Summer 2014

Production of Sustainable Aromatics from Biorenewable Furans

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PRODUCTION OF SUSTAINABLE AROMATICS
FROM BIORENEWABLE FURANS

A Dissertation Presented

By

CHRISTOPHER LUKE WILLIAMS

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 2014

Department of Chemical Engineering
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FROM BIORENEWABLE FURANS

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ACKNOWLEDGEMENTS

I would like to thank my advisor Paul J. Dauenhauer for the time and effort he spent guiding me through the first few years of my PhD and the effort he put into acquiring funds for me to conduct my research. Thanks are also due to my official committee members Wei Fan and Ashwin Ramasubramaniam for their helpful input throughout my various research projects.

I also owe much to my colleagues in the Department of Chemical Engineering for always being there to bounce an idea off of or to join me in my extracurricular activities. In particular I would like to thank Sara Green for her companionship as well as everyone who joined me for all of the road biking, rock climbing, and board game nights over the last five years.

Last but not least I would like to thank my parents Sandy and Eric Williams who have always encouraged me to further my education and pursue my desires. I would also like to thank my brothers Michael and Jesse for providing different perspectives on life.
ABSTRACT

PRODUCTION OF SUSTAINABLE AROMATICS FROM BIORENEWABLE FURANS

SEPTEMBER 2014

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Directed by: Professor Paul J. Dauenhauer

Increasing demand for renewable and domestic energy and materials has led to an accelerated research effort in developing biomass-derived fuels and chemicals. The North American shale gas revolution can provide a domestic source for the manufacture of four of the five major products of the world chemical industry: methanol, ethylene, ammonia, and propylene. However this emerging domestic resource lacks a conversion pathway to the fifth major chemical building block; the larger C6 aromatics benzene, toluene, and xylene (BTX). One sustainable feedstock for renewable C6 aromatic chemicals is sugars produced by the saccharification of biopolymers (e.g., cellulose, hemicellulose). The catalytic conversion of these sugars to high value commodity chemicals, like p-xylene (used in the production of PET plastics), is currently a research area of great interest. The last step in the production of p-xylene from biomass derived glucose involves the conversion of 2,5-dimethylfuran (DMF) and ethylene to p-xylene, which proceeds via a Diels-Alder cycloaddition followed by dehydration.

This thesis presents a novel catalytic system for the production of p-xylene from
DMF and ethylene. Potential transport limitations between the liquid reaction solution and ethylene gas as well as through the pores of the zeolite catalyst have been investigated and altered such that the system is kinetically limited. Competing side reactions have been characterized, and minimized, to achieve high yields of p-xylene. Additionally, a possible mechanism has been developed that takes into account both of the reaction steps: Diels-Alder cycloaddition and dehydration.

Results have demonstrated a 90% yield of p-xylene through optimization of the catalyst and reaction conditions. The production of renewable p-xylene has also been shown to occur at high selectivity and without isomerization to less valuable o,m-xylenes. Careful testing of the principal reaction components revealed the source of isomerization inhibition is very likely the reactant DMF. The precise mechanism of inhibition was further studied through the use of diffuse reflectance infrared spectroscopy (DRIFTS). This study shows preferential binding of DMF over p-xylene to the Brønsted acid sites necessary for promoting isomerization chemistry. Additionally, evidence suggesting a cationic polymerization of DMF on the Brønsted acid sites of H-Y zeolite has been revealed through the use of thermogravimetric analysis (TGA). Reaction kinetics for the Diels-Alder cycloaddition and dehydration steps have also been quantified, revealing first order kinetics in DMF and ethylene. The feasibility of catalyst regeneration has been investigated through the use of x-ray diffraction (XRD) and $^{27}$Al-NMR. This analysis indicates that the zeolite catalyst remains structurally sound after reaction and that there is minimal degradation of the catalytically active Brønsted acid sites. Finally, possible reaction mechanisms have been developed through careful manipulation of the reaction system and an in depth understanding of the catalysis.
This increased understanding of the transformation of DMF and ethylene to $p$-xylene will aid in the development of a variety of renewable aromatics from biomass derived furans.
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CHAPTER 1

