of this thesis, addresses unresolved issues, and proposes possible directions for future research.

7.2 Dissertation Summary

In chapter 3, a route for the production of phthalic anhydride from lignocellulosic biomass is described. From a process development perspective, the main advantage of this route is its use of the dehydration product of hemicellulose, furfural. This is advantageous because furfural production was commercialized in the early 1900's and it is produced at the rate of 300,000 tons per year from biomass [6]. For the process considered in this thesis, the furfural derived molecules, furan and maleic anhydride, were chosen as the starting materials because they are or can be commercially produced at large scales (>10,000 tons). For this transformation, furan and maleic anhydride were converted in a two-step reaction protocol of Diels-Alder followed by dehydration reactions to phthalic anhydride.

The Diels-Alder reactions in chapter 3 were run under solvent-free conditions and without catalysts. Running reactions without solvent decreases separation and solvent costs and reduces environmental impact of the process. For this reaction, a 96% yield to the Diels-Alder product of furan and maleic anhydride, *exo*-4,10-dioxatricyclo[5.2.1.0]dec-8-ene-3,5-dione, was obtained after 4 h of reaction in a 600 mL batch Parr reactor initially at 25 °C. Because some solvent-free reactions thermally runaway, thermodynamic parameters were experimentally determined to assess the safety of the process. This was done by varying the reactant amounts and determining the thermodynamic parameters of the retro-Diels-Alder reaction. It was found that doubling and tripling the reactant amounts for this reversible reaction did not affect the

peak reactor temperature of around 92 °C. This was consistent with the thermodynamic parameters and the calculated adiabatic temperature rise, ΔT_{ad} , of about 150 °C as determined from the van't Hoff plot. After 4 h of reaction, it was found that the reactor temperature returned to about 35 °C. Further analysis was performed to determine if the 'on-water' effect is applicable to this reaction. The addition of small amounts of water (< 20 wt. %) to the reactor decreased the peak reactor temperature but did not increase the rate of the reaction. The addition of water to the reaction also led to the hydrolysis side reactions of maleic anhydride and phthalic anhydride to maleic acid and phthalic acid. Because of these negative results, the addition of water was not considered to be useful and the solvent-free approach was favored. The solvent-free reaction is scalable and allows for the production of the Diels-Alder product at high yields and at the hundreds of thousands of tons per year scale.

An important process discovery which is discussed in chapter 3 is the dehydration reaction of the Diels-Alder products, or oxanorbornene molecules necessary for production of aromatics [7]. The homogeneous dehydration reaction of the Diels-Alder product of furan and maleic anhydride, *exo*-4,10-dioxa-tricyclo[5.2.1.0]dec-8-ene-3,5-dione, is not selective when run in acids. For example, running the reaction in neat MSA at 25 °C yields only a 14% selectivity to phthalic anhydride at 100% conversion after 3 h of reaction. Low selectivity (<10%) to the aromatic products, phthalic anhydride and phthalic acid, was also found for dehydration reactions run in

sulfuric, phosphoric, and nitric acid at 100% conversion. qNMR experiments were used to show that the main side reaction channels for the dehydration of oxanorbornene molecules are retro-Diels-Alder and polymerization reactions. Dehydration reactions run in a binary mixture of MSA and acetic anhydride afforded an 87% selectivity to the aromatic products phthalic anhydride and acid at 100% conversion. MSA and acetic anhydride react at 25 °C to form acetyl methanesulfonate, a strong acylating agent [8]. In the presence of this acylating agent and acetic anhydride, it was discovered that the reaction mechanism proceeded through a different pathway when using the binary mixture of MSA and acetic anhydride as the dehydration medium as compared to reactions run in neat MSA. This is evidenced by the absence of stable reaction intermediates for reactions run in neat MSA. Following reaction, the aromatic products can be efficiently extracted using toluene as the organic phase. A technoeconomic analysis of the process demonstrated renewable phthalic anhydride production is cost-competitive with the synthetic route [9]. This new chemistry can contribute to the resolution of emerging challenges in biomass conversion.

In chapter 4, a route for the production of benzoic acid from lignocellulosic biomass is described. From a process development perspective, the main advantage of this route is its use of biomass-derived molecules which are obtained in high-yield and commercially produced at large scales. Benzoic acid can be industrially transformed to many consumer polymers such as nylon-6, epoxy resins, phenolic resins, and

carbonates [10]. For this transformation, furan and methyl acrylate or acrylic acid were converted by Diels-Alder followed by dehydration reactions to methyl benzoate or benzoic acid [11].

The one-step sequential Diels-Alder and dehydration reactions of furan and methyl acrylate were found to be unselective in *n*-heptane. For all heterogeneous catalysts tested no aromatic products were detected. This included both microporous and mesoporous materials at methyl acrylate conversions of up to 11%. In all cases, catalysts fouled due to the polymerization of the reactants. Because of the sensitivity of the reactants to the Brønsted and Lewis acid at the temperatures tested (150 and 200 °C) the one-step reaction was not further pursued. For this transformation, furan and maleic anhydride were converted in a two-step reaction protocol of Diels-Alder followed by dehydration reactions to phthalic anhydride.

Diels-Alder reactions in chapter 4 were run under solvent-free conditions. However, unlike the Diels-Alder reaction of furan and maleic anhydride, the Diels-Alder reactions of furan and methyl acrylate or acrylic acid are slow at 25 °C. For example, Diels-Alder reactions of furan and methyl acrylate or acrylic acid run at 25 °C yielded no detectable amounts of Diels-Alder product after 24 h of reaction. To catalyze the reactions of furan and acrylic acid or methyl acrylate, Lewis acidic zeolites were used. Hf-, Zr-, or Sn-containing zeolite Beta was found to provide a 50% yield of the Diels-Alder product of furan and acrylic acid and 25% yield of the Diels-Alder product of furan and methyl acrylate. In addition, these microporous materials

catalyzed the Diels-Alder reactions of furans with no detectable side products at 25 °C and at rates one hundred times those of previously reported catalyst for this reaction [12]. A temperature programmed reaction procedure was coded in MATLAB to minimize reaction time and optimize yield of the Diels-Alder products based on experimentally determined kinetic and thermodynamic parameters.

Characterization of the catalyst provides insights into the high activity. TPD-TGA experiments which used diethyl ether as a probe molecule revealed the formation of 1:1 complexes between the Lewis acid site and diethyl ether for Hf-, Zr-, Sn-Beta zeolites. This was not observed for Hf-, Zr-, and Sn- impregnated zeolites which contained oxide clusters which blocked some of the pores of the zeolite. FTIR spectra of acetonitrile-d₃ adsorbed on M-Beta zeolites showed higher frequency peaks at 2302, 2301, and 2305 cm⁻¹ corresponding to an acetonitrile-d₃ (C-N) stretch associated with acetonitrile-d₃ interaction with the Lewis acid site. This higher frequency shift was previously found Sn-Beta samples containing Sn in the framework of the zeolite Beta structure [13]. FTIR spectra of acetonitrile-d₃ on EF-M-Beta, prepared by impregnation of the metal precursor after zeolite crystallization, were identical to those for Si-Beta, a result that is consistent with no Lewis acids present which interact with the acetonitrile-d₃ in these samples. The observed turnover frequencies of the Diels-Alder reaction and the high-frequency ν (C-N) stretch only found for M-Beta samples from FTIR experiments provide a relationship between catalyst activity and spectroscopic results.

The dehydration of the Diels-Alder product of furan and methyl acrylate was run in a binary mixture of MSA and acetic anhydride. The Diels-Alder product was dehydrated with a 96% selectivity to methyl benzoate at 100% conversion in the binary mixture for the reaction run at 25 °C for 2 h followed by a temperature increase to 80 °C for 1 h at an endo:exo ratio of 0.43. Increasing the concentration of the reactant from 0.13 to 0.65 M at the same endo:exo ratio decreased methyl benzoate selectivity from 96 to 83% at 100% conversion. The stereochemical composition of the reactant on the does not have an effect on selectivity. Increasing the endo:exo ratio from 0.43 to 1.89 at a 0.65 M concentration of reactant led to a 89% selectivity to methyl benzoate at 100% conversion. Reactions run in neat MSA resulted in a 1.7% selectivity to methyl benzoate at 100% conversion. Running using the Diels-Alder adduct of furan and acrylic acid as the reactant, led to a drop in the selectivity of aromatics from 96% to 43% at 100% conversion under identical conditions of temperature, concentration and time. The selective process discussed in chapter 4 allows for the production of benzene derived polymers from molecules obtained in high yield from lignocellulosic biomass.

In chapter 5, a catalytic route for the production of *p*-xylene from lignocellulosic biomass is discussed. *p*-Xylene is an important chemical used for the manufacture of PET, a polymer produced at a rate of over 31 million tons per year for plastic bottle and textile manufacture [14]. *p*-Xylene was synthesized *via* the Diels-Alder cycloaddition of 2,5-dimethylfuran (DMF) and ethylene to form 1,4-dimethyl-7-

oxabicyclo[2.2.1]hept-2-ene (oxanorbornene) which is subsequently dehydrated to *p*-xylene over solid acid catalysts [15]. For the reaction of DMF and ethylene, three side reactions decrease *p*-xylene selectivity: hydrolysis of DMF to 2,5-hexanedione, alkylation of reaction intermediates by ethylene, and Friedel-Crafts-type reactions of dehydration intermediates resulting in oligomer formation. The rates of the latter two reactions, which are irreversible, may be decreased by tuning the acidity of the catalyst [16]. The selectivity to *p*-xylene decreases with increasing DMF concentration [17].

Metal-exchanged faujasites are solid Lewis acids that can catalyze both Diels-Alder and dehydration reactions. At 250 °C, NaX catalyzes *p*-xylene synthesis with 96% selectivity at 10% DMF conversion. High selectivity to *p*-xylene (> 90%) is maintained at conversions greater than 30%. This result is a major improvement over the 35% selectivity to *p*-xylene obtained for HY zeolite. These catalysts are more selective than the framework Lewis acidic molecular sieves, Sn- and Zr-BEA, which yield a ~75% selectivity to *p*-xylene at 30% DMF conversion using *n*-heptane as solvent [18]. The experimental results indicate that the increase in *p*-xylene selectivity associated with Lewis acidic faujasite catalyst is due to a combination of the effects of Lewis acid type, strength, and extraframework position in the faujasite framework.

Selectivity to the alkylated and hydrolysis by-products, 1-methyl-4-propylbenzene and 2,5-hexanedione, increases from metal-exchanged faujasites with silicon to aluminum ratios of 40 to 2.55 and decreases from metal-exchanged faujasites with silicon to aluminum ratios of 2.55 to 1.25. Cations only occupy the less

accessible site I', located in double six-membered ring for materials with silicon to aluminum ratios of 40 [19]. With decreasing silicon to aluminum ratios (2.55 and 1.25), extraframework cations begin to occupy the more exposed sites II and III which become less acidic with decreasing silicon to aluminum ratio of the framework [20]. These results show how important the combination of the effects of Lewis acid strength, accessibility, and extraframework position contribute to the observed selectivity trends to by-products. From a process development perspective, the selective synthesis of *p*-xylene without solvent eliminates some process separation steps and make the process more environmentally friendly.

In chapter 6, a route for the production of HMF and its ethers from lignocellulosic biomass is described. This route uses a high-yield cellulose-derived molecule, glucose, for HMF synthesis in a monophasic system. Running the cascade reaction in a low boiling point (<100 °C) monophasic system using heterogeneous catalysts offers advantages in process design and product separation and decrease the cost of a continuous process. To this end, glucose was converted to 5-(ethoxymethyl)furfural (EMF) in ethanol with 31% selectivity at 100% conversion using heterogeneous Lewis and a Brønsted acid combinations [21]. In ethanol the Lewis acid Sn-Beta zeolite catalyzes the isomerization of glucose to fructose and the solid Brønsted acid, Amberlyst 131, catalyzes the dehydration of fructose to HMF and the subsequent etherification to EMF. The overall reaction can be separated into individual components in order to establish why the mass balance is not closed. In this cascade

reaction, nearly 100% of the fructose produced by isomerization is rapidly converted to EMF, implying that a process that efficiently isomerizes glucose would lead to the more selective synthesis of furans.

The addition of small weight percent of water (7.5%) increased the selectivity of the glucose isomerization reaction. It was found that glucose can be converted to furans (HMF and IMF) with a selectivity of 88% at 60% glucose conversion using mixtures of Sn-Beta zeolite (Lewis acid) and Amberlyst 15 (Brønsted acid) catalysts in isopropanol. The cascade reaction was run in ethanol and isopropanol using any of the materials: Sn-MCM-41, Sn-Beta, Hf-Beta, and Zr-Beta and polymeric Brønsted acid catalysts.

At larger conversion (97%), selectivity to furans decreased to 39% due to humin formation. Increasing the temperature of reaction from 120 to 140 °C in a solution of 7.5 wt. % water in isopropanol increases glucose conversion from 52 to 63% and decreases the total carbon balance from 70 to 57% after 2 h of reaction. The furans' selectivity also decreases from 43 to 32% when the reaction is catalyzed by Sn-Beta and Amberlyst 70. Mixtures of Lewis acidic molecular sieves Zr- or Hf-Beta and Amberlyst 70 also catalyze the cascade reaction with lower glucose conversion in solutions of 7.5 wt. % water in isopropanol as compared to reactions run with Sn-Beta and Amberlyst 70. At a 150:1 glucose to Lewis acid molar ratio, Zr-Beta catalyzed 10% sugar conversion at a furan selectivity of 44% after 8 h of reaction at 110 °C. Hf-Beta and Amberlyst 70 catalyzed the cascade reaction with 24% sugar conversion at

55% furan selectivity at identical conditions. Sugar conversion and furan selectivity were greater when using Sn-Beta as the Lewis acid catalyst and Amberlyst 70 as the Brønsted acid.

The results presented in chapter 6 are an improvement for the conversion of glucose to furans in alcoholic solvents with respect to reported results on glucose conversion in ethanol. When the cascade reaction is run in ethanol-water solvent catalyzed by the homogeneous catalyst, AlCl_3 , in microwave reactors, nearly identical yields to furans were measured, but at 20% greater conversion [22]. The discussed protocol simplifies the reaction procedure and is more selective than alternative one-reactor, two-step reaction protocol for EMF synthesis with the sequential addition of dealuminated Beta zeolite followed by Amberlyst-15, which achieves a 53 % furans selectivity at 87% glucose conversion in ethanol [23]. The use of a heterogeneous catalyst free of strong Brønsted acids decreases oligomerization side reactions in the pores of the zeolite. The lab-scale process described in chapter 6 for glucose conversion monophasic system using heterogeneous catalysts could offer advantages in process design, product separation, and decrease the cost of a continuous process for HMF production.

7.3 Recommendations for Future Studies

This thesis describes the discovery of lab-scale processes for the conversion of high-yield lignocellulose derived molecules to aromatics and furans. The results in this thesis can be used to solve emerging challenges in biomass conversion. Future work regarding this topic can focus on optimizing the proposed processes through

alterations in catalyst design, solvent choice, and feedstock. Recommendations are also given for the investigation of additional routes to produce chemicals that can be explored for the conversion of lignocellulose to chemicals and fuels.

7.3.1 Dehydration of Diels-Alder Reaction Products of Furans

The dehydration of Diels-Alder reaction products of furans is an important reaction in the field of biomass conversion as furan and 2-methylfuran are molecules industrially manufactured from furfural. The yields of dehydration reactions of Diels-Alder reaction products of unsubstituted furans were previously low (<60%) and these reactions were often run using corrosive acids such as sulfuric acid and/or at temperatures below 10 °C [24-26]. In chapters 3 and 4, a new process, which utilizes anhydrides, is described for the selective dehydration of Diels-Alder reaction products of furans to aromatic molecules [7, 11]. Using this approach nearly quantitative yields to the Diels-Alder products can be achieved. Mechanistic studies utilizing the structures of isolated, stable reaction intermediates demonstrate the benefits of an anhydride as compared to an acid promoted dehydration of Diels-Alder products. A 96% yield of the dehydration of a Diels-Alder reaction product of furan was measured [11]. The aromatic molecule yield was found not to be significantly affected by reactant concentration or the stereochemical composition of the reactant. The results presented in these chapters are a significant advance in the dehydration of Diels-Alder products of furan as there were no published results on this reaction.