PRODUCTION OF RENEWABLE CHEMICALS
FROM BIOMASS

1.1. The Need for Renewable Chemicals

Public concern for renewable and domestic fuels and chemicals has continued to grow in recent decades. This change in public attitude is in part caused by increasingly accurate climate studies by the International Panel on Climate Change (IPCC) to which give progressively more dire warnings on the effects of global climate change.\(^1\) This increased demand has led to an accelerated research effort in the development of renewable pathways to replace chemical currently derived from fossil fuels.\(^2\) However, the concern over the climate is not the only factor driving research efforts towards renewable chemical production. Civil unrest in the nations which supply the majority of the fossil fuel based chemicals has increased the price of these chemical feed stocks and lead towards increased consumer demand for sustainable products combined with a focus on national energy independence.\(^3,4\) As illustrated in Figure 1.1 below this increase the price of natural gas in the United States has coincided with a greater number of publications in the field of biomass catalysis which is geared towards the production of renewable fuels and chemicals.\(^5\)
Figure 1.1 The past decade has seen a drastic increase in the number of publications on biomass and catalysis as the price of natural gas has increased.\textsuperscript{6}

As interest in utilizing biomass for sustainable fuels and chemicals has increased, several questions have arose. Should research focus on the production of fuels or chemicals? Even once the question of fuels or chemicals is answered the next question becomes which type of fuels or chemicals should be focused on? The following section will provide one set of answers to the questions posed above. However, as with most complicated questions there will be multiple answers and in the end a diverse set of solutions will be implemented.

To effectively replace transportation fuels with biomass sources would require the energy input into growing, harvesting, and converting the biomass into fuels to be on par with that of the petroleum sources. Additionally, the conversion of biomass to fuels and chemicals will be limited by the land required to produce the fuels and the efficiency at which biomass can convert sunlight into usable fuels. It has been predicted that even if biomass could match fossil fuels joule for joule in energy only 15\% of the global fossil fuel CO\textsubscript{2} emissions could be replaced with biomass.\textsuperscript{7} While
about 75% of a barrel of crude oil goes towards transportation fuels only 2.5% goes towards petrochemical feedstocks.\textsuperscript{8} When the value of these two products is taken into account it can be seen that chemicals are much more valuable than fuels. Since chemicals from biomass are much more valuable than fuels and their overall production volume is much lower both the economic motivation and ability to replace a higher volume of the market with renewable sources will drive chemical production from biomass. Hopefully, the lessons learned from the production of chemicals from biomass could be applied to the future production of biomass derived fuels.

If focus shifts to the production of chemicals from biomass the next question becomes what chemicals should be produced? Currently, global energy demand for the chemical industry is 15 EJ per year, comprising 30% of total industrial energy demand worldwide.\textsuperscript{9} Only five major products dominate chemical production in terms of volume and energy consumption including: benzene/toluene/xylenes (BTX), methanol, ethylene, ammonia, and propylene.\textsuperscript{8} An illustration of the energy consumed versus production volume of the world’s major chemicals can be seen below in Figure 1.2. An analysis of this plot gives several chemicals that could be target for production from biomass. However, many of these high volume chemicals, such as methanol and ethylene, cannot be made very readily from biomass due to the fact that biomass is highly functionalized and contains larger molecular weight species. Recent studies have suggested that target chemicals from biomass derived sugars could include chemicals like 2,5- furandicarboxylic acid.\textsuperscript{10} It is the production of biomass derived furans that could lead us to one of the world’s major chemicals; the benzene, toluene, xylene (BTX) family of aromatics.
Figure 1.2 The modern global chemical industry produces large volumes of methanol, propylene, ethylene, ammonia, and the BTX family of aromatics.\textsuperscript{9}

The emerging North American shale gas revolution can significantly contribute to four these products, with high production of low molecular weight chemicals (e.g. C2 and C3 compounds).\textsuperscript{9,11} However, production of larger molecules in the BTX family will not likely be replaced with shale gas derivatives and will rely on the larger chemicals, such as C6 sugars, obtained from biomass.\textsuperscript{12,13} These C6 sugars are ideally suited too production by hydrolysis of the cellulosic fraction of biomass. Cellulose and hemicellulose make up as much as 70 wt% of lignocellulosic biomass and are comprised of five (e.g., xylose) and six-carbon sugars (glucose).\textsuperscript{3} These sugars, obtained by saccharification of biopolymers (e.g., cellulose, hemicellulose), are considered the primary feedstocks for renewable chemical processes.\textsuperscript{14} Figure 1.3 below provides a clear visual representation of the influence that shale gas production could have on the production of large aromatics from biomass.
Figure 1.3 Biomass has the potential to produce C4 hydrocarbons and aromatics that cannot be readily produced from shale gas and constitute a large part of the global chemical production.\textsuperscript{11}