Technoeconomic analysis of the proposed phthalic anhydride production process demonstrates that this route is promising [9]. Starting from both hemicellulose solutions and corn stover, the conversion of these biomass feedstocks to phthalic anhydride was found to be cost-competitive with the production route of oil based phthalic anhydride. A closer investigation of the proposed processes demonstrates that acetic acid regenerated to acetic anhydride via ketene is one major cost of the process [27]. Future work regarding this process should be directed at further understanding the mechanism of the reaction, the investigation of solid-phase acylating reagents, and other reagents such as etherification reagents.

In chapter 4, the change in the functional group of the Diels-Alder product from methyl ester to carboxylic acid decreased the selectivity to the respective aromatic product from 96 to 43% at 100% conversion. Further mechanistic studies can be done to understand why this is the case. For example, the functional group of the methanesulfonate may be changed to an ethyl group. In addition, the substitution of the Diels-Alder product may be changed, the yield of the reaction measured, and stable intermediates isolated. The results of these studies may provide a broader view of the reaction including steric effects for the dehydration of Diels-Alder products for aromatics synthesis.

The results from the additional mechanistic studies may be used to aid in the development of processes that use solids for the dehydration of Diels-Alder products. For example, recyclable solid-phase acylating reagents may be used. These materials, which are often polymers can transfer acyl groups at room temperature [28]. This

approach, which uses solid-phase acylating reagents, may decrease the cost of product separation and solvent recycle. Another possible process improvement is the optimization of reactant concentration while minimizing the production of side product. If optimal reaction conditions and solvent are chosen it may eliminate or significantly decrease the use of MSA.

Other reagents besides acylating reagents may be used such as etherification reagents. However, it must be noted that the use of acid to promote the dehydration of Diels-Alder products is not selective. The use of these alternative reagents may be less expensive than the use of anhydrides for the overall process.

7.3.2 Lewis Acid Catalysts for Diels-Alder Reaction of Furans

In chapter 4, it was shown that microporous Lewis acids are excellent catalysts for the Diels-Alder reactions of furans and acrylates. One reason for this is that these materials do not catalyze side reactions of furans and acrylates at the temperatures of reaction and at good turnover frequencies. The Diels-Alder reaction of furans is an important reaction for the conversion of these compound to aromatic molecules, the synthesis of pharmaceuticals, and a variety of other important molecules.

Future work related to this topic should center on the investigation of cheap, readily accessible materials which are active for the catalysis of Diels-Alder reaction of furans. Some candidate materials include ZrO_2 and HfO_2 (Figure 7.1). Microporous materials such Hf-, Zr-, and Sn-Beta often require hydrofluoric acid as the mineralization agent during synthesis, which is toxic [13]. As demonstrated in chapter 4, nanosized HfO_2 of the monoclinic phase is a good catalyst for the solvent-free

Diels-Alder reaction of furan and acrylic acid. An investigation of the effect of the extent of hydroxylation can be related to the activity of these catalysts. For these materials krypton adsorption is required to determine an accurate surface area. Additional methods like TPD-TGA could be used to calculate the number of accessible sites for these particles as it avoids any assumptions on which crystal facet is present on the surface, its activity, and be able to distinguish different sites present on these particles. The expected number of Hf atoms in 1 nm^2 for the $(-1 \ 1 \ 1)$ surface is 10.1.

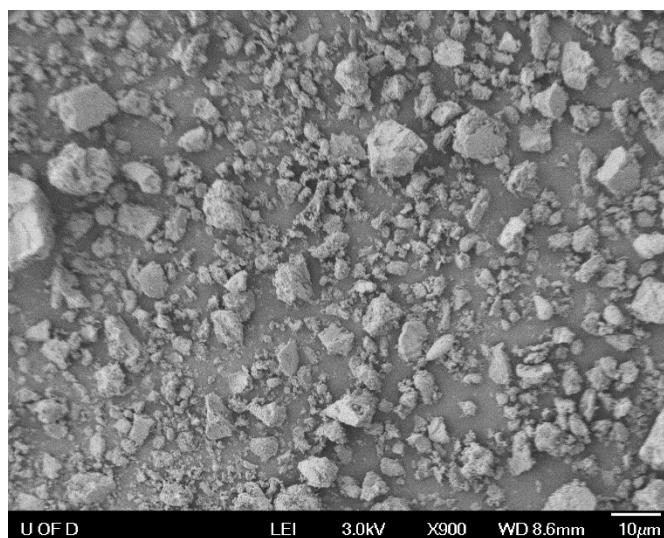


Figure 7.1 SEM image of ZrO_2

The synthesis method of these oxide materials may also be tailored to increase the number of surface atoms by altering synthesis temperature, metal precursor, and solvent.

7.3.3 Synthesis of Other Aromatic Molecules from Lignocellulosic Biomass

The results from chapter 3 and 4 can be used in the development of other processes for the production of aromatic molecules from furfural. These processes can be very selective, use industrially manufactured feedstocks, and its products are commercially manufactured.

Since the publication of the results in chapter 3 on the dehydration of Diels-Alder products of furans, additional work has been done utilizing the use of mixed anhydride for aromatics production. A biobased route to terephthalic acid from furfural was proposed. For the dehydration, a mixture of trifluoromethanesulfonic acid and acetic anhydride was employed giving an 84% yield to phthalic anhydride. Phthalic anhydride was hydrolyzed to dipotassium phthalate and converted to terephthalic acid [29]. In an alternative approach to deal with the challenge in the dehydration of Diels-Alder products, a three step strategy was studied which included a mild intermediate hydrogenation step of the Diels-Alder product which was subsequently dehydrogenated [30].

Other aromatic molecules of interest include styrene, toluene, benzophenone, and benzaldehyde. These molecules can potentially be synthesized by the Diels-Alder reaction of furan with various dienophiles such as methyl vinyl ketone followed by dehydration of the Diels-Alder product. Additional hydrogenation, decarboxylation, and dehydrogenation steps may be required.

7.3.4 Lewis Acid Catalysts for Renewable *p*-Xylene Synthesis

Work can also be done to find a more active heterogeneous catalyst for the solvent-free reaction of DMF and ethylene to *p*-xylene discussed in chapter 5. This increase in activity should not come at the cost on a significant decrease in selectivity. One such material is CIT-6 (Zn-Beta) which has been shown to enable chemistries previously not accessible with framework Sn-, Ti-, and Zr- based Lewis acid sites [31]. The solvent-free reaction may be monitored to look for intermediates to further understand the reaction mechanism.

7.4 Dissertation Accomplishments

In summary, the work presented in this thesis has shown several lab-scale processes for the production of aromatics and furans from lignocellulosic biomass. The processes presented in chapters 3 and 4 focus on the conversion of high-yield hemicellulose derived feedstocks, such as furan, to phthalic anhydride and benzoic acid. A new discovery was made regarding the dehydration of Diels-Alder products of furans which allows for nearly quantitative yields of aromatics. In chapter 4, it is demonstrated that the Diels-Alder reactions of furans and acrylates can be catalyzed by microporous Lewis acids of the zeolite Beta morphology. These microporous materials exhibit TOFs for these reactions that are one hundred times greater than the best heterogeneous catalyst reported for this reaction with no side products detected [12]. In chapter 5, it was demonstrated metal-exchanged faujasites catalyze the conversion of DMF and ethylene to *p*-xylene at 90% selectivity at 30% DMF conversion. The catalysts, which contain extraframework Lewis acids, were found to

be reusable. Finally, in chapter 6, a production route to HMF from glucose catalyzed by heterogeneous catalysts in low boiling point ($<100\text{ }^{\circ}\text{C}$) alcoholic solvents is discussed. It was found that glucose can be converted to furans (HMF and IMF) with an 88% selectivity at 60% glucose conversion when using mixtures of Sn-Beta zeolite (Lewis acid) and Amberlyst 15 (Brønsted acid) catalysts in isopropanol. The results presented in this thesis may be used to aid in the development of other processes for the production of chemicals and fuels from biomass.

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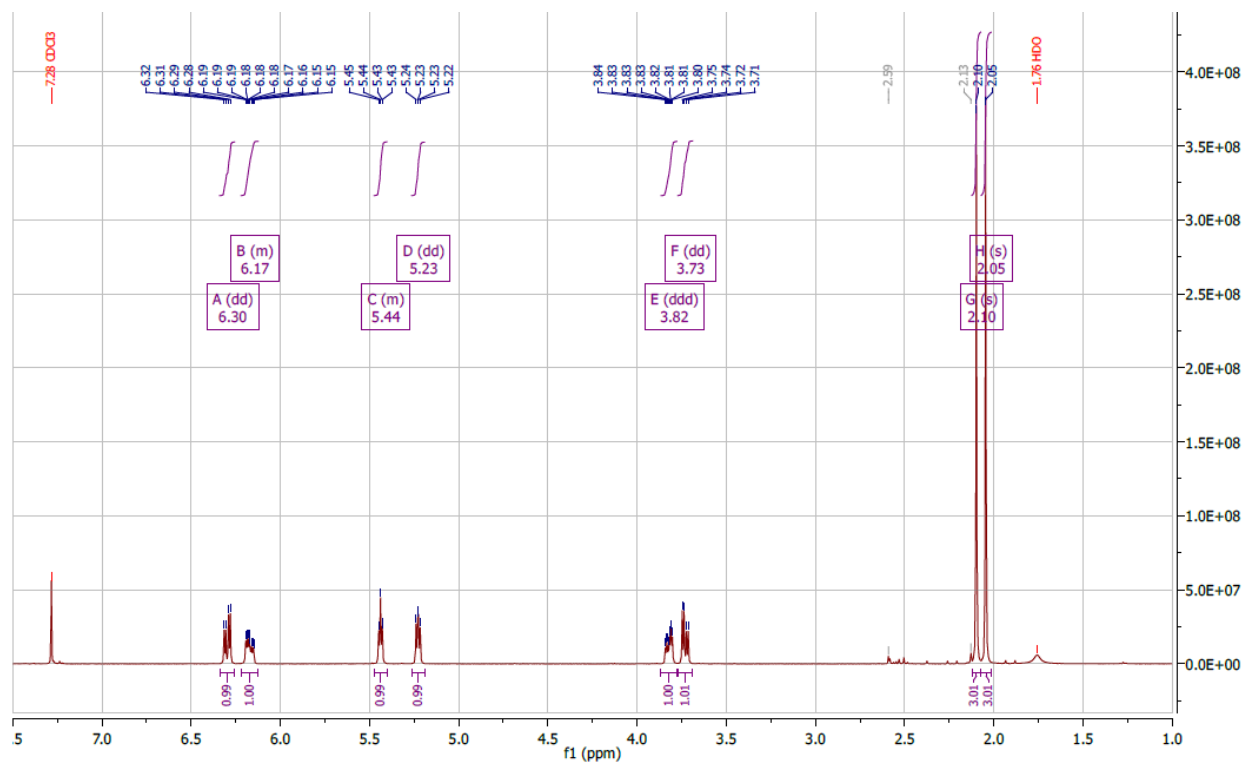
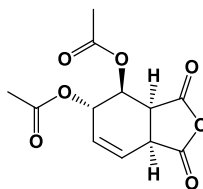
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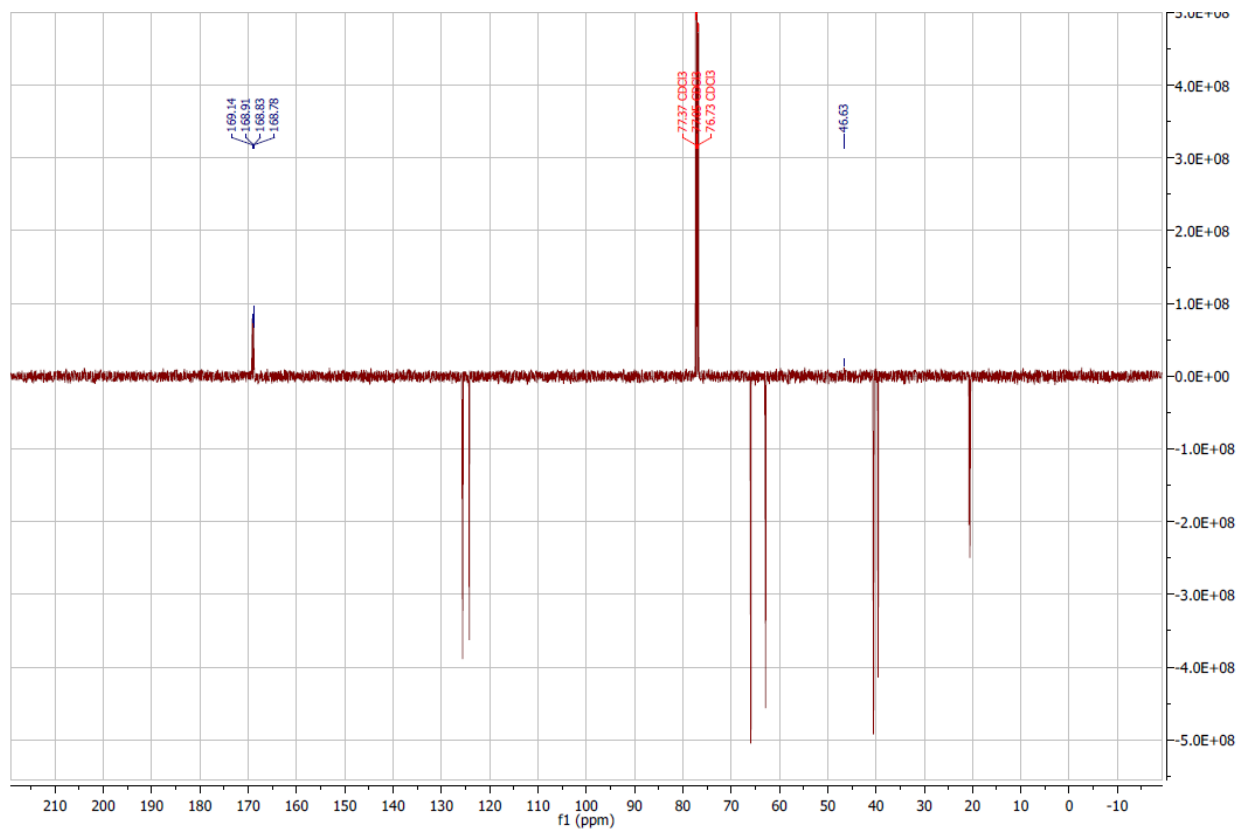
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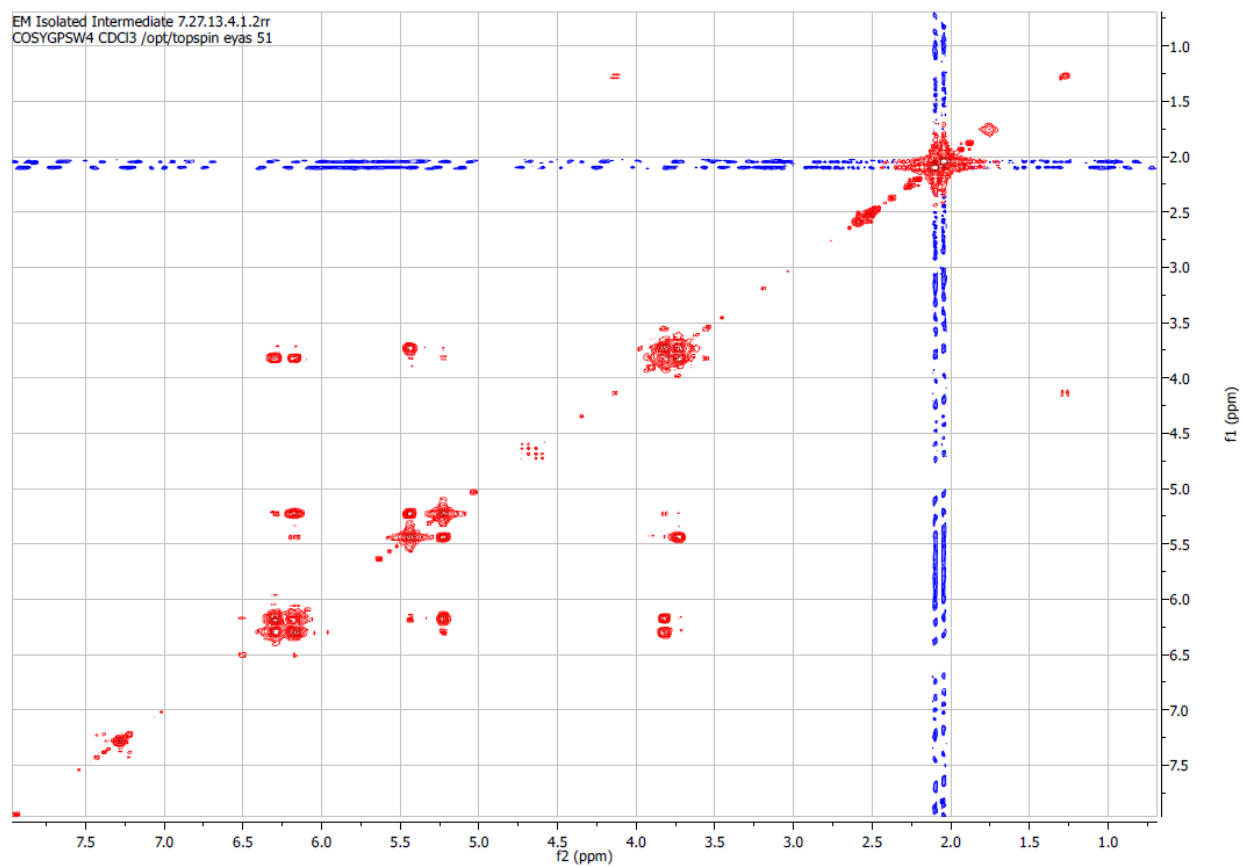
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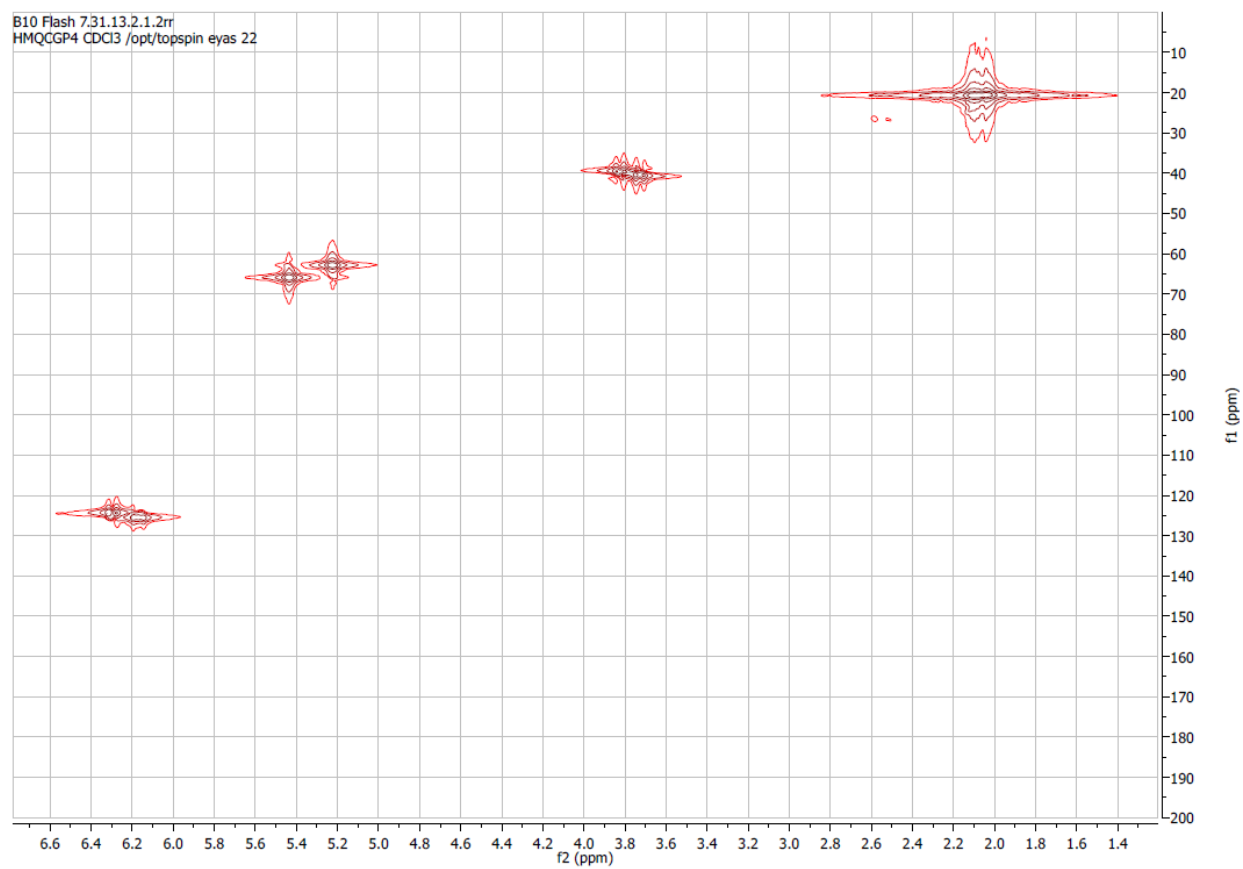
Appendix A

NMR CHARACTERIZATION OF REACTION INTERMEDIATE AND ANALYSIS OF DIELS-ALDER REACTION FOR RENEWABLE PHTHALIC ANHYDRIDE PRODUCTION









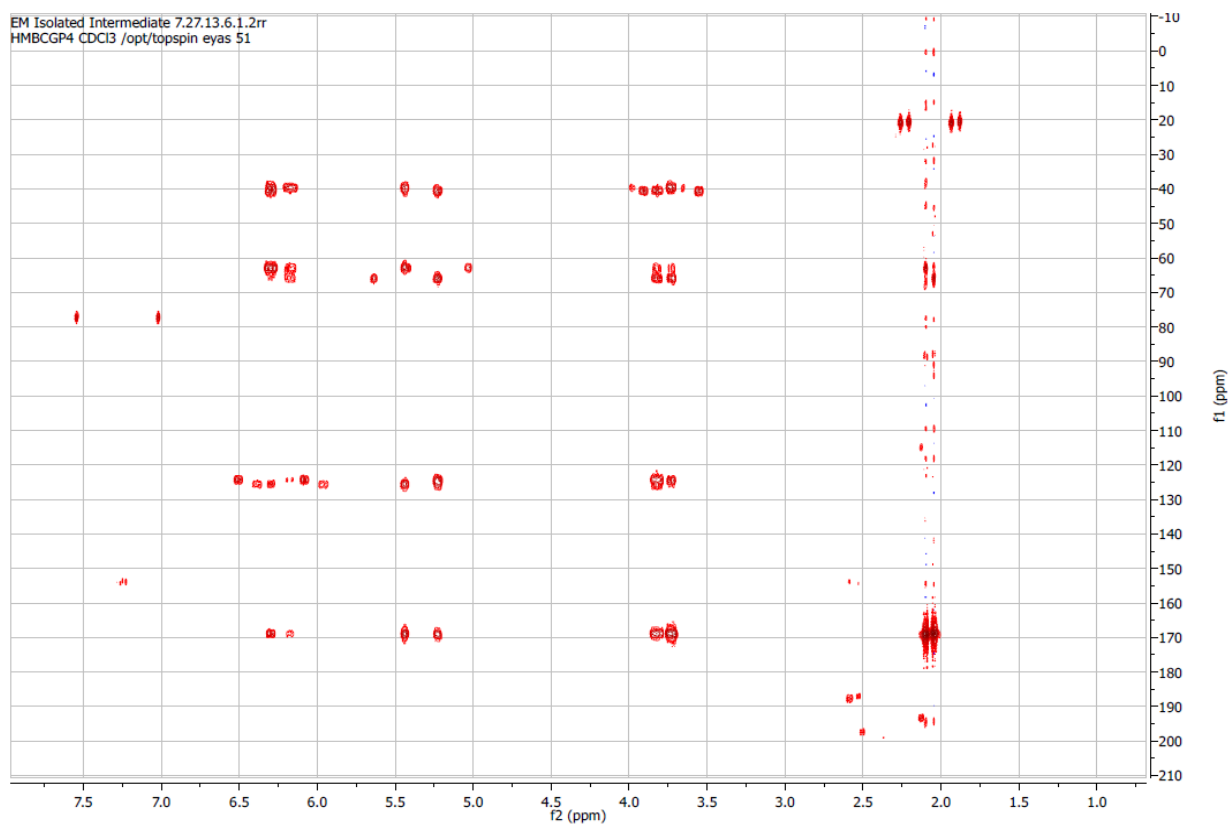


Figure A1. NMR spectra of the reaction intermediate, (rac) (3aS,4S,5S,7aS)-1,3-dioxo-1,3,3a,4,5,7a-hexahydroisobenzofuran-4,5-diyl diacetate in CDCl₃.

Diels-Alder Reaction

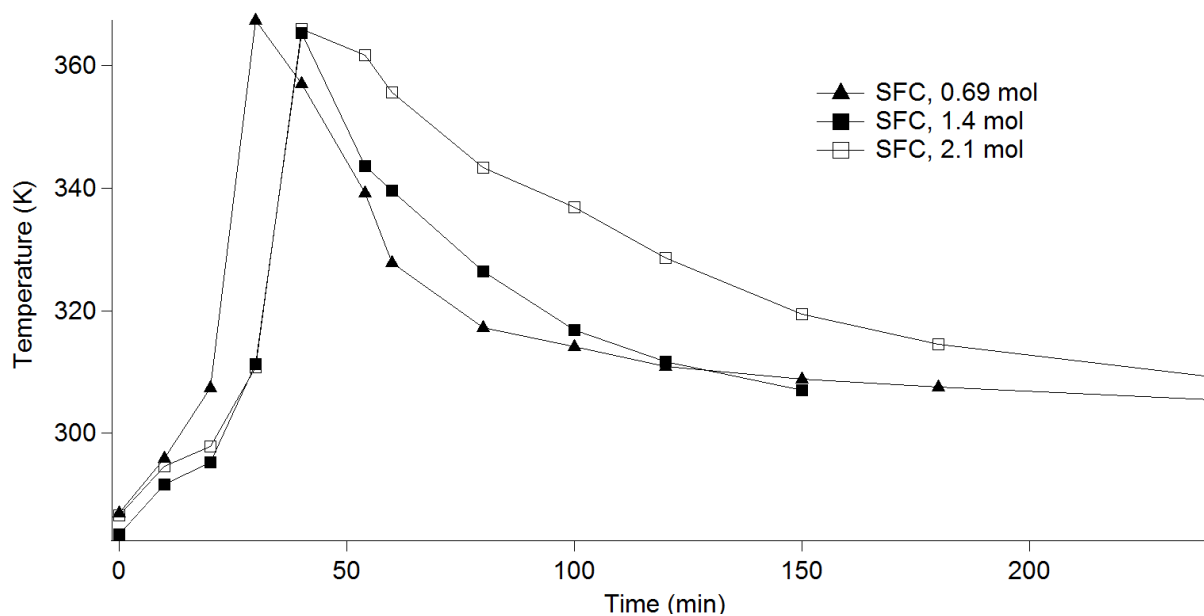


Figure A2 (a). Temperature of the Diels-Alder reaction of furan and maleic anhydride as a function of time under solvent-free conditions (SFC).

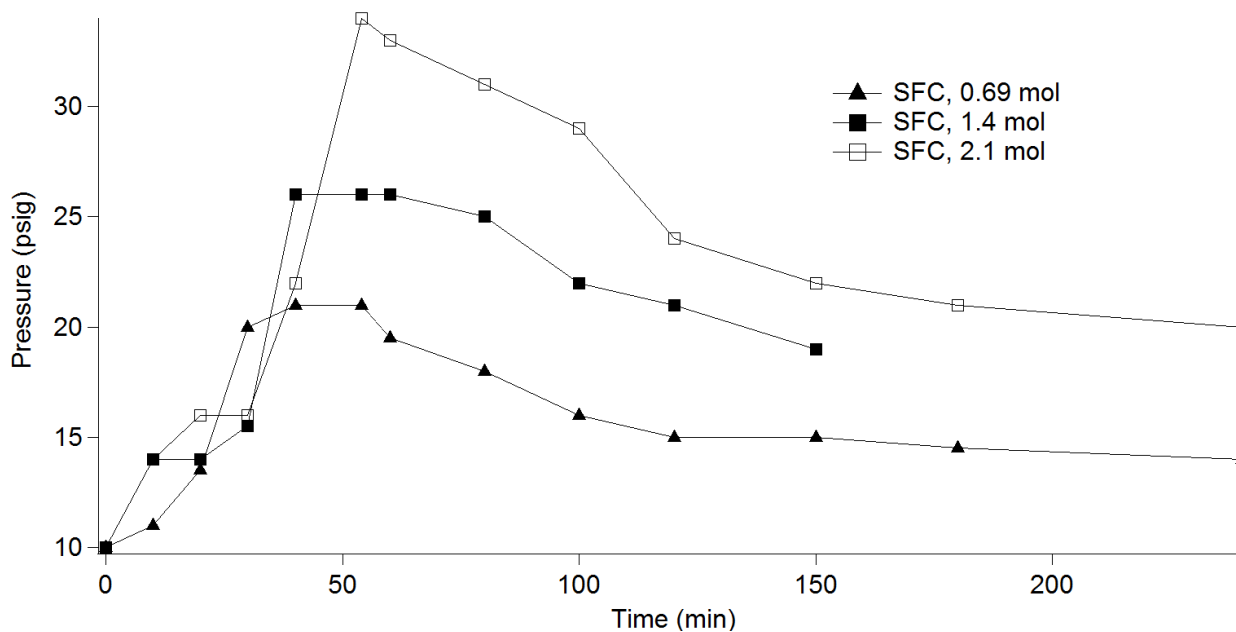
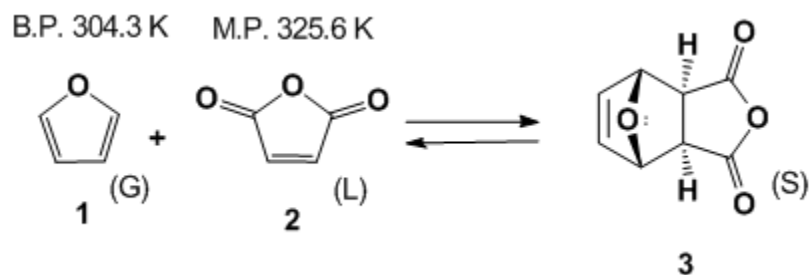


Figure A2 (b). Pressure of the Diels-Alder reaction of furan and maleic anhydride as a function of time under SFC.

Oxanorbornene Dicarboxylic Anhydride (3) Equilibrium Experiments



For reactions involving combined chemical and phase equilibrium, the equality of the partial molar Gibbs free energy of each species in all phases at equilibrium assures that if the chemical equilibrium criterion is satisfied in any one phase, it will be satisfied in all phases.¹

$$K_{eq} = \frac{a_3}{a_1 a_2} = \frac{1}{\left(\frac{P_{furan}}{1bar}\right) * 1} \quad [Eqn. A1]$$

Correcting for the pressure of N₂, the pressure of furan was determined and used to calculate K_{eq}.