It is into this framework that the production of high value aromatic chemicals from biorenewable sugars could help pave the way for future sustainable materials and fuels. The BTX market is a viable initial target for renewable chemicals because the 100 billion dollar a year world market values provides financial incentive. The next step is choosing an appropriate target: benzene, toluene, or p-xylene.

1.2. One Pathway from Biomass to p-Xylene:

One important BTX chemical requiring a low-cost, thermochemical process for renewable production is p-xylene.\textsuperscript{15} p-Xylene is currently oxidized to Terephthalic Acid (PTA), the building block for polyethylene terephthalate (PET) which is used to manufacture plastic bottles, clothing, automobiles, and food packaging. Production of p-xylene or PTA directly from biomass has the benefit that it can be directly integrated into the existing chemical and product infrastructure.\textsuperscript{16,17} p-Xylene is currently produced from the separation of aromatic mixtures (isomers of xylene and ethylbenzene) from the naptha fraction of petroleum. p-Xylene can also be selectively produced from toluene through
the use of ZSM-5 catalysts\textsuperscript{18,19} in combination with membrane separation.\textsuperscript{19,20} New processes are currently being implemented to produce \textit{p}-xylene from renewable resources using a hybrid process that combines fermentation and heterogeneous catalysis.\textsuperscript{6,21–23} Many of these new processes are finding current market applications for the production of renewable PET and its monomer precursors.\textsuperscript{24–26} \textit{p}-Xylene potentially can be produced renewably from glucose as shown in Scheme 1.1.

Scheme 1.1 The production of renewable \textit{p}-xylene from glucose. Isomerization of glucose to fructose, followed by dehydration and hydrogenolysis to Dimethylfuran (DMF), comprises the first two steps. The fourth step to produce \textit{p}-xylene proceeds in two parts: cycloaddition and dehydration.

Isomerization of glucose to fructose can be performed using biological (i.e., enzymes) or thermochemical catalysts including base catalysts\textsuperscript{27} or Lewis acid heterogeneous catalysts such as Sn-Beta.\textsuperscript{28} Fructose can then be converted to hydroxymethylfurfural,\textsuperscript{29} which can be hydrodeoxygenated to produce dimethylfuran\textsuperscript{30} in an overall process designed to produce biofuels. In order to produce \textit{p}-xylene, dimethylfuran must then be converted in two-steps: Diels-Alder cycloaddition of ethylene followed by dehydration.\textsuperscript{26}

In this scheme, the conversion of dimethylfuran to \textit{p}-xylene by a two-step reaction (cycloaddition followed by dehydration) is crucial for the efficient production of
high-value chemicals from biomass-derived sugars. However, the precise chemical mechanism producing $p$-xylene and side products as well as heterogeneous catalysts that easily integrate the selective conversion of dimethylfuran to $p$-xylene is lacking. The initial step in the conversion of dimethylfuran to $p$-xylene is thought to occur by the Diels-Alder reaction\textsuperscript{31} with ethylene as the dienophile. It is known that furans undergo [4+2]-cycloaddition with a number of dienophiles including alkynes and alkenes, but the reaction environment and functionality of the diene/dienophile leads to significant variation in activity and stereochemistry.\textsuperscript{32} Employing ethylene as the dienophile in Diels-Alder processes is inherently difficult; ethylene lacks an electron withdrawing group which promotes the reaction by closing the HOMO-LUMO gap of the interacting molecules. For a large number of substituted furans, [4+2]-cycloaddition with an alkene results in the formation of an oxabicyclic cycloadduct.\textsuperscript{33,34} This step has been catalyzed by a number of Lewis acids including ZnCl\textsubscript{2},\textsuperscript{35} ZnI\textsubscript{2},\textsuperscript{35} and Et\textsubscript{2}AlCl.\textsuperscript{36} Similarly, cycloaddition of other dienes/dienophiles has been catalyzed by zeolites such as Y, beta and ZSM-5,\textsuperscript{37} some of which were exchanged with cations such as sodium\textsuperscript{38} or copper.\textsuperscript{39}

In Scheme 1.2 below, the conversion of dimethylfuran to $p$-xylene by a two-step reaction (cycloaddition followed by dehydration) is crucial for the efficient production of high-value chemicals from biomass-derived sugars.
Scheme 1.2 DMF and ethylene undergo Diels-Alder cycloaddition to an oxabicyclic intermediate. The cycloadduct is then dehydrated to form the desired product, \( p \)-xylene, and water.