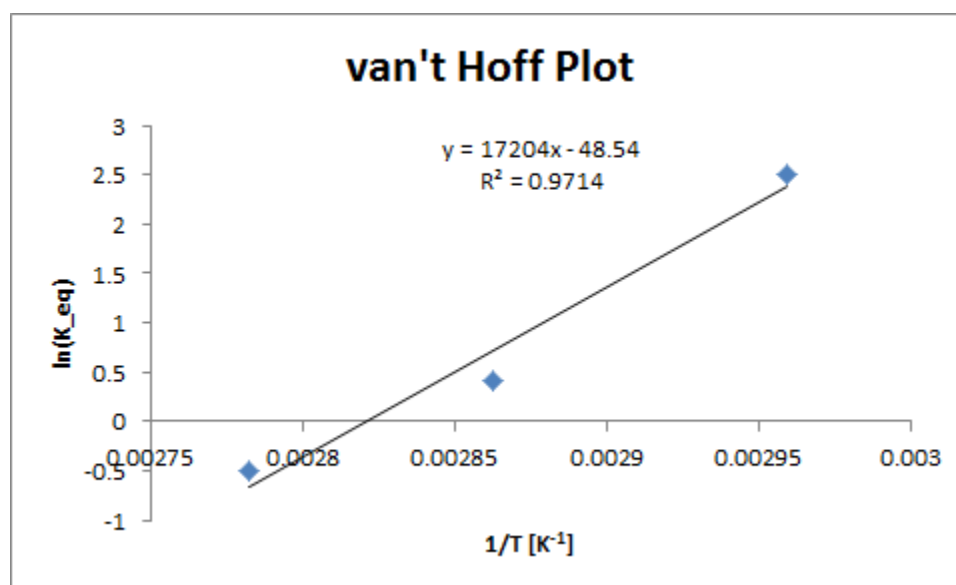


Figure A3 (a). van't Hoff plot of the equilibrium constant of the Diels-Alder reaction of furan and maleic anhydride vs. $1/T$.

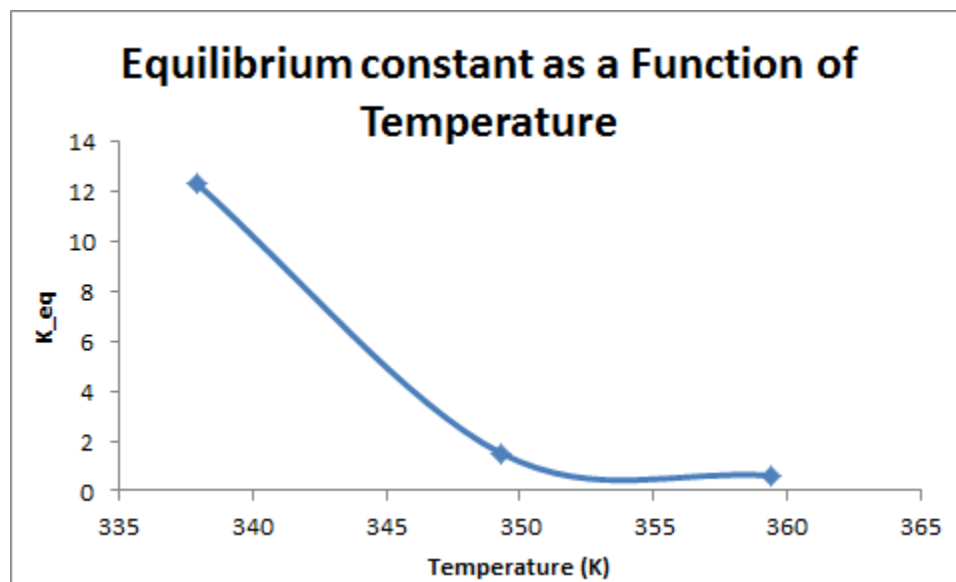


Figure A3 (b). Plot of the equilibrium constant of the Diels-Alder reaction of furan and maleic anhydride in the forward direction vs. Temperature.

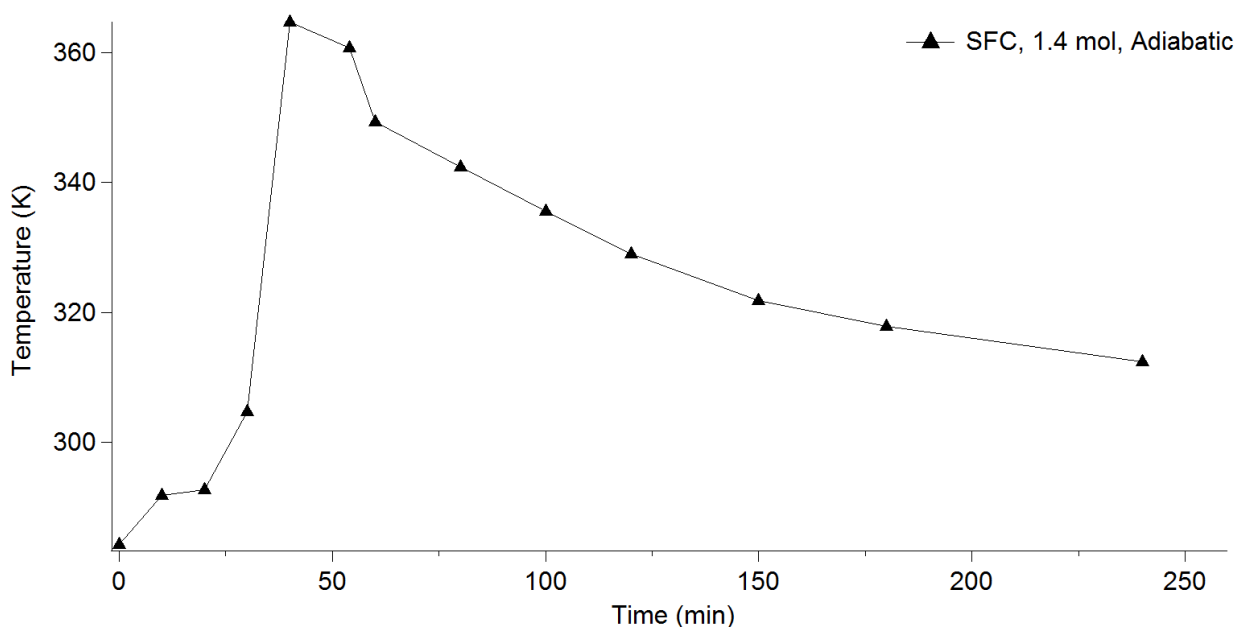
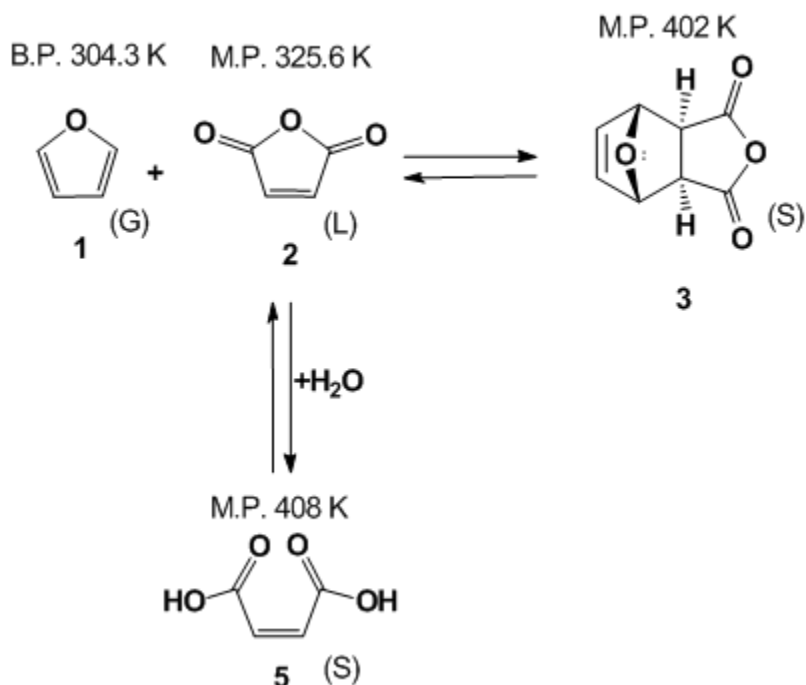


Figure A4. Temperature of the Diels-Alder reaction of furan and maleic anhydride as a function of time under pseudo-adiabatic conditions.

Equilibrium Experiments run in the Presence of Water



^1H NMR taken following completion of the equilibrium experiments revealed the compounds shown above. Oxanorbornene dicarboxylic acid was not detected, therefore the Diels-Alder reaction of furan and maleic acid was not considered.

. The equilibrium constant is given by:

$$K_{eq} = \frac{a_3}{a_1 a_5} = \frac{1}{\left(\frac{P_{furan}}{1\text{bar}}\right) * 1} \quad [Eqn. A2]$$

For this reaction at the same temperature, the equilibrium constant remains the same as in figure A4, however maleic anhydride reacts with water to form maleic acid. Correspondingly, the pressure of furan increases at the same temperature. This is what is seen in figure A6.

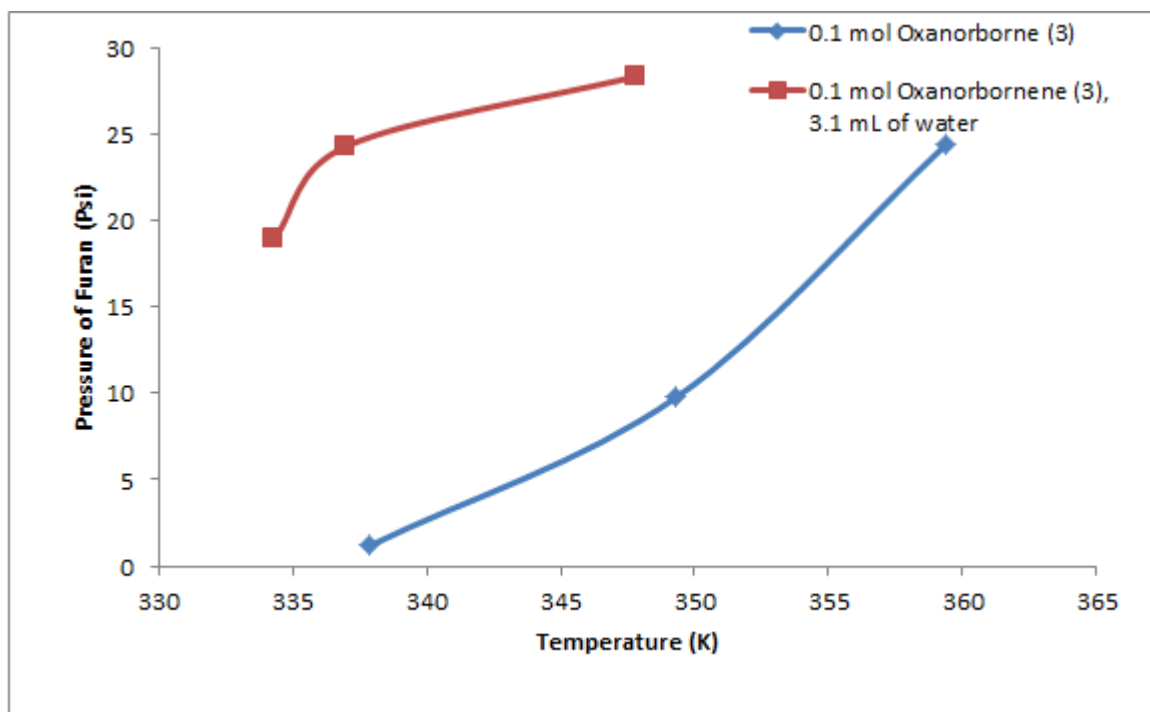


Figure A5. Partial pressure of furan at different temperatures in the presence and absence of water.

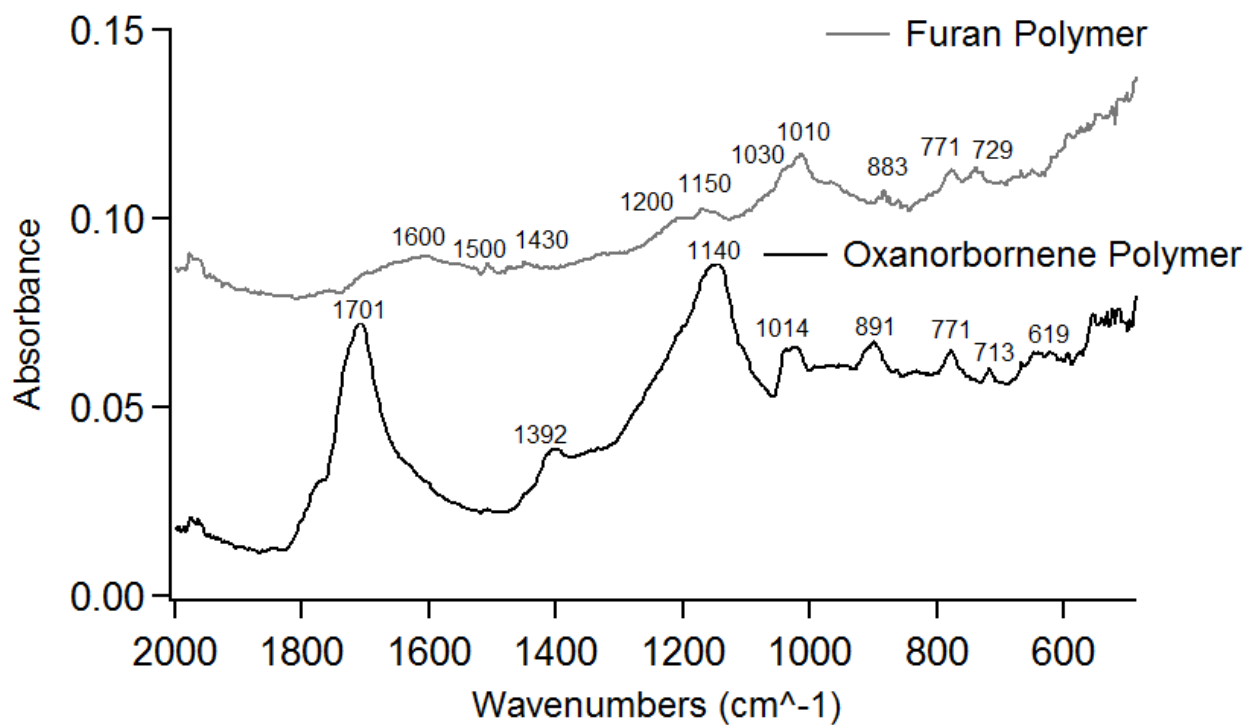


Figure A6. ATR-IR Spectrum of the oxanorbornene polymer and furan polymer prepared by reaction at 298 K for 3 hrs followed by precipitation and washing with ice-cold water.

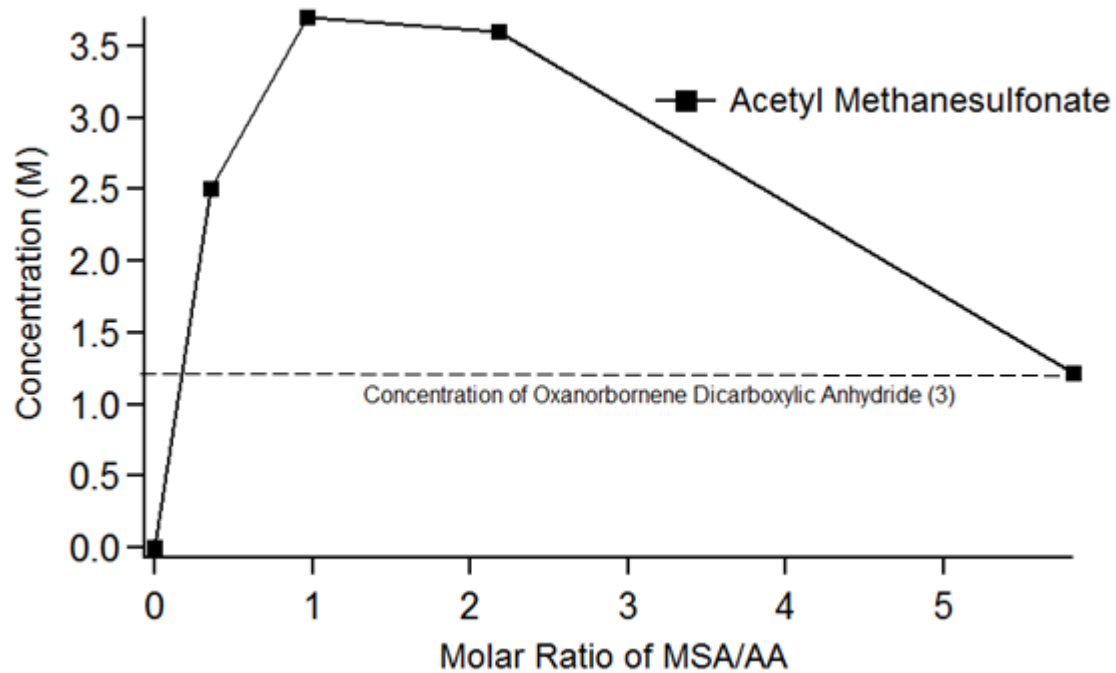


Figure A7. Concentration of acetyl methanesulfonate as a function of the molar ratio of MSA/acetic Anhydride (total solution volume kept constant at 5 mL) following 5 minutes of reaction.

Appendix B

CATALYST CHARACTERIZATION AND KINETIC ANALYSIS FOR BENZOIC ACID SYNTHESIS

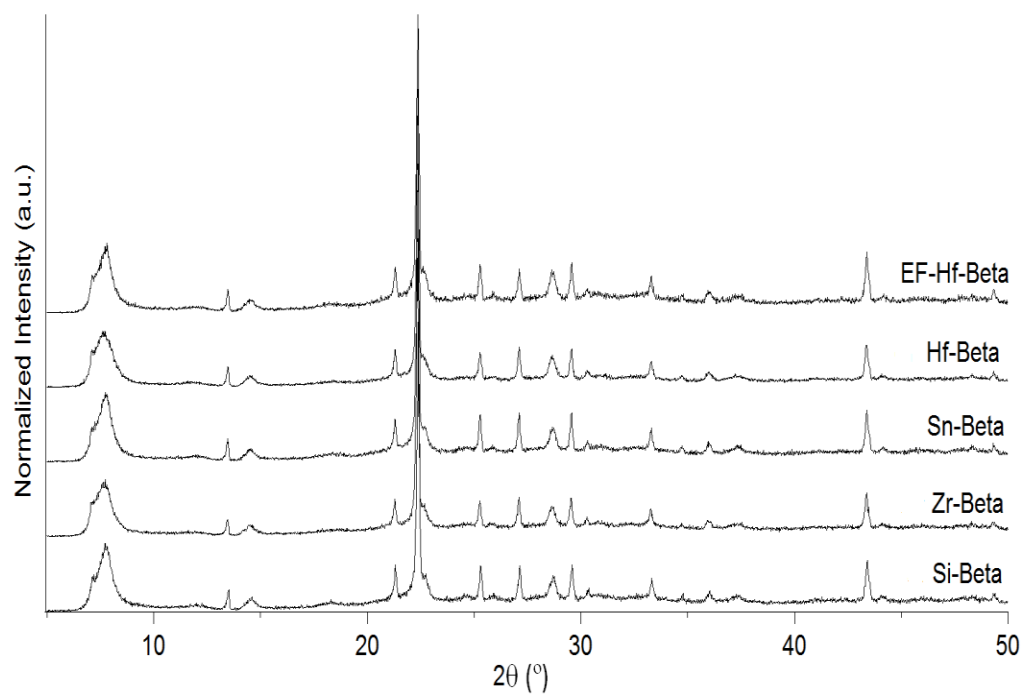


Figure B1. Powder X-ray diffraction patterns of Si-Beta, Zr-Beta (Si/Zr=325), Sn-Beta (Si/Sn=230), Hf-Beta (Si/Hf=219), and EF-Hf-Beta (Si/Hf=200) zeolites.

Table B1. Textural properties of catalyst samples.

Sample	microporous volume (cm ³ g ⁻¹) ^a	external surface area (m ² g ⁻¹) ^a
Hf-Beta (Si/Hf=219)	0.18	67.75
Zr-Beta (Si/Zr=325)	0.19	69.69
Sn-Beta (Si/Sn=230)	0.19	93.15
Si-Beta	0.20	58.32
EF-Hf-Beta (Si/Hf~200)	0.21	24.91
EF-Zr-Beta (Si/Zr~200)	0.21	30.60

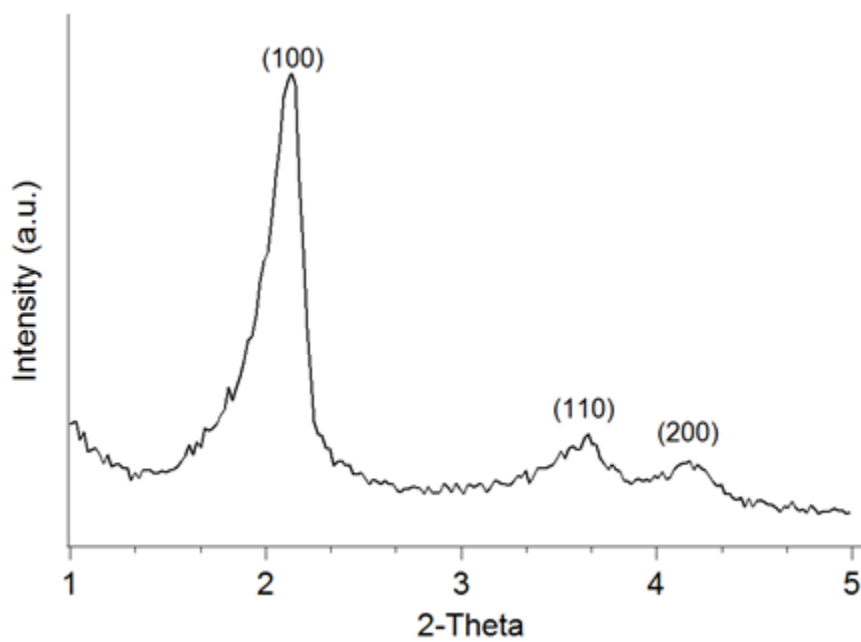
^aDetermined using the t-plot method.

Figure B2. Powder X-ray diffraction pattern of Sn-MCM-41 (Si/Sn=50).

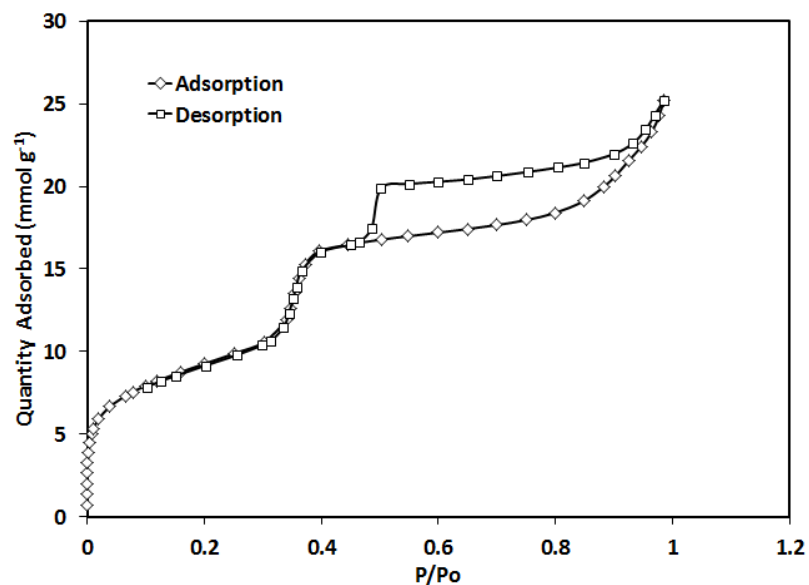


Figure B3. Nitrogen adsorption-desorption isotherm of Sn-MCM-41.

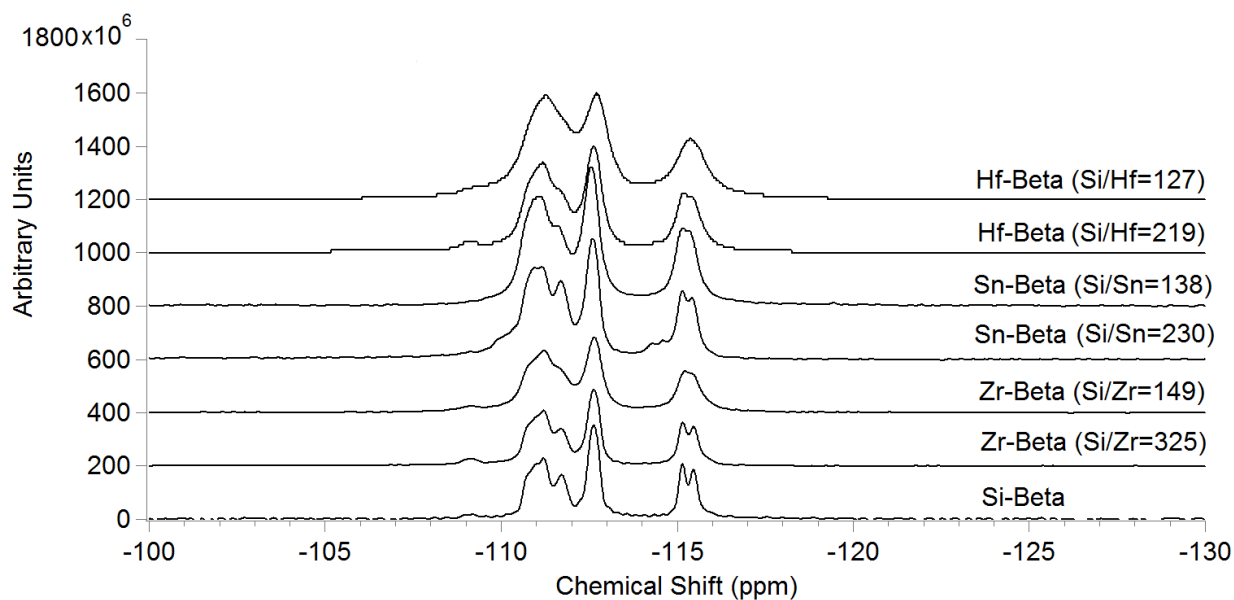


Figure B4. ^{29}Si NMR of Hf, Sn, Zr and Si-Beta zeolites.

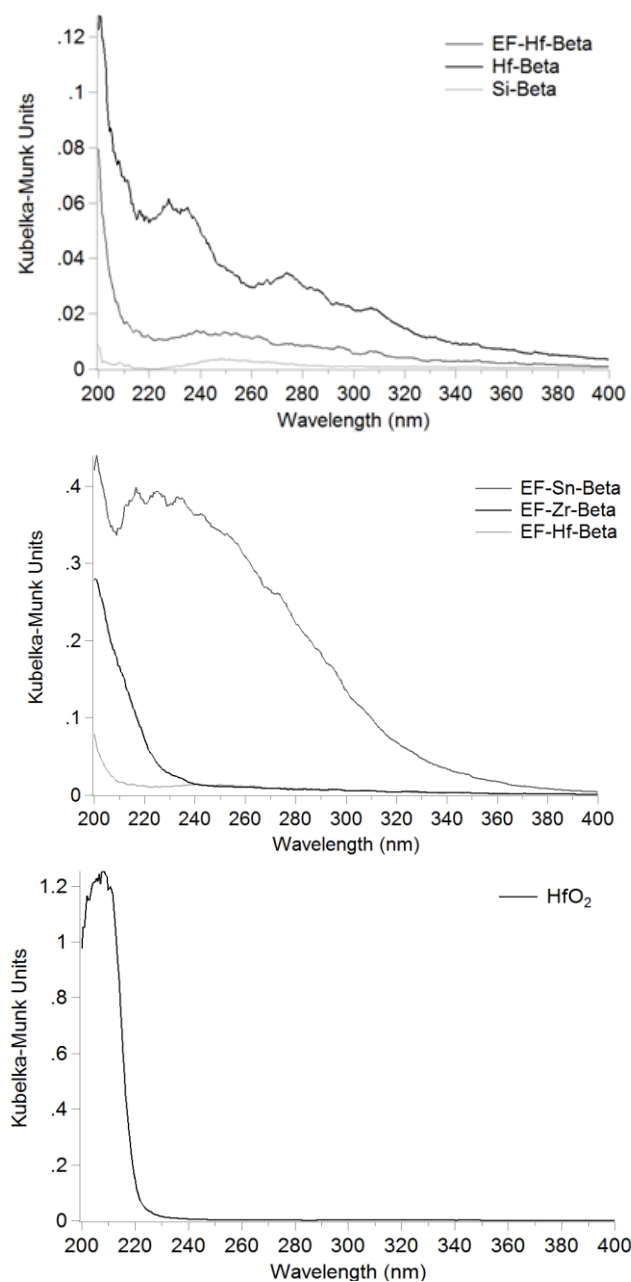


Figure B5. Reflectance UV-Vis spectra of Si, Hf, EF-Hf, EF-Zr, and EF-Sn-Beta zeolites.

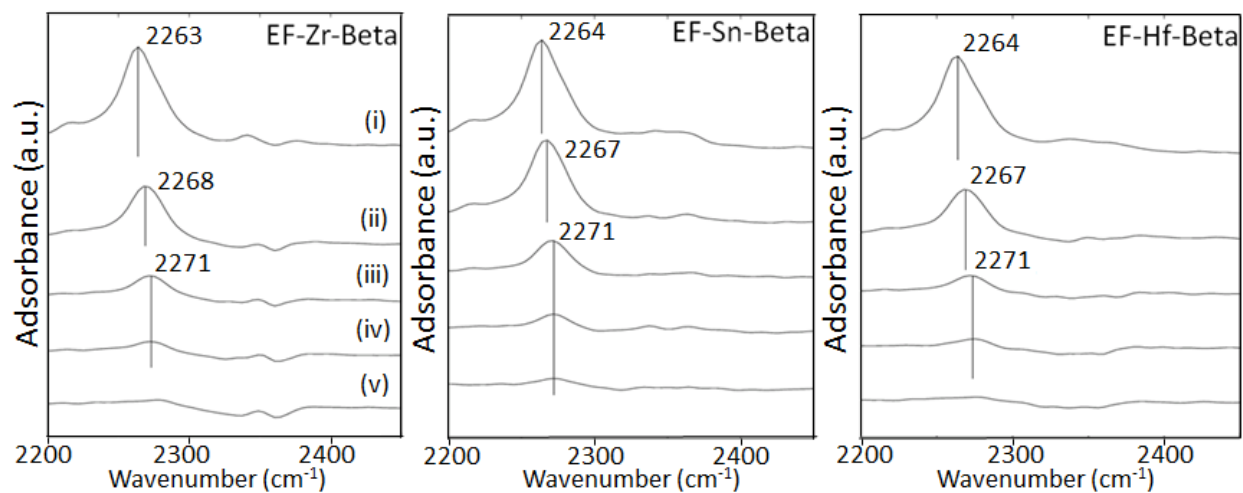


Figure B6. FTIR spectra of EF-M-Beta (Si/M~200) (i) in pure He flow at RT immediately after removing CD₃CN vapor; in He flow after heating to 333 K for (ii) 1 min; (iii) 2 min; (iv) 3 min; (v) 5 min.

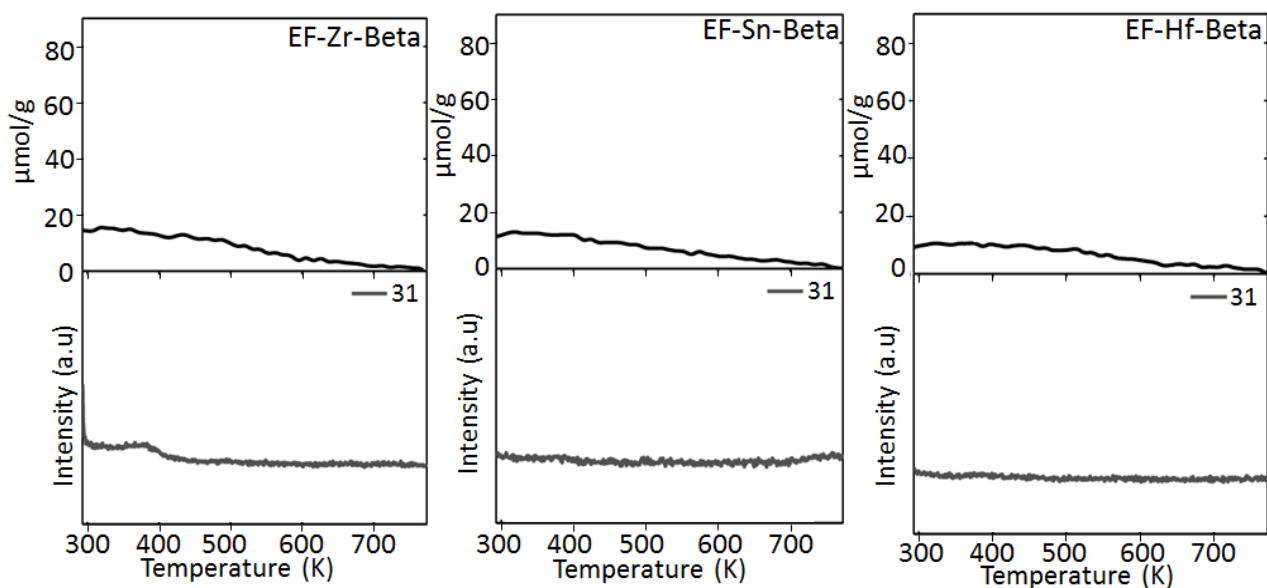


Figure B7. TPD (lower curves) and TGA (upper curves) traces of diethyl ether dosed onto EF-M-Beta samples (M=Zr, Sn, and Hf) with Si/M~200. Diethyl ether was monitored in the mass spectra by its $m/e=31$ peak.

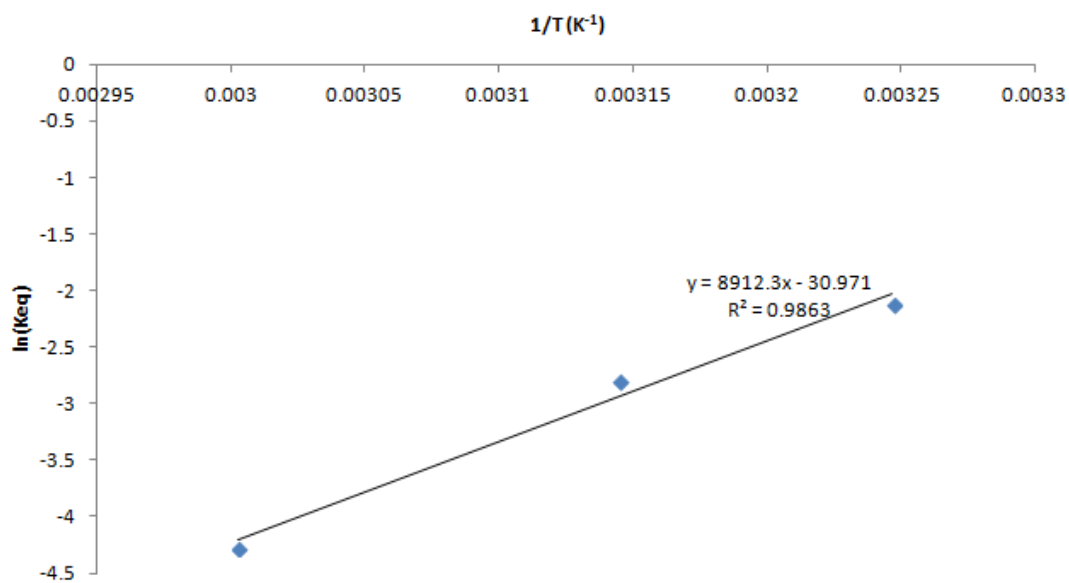


Figure B8. Van't Hoff plot. The ΔH_{rxn} and ΔS_{rxn} of the Diels-Alder reaction of furan and methyl acrylate was calculated to be $-74.1 \text{ kJ mol}^{-1}$ and $-0.257 \text{ kJ mol}^{-1} \text{ K}^{-1}$.

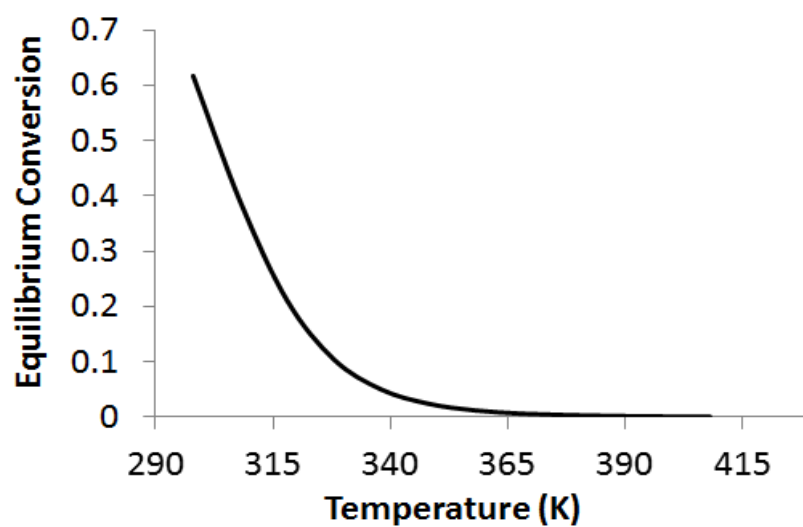


Figure B9. Calculated equilibrium conversion vs. temperature for the Diels-Alder reaction of furan and methyl acrylate under solvent free conditions ($\Delta H_{\text{rxn}} = -74.1 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{rxn}} = -0.257 \text{ kJ mol}^{-1} \text{ K}^{-1}$, initial molar ratio of furan to methyl acrylate of 5.28).

Table S2 Diels-Alder Reaction of Furan and Methyl Acrylate Catalyzed by Hf-, Zr- and Sn- zeolite Beta and other Materials^a

Catalyst (Si/M ratio)	<i>M:Hf Molar Ratio^b</i>	Yield (%) ^c	Turnover Frequency [h ⁻¹] ^d
Hf-Beta (219)	1.0	25	1.9 (1.8)
Sn-Beta (230)	1.0	25	2.0 (1.8)
Zr-Beta (325)	0.68	22	2.4 (2.2)
Hf-Beta (127)	1.7	13	0.57 (0.48)
Sn-Beta (134)	1.6	20	0.94 (0.85)
Zr-Beta (149)	1.5	17	0.88 (0.78)
H-Al-Beta (4)	12	31	0.19
Si-Beta	-	1.9	-

Reactions were run under solvent free conditions at 298 K for 24 h. 6.9 mmol of furan and 1.36 mmol of methyl acrylate and 0.10 g of zeolite Beta catalyst corresponding to 0.0075 mmol loading of Hf or 0.55 mol% Hf with respect to methyl acrylate (Si/Hf=219). Metal contents of the zeolites in bold were determined by ICP-OES. An identical mass of Si-Beta catalyst was used compared to the amount of metal containing zeolite catalysts.

a-Reactions run without a catalyst gave no yield of oxanorbornene under these reaction conditions.

b-The molar ratio is defined as the moles of metal, M, in the catalyst (M=Hf, Zr, Sn, Al or Zn) divided by the moles of Hf in Hf-Beta.

c-Percent yield of oxanorbornene products.

d-Turnover frequency calculated by moles of oxanorbornene produced divided by moles of metal in catalyst. Values in parenthesis are turnover frequencies calculated after subtracting the yield of product associated with Si-Beta.

*M-Beta (~100) samples were prepared using a seeded synthesis method.

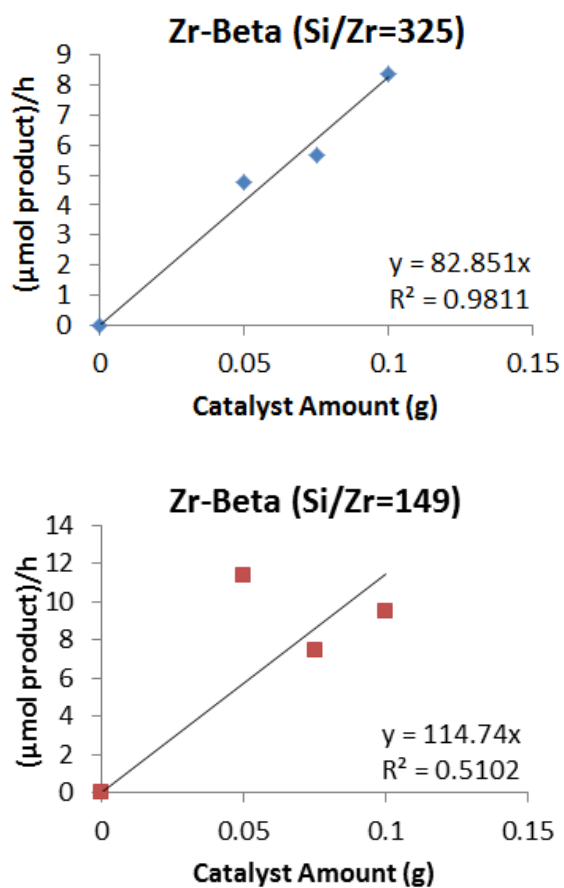


Figure B10. Effect of catalyst amount on μmol product produced per hour. 6.9 mmoles of furan and 1.36 mmol of methyl acrylate were reacted at 25 °C for 6 h with addition of the Zr-Beta catalyst. Si-Beta zeolite showed no product production under these conditions.

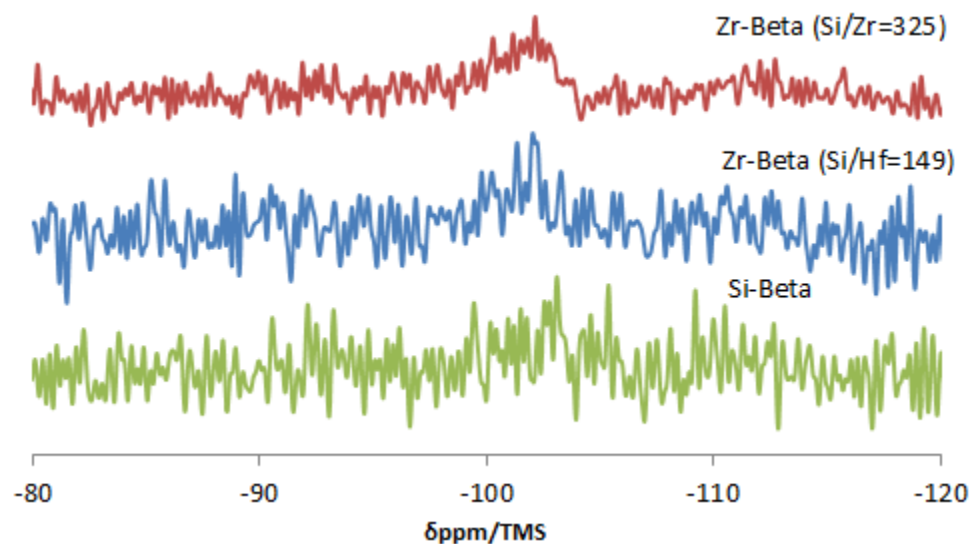


Figure B11. ^1H - ^{29}Si CP-MAS NMR spectra of Si-Beta, Zr-Beta (Si/Zr=325) and Zr-Beta (Si/Zr=149).

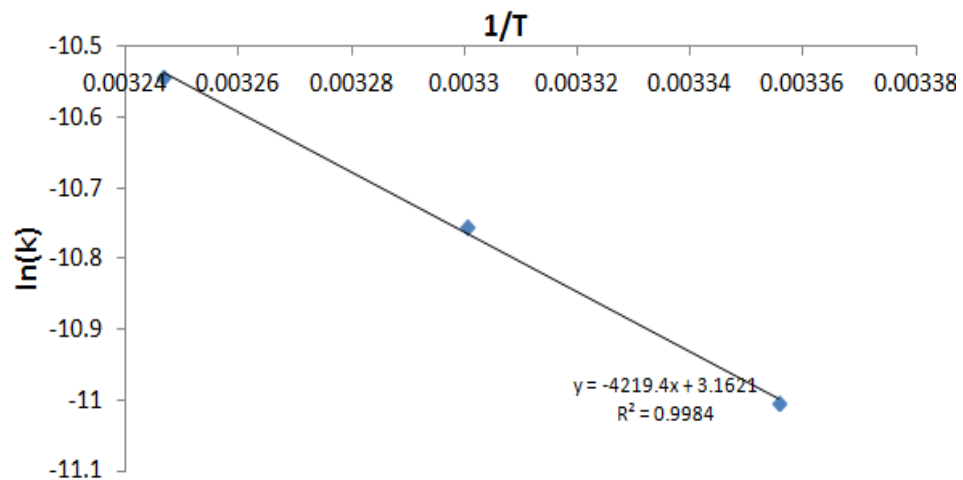
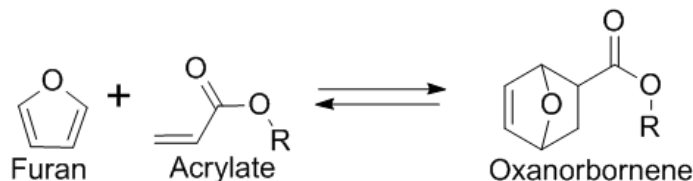


Figure B12. Arrhenius plot. The activation energy of the Diels-Alder reaction of furan and methyl acrylate was found to be 35.1 kJ mol^{-1} with a pre-exponential factor of $23.6 \text{ moles g cat.}^{-1}\text{sec}^{-1}\text{L}^{-1}$.

Designing optimum reaction temperature programs for the Diels-Alder reaction of furan and acrylates

We derive a mathematical equation to calculate optimum reaction temperature programs to maximize product yield and minimize reaction time of Diels-Alder reactions assuming a constant volume, elementary, second order reversible reaction which is first order in the reverse direction. The derived equation (Equation B2), is implemented in a MATLAB code using experimentally obtained kinetic and thermodynamic parameters for the particular Diels-Alder reaction of furan and methyl acrylate to find optimal temperature profiles ($\Delta H_{\text{rxn}} = -74.1$ kJ/mol, $\Delta S_{\text{rxn}} = -0.257$ kJ/(mol K), $E_a^{\text{rxn}} = 35.1$ kJ/mol and $A = 23.6$ mol gcat⁻¹sec⁻¹L⁻¹).

In Scheme B1, the Diels-Alder reactions of interest are depicted.



Scheme B1. Diels-Alder reaction of furan and acrylate. The functional group of the acrylate, R, can be H or CH₃.

Let [A] denote the concentration of the diene (furan), [B] the concentration of the dienophile (acrylate) and [C] the concentration of the product (oxanorbornene). One can begin with the equation for the rate of a reversible reaction which is second order in the forward direction and first order in the reverse direction shown below:

$$r = k^+[A][B] \left(1 - \frac{[C]}{K[A][B]}\right) = r^+ - r^- \quad (\text{Eq B1})$$

Assuming a constant reactor volume and equating the net rate of reaction to the change in concentration of [A], one obtains the following equation:

$$\frac{d[A]}{dt} = -r_A = -k^+[A][B] \left(1 - \frac{[C]}{K[A][B]}\right)$$

One can relate the concentration of [A], [B] and [C] to conversion using the equations below:

$$[A] = [A]_0 - [A]_0 X_A, \quad d[A] = -[A]_0 dX_A$$

$$[B] = [B]_0 - [A]_0 X \text{ and } [C] = [A]_0 X, \text{ where } X_A \text{ is the conversion of } A$$

Substituting these equations into Equation B1:

$$-[A]_0 \frac{d[X_A]}{dt} = -k^+([A]_0 - [A]_0 X_A) ([B]_0 - [A]_0 X_A) \left(1 - \frac{[A]_0 X_A}{K ([A]_0 - [A]_0 X_A)([B]_0 - [A]_0 X_A)}\right)$$

Simplifying the equation above by canceling negatives and dividing by $[A]_0$:

$$\frac{d[X_A]}{dt} = k^+(1 - X_A) ([B]_0 - [A]_0 X_A) \left(1 - \frac{X_A}{K (1 - X_A)([B]_0 - [A]_0 X_A)}\right)$$

Separating variables:

$$\int_{X_{A0}}^{X_A} \frac{d[X_A]}{(1 - X_A) ([B]_0 - [A]_0 X_A) \left(1 - \frac{X_A}{K (1 - X_A)([B]_0 - [A]_0 X_A)}\right)} = \int_0^t k^+ dt$$

Simplifying the denominator on the left-hand side:

$$\int_{X_{A0}}^{X_A} \frac{d[X_A]}{\left((1 - X_A) ([B]_0 - [A]_0 X_A) - \frac{X_A}{K}\right)} = \int_0^t k^+ dt$$

Finally, after integration the equation becomes:

$$\frac{2K \tan^{-1} \left[\frac{[A]_0 K (2X_A - 1) - [B]_0 K - 1}{\sqrt{-[A]_0^2 K^2 + 2[A]_0 K ([B]_0 K - 1) - ([B]_0 K + 1)^2}} \right]}{\sqrt{-[A]_0^2 K^2 + 2[A]_0 K ([B]_0 K - 1) - ([B]_0 K + 1)^2}} \Bigg|_{X_{A0}}^{X_A} = k^+ t \Big|_{t_0}^t$$

Plugging in the integral bounds into the equation above we obtain:

$$\frac{2K \tan^{-1} \left[\frac{[A]_0 K(2X_A - 1) - [B]_0 K - 1}{\sqrt{-[A]_0^2 K^2 + 2[A]_0 K([B]_0 K - 1) - ([B]_0 K + 1)^2}} \right]}{\sqrt{-[A]_0^2 K^2 + 2[A]_0 K([B]_0 K - 1) - ([B]_0 K + 1)^2}} - \frac{2K \tan^{-1} \left[\frac{[A]_0 K(2X_{A0} - 1) - [B]_0 K - 1}{\sqrt{-[A]_0^2 K^2 + 2[A]_0 K([B]_0 K - 1) - ([B]_0 K + 1)^2}} \right]}{\sqrt{-[A]_0^2 K^2 + 2[A]_0 K([B]_0 K - 1) - ([B]_0 K + 1)^2}} = k^+ t - k^+ t_0$$

(Eq B2)

Finally, solving for conversion one obtains the following equation used to find optimal reaction temperature programs for second order reversible Diels-Alder reactions:

$$X_A = \frac{[A]_0 K + [B]_0 K + 1}{2[A]_0 K} + \frac{1}{2[A]_0 K} \tan \left(\frac{2K \tan^{-1} \left(\frac{([B]_0 K + 1 + [A]_0 K(1 - 2X_{A0}))}{\sqrt{2[A]_0 K([B]_0 K - 1) - ([B]_0 K + 1)^2 - [A]_0^2 K^2}} \right) - k^+ t \sqrt{2[A]_0 K([B]_0 K - 1) - ([B]_0 K + 1)^2 - [A]_0^2 K^2} + k^+ t_0 \sqrt{2[A]_0 K([B]_0 K - 1) - ([B]_0 K + 1)^2 - [A]_0^2 K^2}}{2K} \right)$$

(Eq B3)

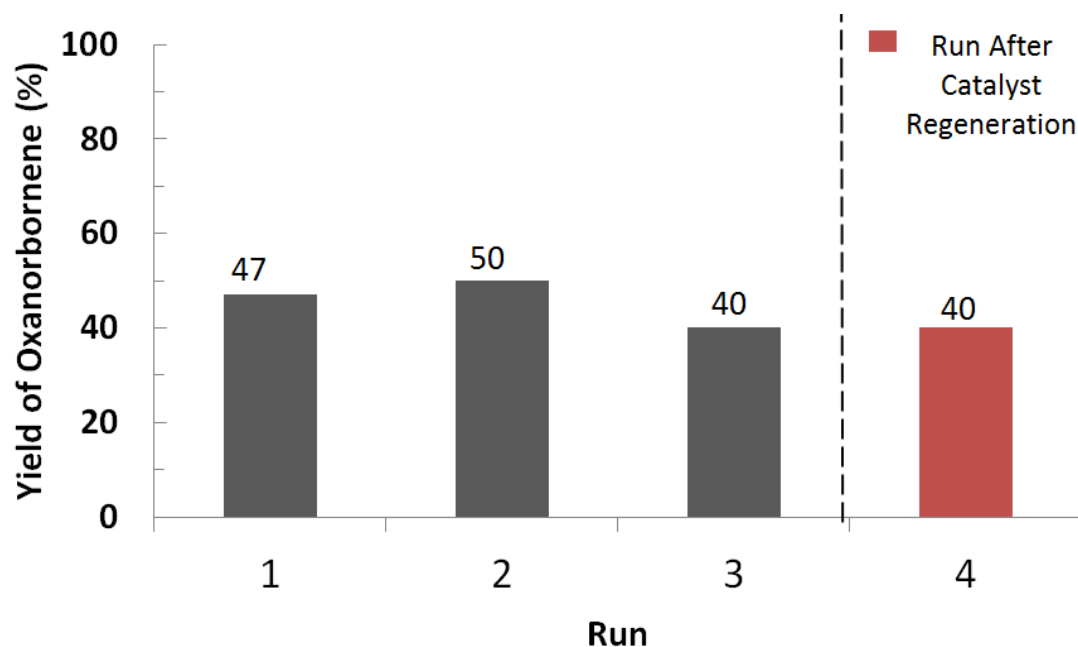


Figure B13. Hf-Beta catalyst reusability and regeneration. Reactions were run at 25 °C for 24 h using a 3.85:1 molar ratio of furan and acrylic acid and a 0.41 mol% loading of Hf relative to acrylic acid. Run 4 denotes yield after catalyst regeneration using an identical calcination treatment for a freshly calcined catalyst. The catalyst was washed in methanol and dried at 120 °C for 24 h between each use and before regeneration.

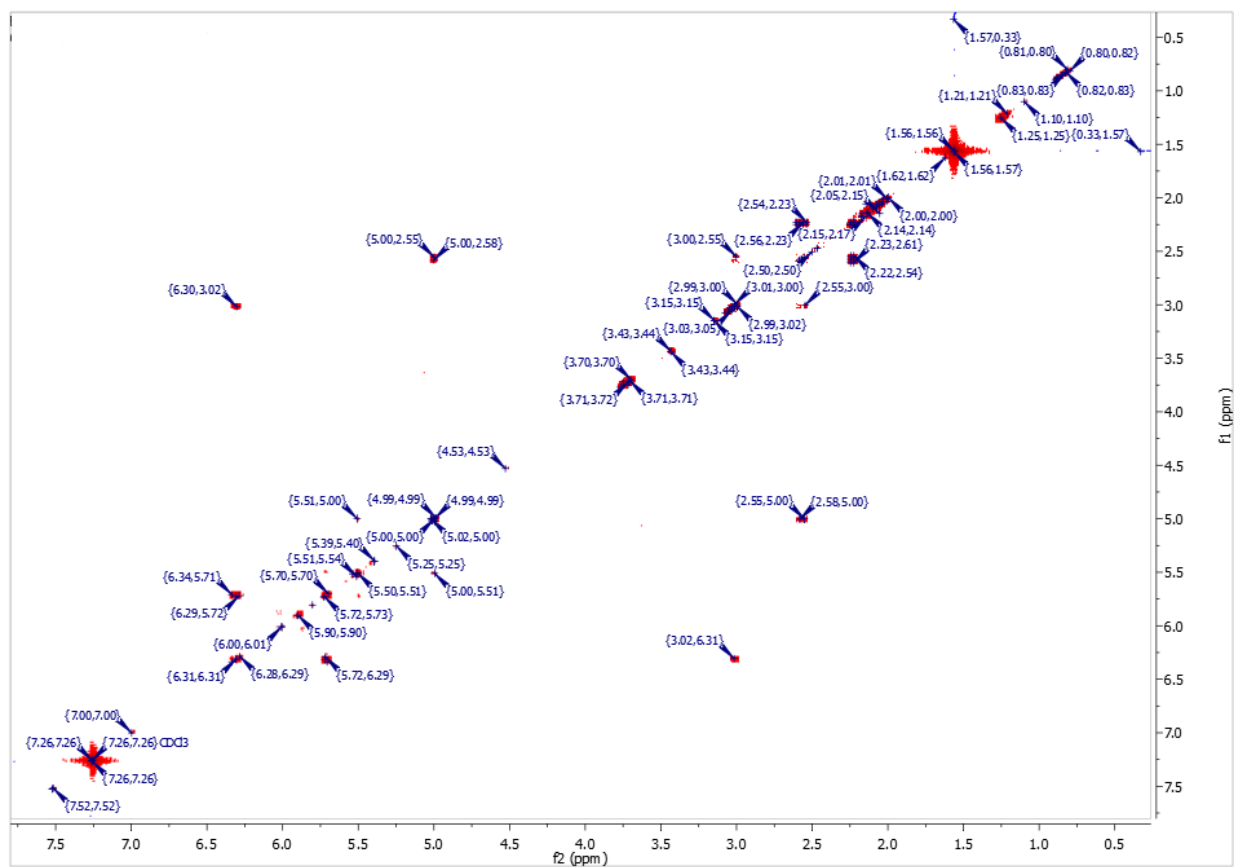


Figure B14. 2D NMR COSY of 4,5-diacetoxycyclohex-2-enecarboxylic acid.

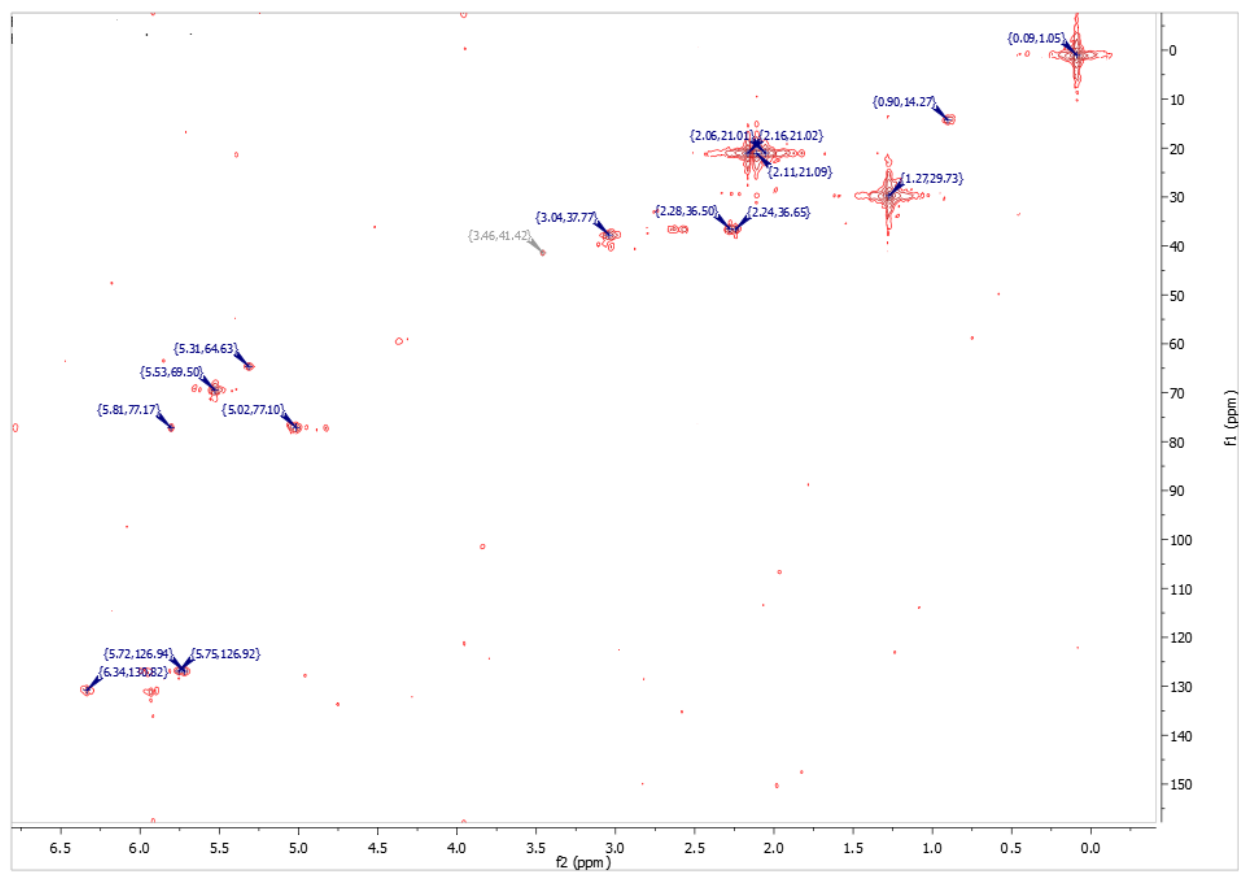


Figure B15. 2D NMR HMQC of 4,5-diacetoxycyclohex-2-enecarboxylic acid.

MATLAB Code

```

syms X

i=0;
K=0.23;
A=2.18; %M
B=11.04; %M
t=3600;
k=1.67E-7; %sec

eqn=('2*K*atan(((A*K*(2*X-1)-B*K-1)/sqrt((-A^2*K^2+2*A*K*(B*K-1)-(B*K+1)^2))))/sqrt((-A^2*K^2+2*A*K*(B*K-1)-(B*K+1)^2))-2*K*atan(((A*K*(2*i-1)-B*K-1)/sqrt((-A^2*K^2+2*A*K*(B*K-1)-(B*K+1)^2))))/sqrt((-A^2*K^2+2*A*K*(B*K-1)-(B*K+1)^2))=k*t-k*t_i');

solve(eqn, X)

(A*K - tan((2*K*atan((B*K + 1 + A*K*(1 - 2*i))/(2*A*K*(B*K - 1) - (B*K + 1)^2 - A^2*K^2)^(1/2)) - k*t*(2*A*K*(B*K - 1) - (B*K + 1)^2 - A^2*K^2)^(1/2) + k*t_i*(2*A*K*(B*K - 1) - (B*K + 1)^2 - A^2*K^2)^(1/2))/(2*K)))*(2*A*K*(B*K - 1) - (B*K + 1)^2 - A^2*K^2)^(1/2) + B*K + 1)/(2*A*K)

%Optimization

%Optimize time and temperature for optimal conversion

%Want the total time to be 24 h
%Want to optimize conversion
%Three temperature steps can be used: 318 K, 308 K, and 298 K

%t1+t2+t3=86400; %Total time is 24 h
p1=0;
totaltime=86400;
step=totaltime/30;

finalconversion=zeros(31,31);
for t1=0:step:totaltime,
p1=p1+1
p2=0;
for t2=0:step:totaltime-t1,
p2=p2+1

t3=totaltime-t2-t1;

```

```

i=0;
T=318;
K=exp(8912*(1/T-1/298))*0.23;
A=2.18; %M
B=11.04; %M
t=t1;
t_i=0;
Aarr=2.36; % L/(mol*sec*0.1 gcat)
E=35080; %activation energy J/mol
R=8.314; %J/(mol*K)
k=Aarr*exp(-E/(R*T));

i=(A*K - tan((2*K*atan((B*K + 1 + A*K*(1 - 2*i))/(2*A*K*(B*K - 1) -
(B*K + 1)^2 - A^2*K^2)^(1/2)) - k*t*(2*A*K*(B*K - 1) - (B*K + 1)^2 -
A^2*K^2)^(1/2) + k*t_i*(2*A*K*(B*K - 1) - (B*K + 1)^2 -
A^2*K^2)^(1/2))/(2*K))*(2*A*K*(B*K - 1) - (B*K + 1)^2 -
A^2*K^2)^(1/2) + B*K + 1)/(2*A*K);

T=308;
K=exp(8912*(1/T-1/298))*0.23;
A=A-2.18*i;
B=B-2.18*i;
t_i=t1;
t=t2+t1;
k=Aarr*exp(-E/(R*T));

i=(A*K - tan((2*K*atan((B*K + 1 + A*K*(1 - 2*i))/(2*A*K*(B*K - 1) -
(B*K + 1)^2 - A^2*K^2)^(1/2)) - k*t*(2*A*K*(B*K - 1) - (B*K + 1)^2 -
A^2*K^2)^(1/2) + k*t_i*(2*A*K*(B*K - 1) - (B*K + 1)^2 -
A^2*K^2)^(1/2))/(2*K))*(2*A*K*(B*K - 1) - (B*K + 1)^2 -
A^2*K^2)^(1/2) + B*K + 1)/(2*A*K);

T=298;
K=exp(8912*(1/T-1/298))*0.23;
A=A-2.18*i;
B=B-2.18*i;
t_i=t2+t1;
t=t3+t2+t1;
k=Aarr*exp(-E/(R*T));

finalconversion(p1,p2)=(A*K - tan((2*K*atan((B*K + 1 + A*K*(1 -
2*i))/(2*A*K*(B*K - 1) - (B*K + 1)^2 - A^2*K^2)^(1/2)) -
k*t*(2*A*K*(B*K - 1) - (B*K + 1)^2 - A^2*K^2)^(1/2) +
k*t_i*(2*A*K*(B*K - 1) - (B*K + 1)^2 -
A^2*K^2)^(1/2))/(2*K))*(2*A*K*(B*K - 1) - (B*K + 1)^2 -
A^2*K^2)^(1/2) + B*K + 1)/(2*A*K)

end
end

```

```
[M, I]=max(finalconversion(:))
```

```
%Optimal does not use 318 K, 14400 at 308 K, 72000 at 298 K
```

Appendix C

STATISTICS OF RENEWABLE P-XYLENE SYNTHESIS

Table C1. TOF of *p*-xylene production rate for a two factors experiment (cation type levels 1: Na⁺, 2: Ag⁺, 3: Li⁺ and framework type levels; 1: X and 2: Y) run with two replicates. Y zeolites have a silicon to aluminum ratio of 2.55 and X zeolites have a silicon to aluminum ratio of 1.25.

Run order	Cation type	Framework type	TOF of <i>p</i> -xylene production (site ⁻¹ h ⁻¹)
1	Ag	Y	1.63
2	Na	X	0.904
3	Li	X	0.573
4	Li	Y	0.835
5	Ag	X	1.84
6	Na	Y	1.35
7	Li	X	0.629
8	Na	Y	1.35
9	Na	X	1.09
10	Li	Y	0.830
11	Ag	X	1.79
12	Ag	Y	1.61

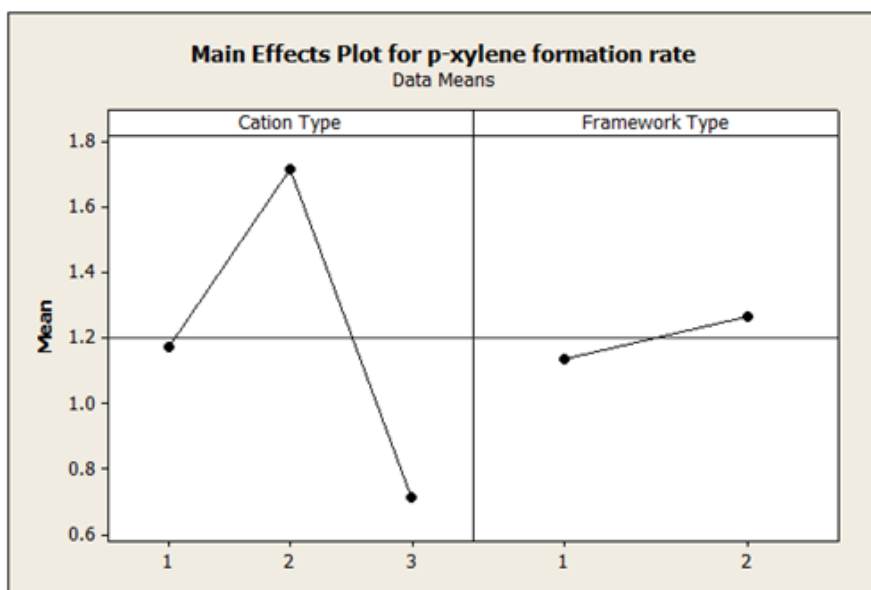


Figure C1. Main effects plot for the TOF of *p*-xylene production. Cation type level 1: Na, 2: Ag, 3: Li; Framework type level 1: X, 2:Y.

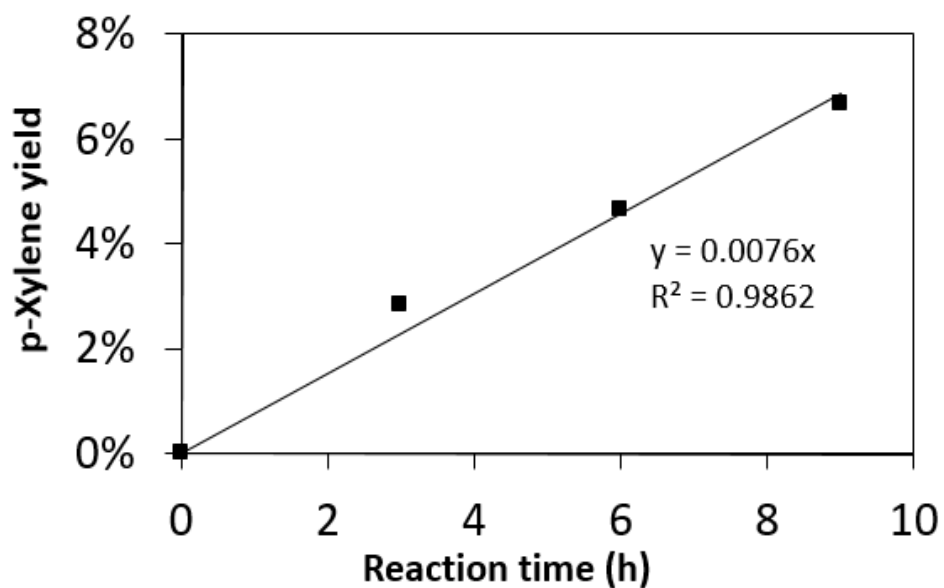


Figure C2. Yield profile for *p*-xylene production for the solvent-free reaction of DMF and ethylene at 250 °C catalyzed by NaX zeolite.

Appendix D

ADDITIONAL REACTIONS FOR FURANICS SYNTHESIS FROM GLUCOSE IN ALCOHOLIC SOLVENTS CATALYZED BY LEWIS ACIDIC BETA ZEOLITES

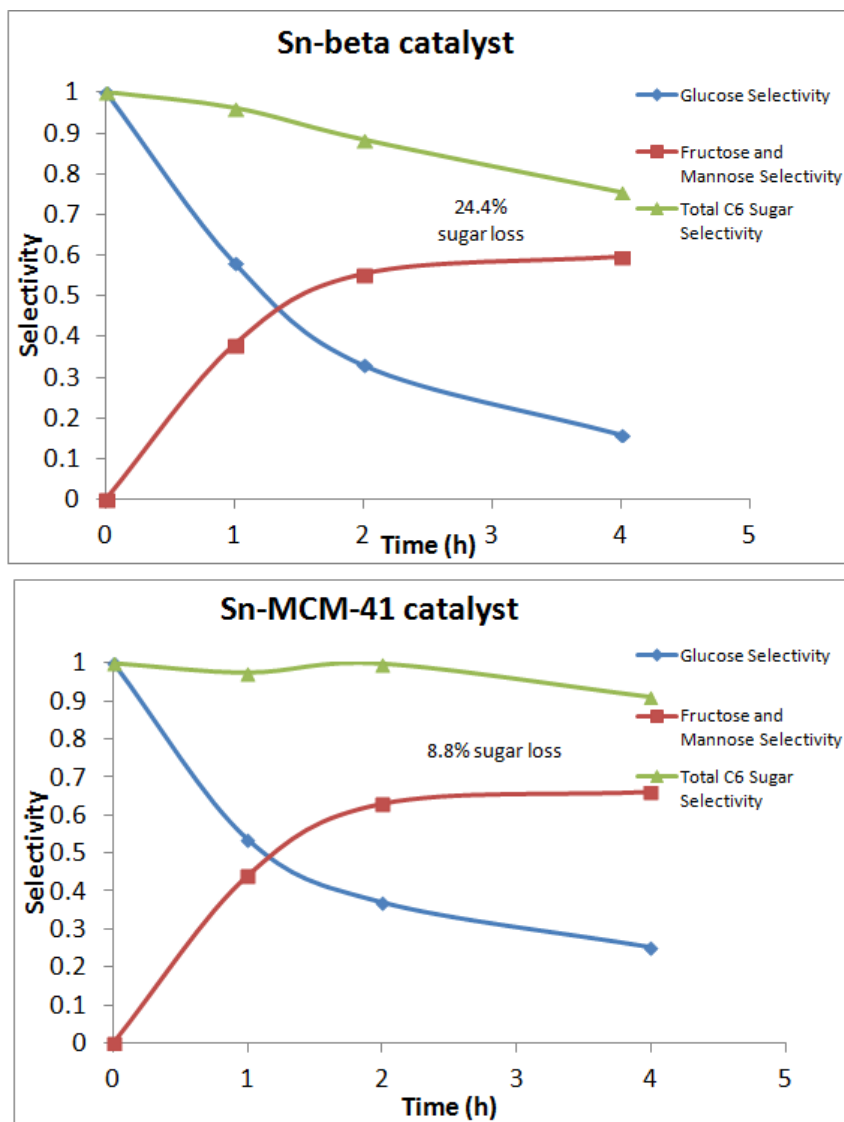


Figure D1. Glucose isomerization experiments run with Sn-beta or Sn-MCM-41.

Experiments were run at 363 K at a 0.159 M of glucose with 0.06 g of Sn-beta

(Si/Sn=100) or 0.03 g of Sn-MCM-41 (Si/Sn=50).

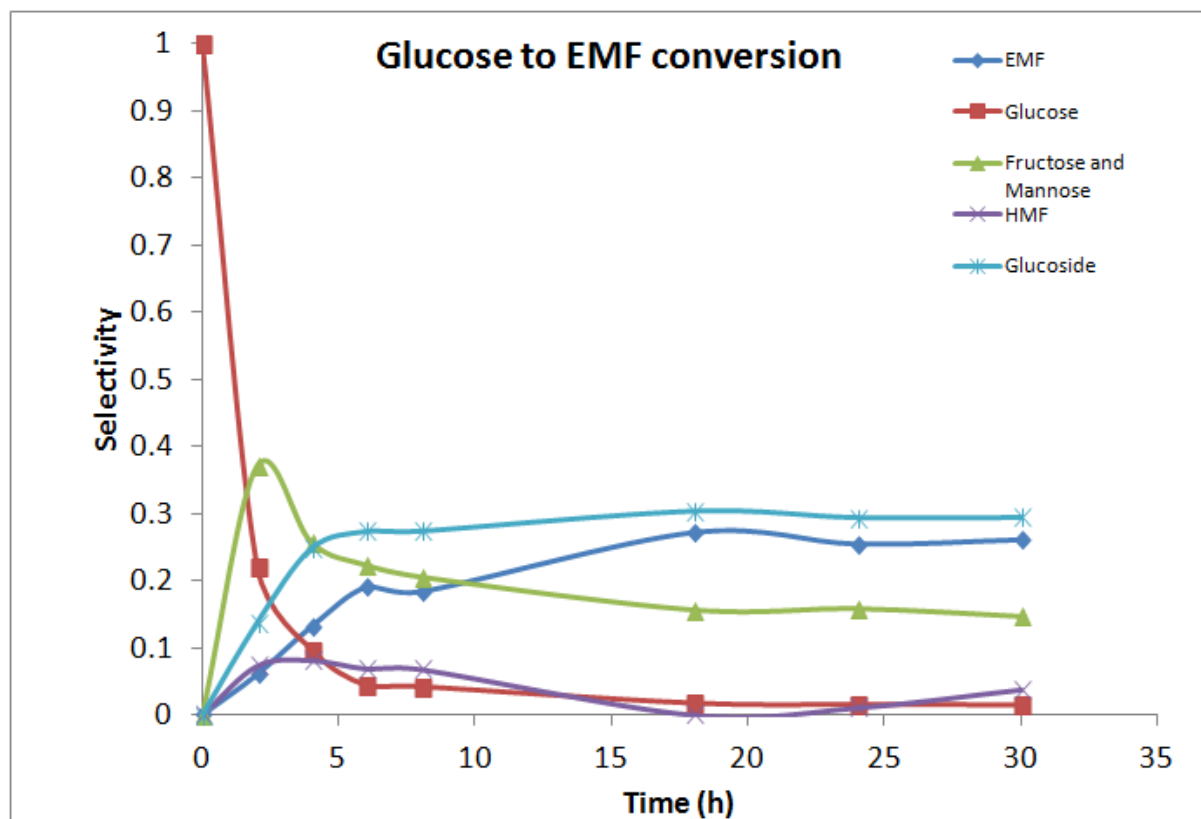


Figure D2. Glucose conversion to EMF using Sn-MCM-41 and amberlyst 15 in

ethanol. Experiments were run at 363 K at a 0.159 M of glucose with 0.1 g of Sn-

MCM-41 (Si/Sn=50) and 0.02 g of amberlyst 15.

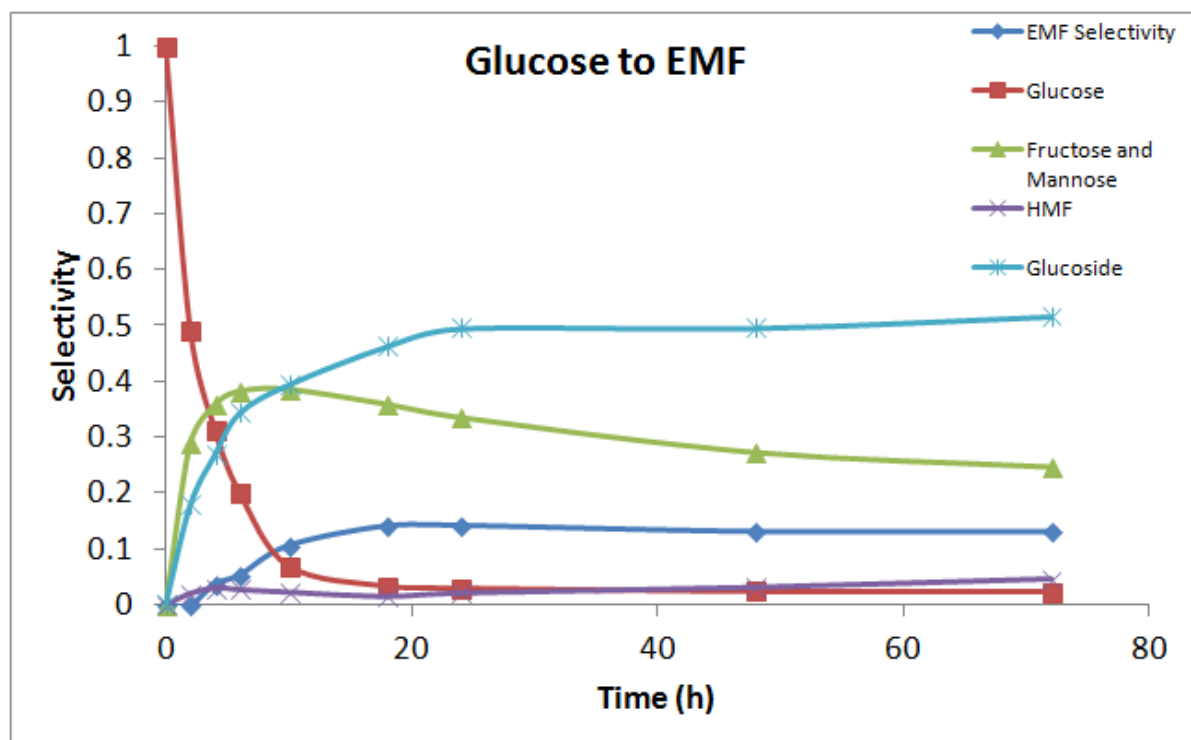


Figure D3. Glucose conversion to EMF using Sn-MCM-41 and amberlyst 15 in ethanol. Experiments were run at 343 K at a 0.159 M of glucose with 0.1 g of Sn-MCM-41 (Si/Sn=50) and 0.1 g of amberlyst 15.

Appendix E

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Renewable production of phthalic anhydride from biomass-derived furan and maleic anhydride

E. Mahmoud, D. A. Watson and R. F. Lobo, *Green Chem.*, 2014, **16**, 167
DOI: 10.1039/C3GC41655K

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Date: Nov 1, 2015

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