One important chemical, \( p \)-xylene, is used for the production of terephthalic acid\(^{16} \), a monomer for polyester and polyethylene terephthalate plastics (e.g., plastic bottles).\(^{17} \) \( p \)-Xylene is currently produced from the separation of aromatic mixtures (isomers of xylene and ethylbenzene) from the naptha fraction of petroleum. \( p \)-Xylene can also be selectively produced from toluene through the use of ZSM-5 catalysts\(^{18,19} \) in combination with membrane separation.\(^{20,19} \) New processes are currently being implemented to produce \( p \)-xylene from renewable resources using a hybrid process that combines fermentation and heterogeneous catalysis.\(^{21–24} \)
CHAPTER 2

METHODS AND MATERIALS FOR THE PRODUCTION OF RENEWABLE AROMATICS

The production of p-xylene from DMF and ethylene requires the use of high pressure and high temperature reactors that efficiently mix a three phase system. The three phases present are the liquid DMF, which can be diluted in an aliphatic solvent such as n-heptane, gaseous ethylene, and the solid acid catalyst, such as a zeolite, that facilitates the efficient dehydration of the cycloadduct. The following section describes the methods and materials that allows one to produce renewable aromatic from furans.

2.1. Experimental Methods for Liquid Phase Reactions

2.1.1. The Parr Reaction Vessel System

![Image of Parr reaction vessel with gas dispersion impeller, sample tube, and double block sampling system.]

Figure 2.1 Parr reaction vessel with gas dispersion impeller, sample tube, and double block sampling system.
The reaction vessels were supplied by Parr Instruments and included several reactor in the 4560 series. They were equipped with gas entrainment stirrers and 4848 series controller with temperature and pressure displays as well as a tachometer. The reaction sampling system was designed such that a sample can be collected at reaction conditions without exposing the vessel contents to the atmosphere, ensuring proper containment and safety. The sampling procedure was also planned to minimize sample cross-contamination inside the sample tube as well as between the three reactor connected in parallel. Before each sample was taken all gas inlets were closed to ensure that pressure fluctuation in one vessel did not affect the others. The first sample of each time point was drawn and sent to waste before the second sample was taken and filtered through a 0.22μm filter, to remove any catalyst lost during sampling, before being sent to analysis. The reactor was then brought back to operating pressure (about 50psi is lost during removal of a standard 2ml sample) before all of the other vessels were opened. The gas inlet was left open during the reaction to ensure a constant ethylene supply throughout the reactions with an excess flow shutoff valve in place in case of reactor leaks.
2.1.2. Gas to Liquid Mass Transfer in the Catalytic System

Figure 2.2 Investigation of mass transfer limitations of the ethylene gas to the reactant liquid. The second Damköhler number \((k_{\text{rxn}}/k_{\text{la}})\) is 0.0006 \(< 0.1\) which indicates that no mass transfer limitations exist between the gas and liquid phases.

To ensure that the experiment was not mass transfer limited, the Damköhler number was determined. A series of kinetic data was measured for the H-Y catalyst at 300 °C and the change in DMF concentration with time was used to obtain the greatest possible reaction rate \((k_{\text{rxn}})\). Mass transfer tests were performed by adding 50mL of heptane to the Parr reactor and pressurizing to 800 psi ethylene. Once the reactor was at pressure the gas dispersion impeller was turned to 1000 rpm and the pressure of the system was monitored. Temporal pressure changes were measured every \(1/15^{th}\) of a second to obtain a \(k_{\text{la}}\) value. The Damköhler number is the ratio of the \(k_{\text{rxn}}/k_{\text{la}}\) and gives a value of 0.0006 which is well below the value of 0.1 and indicates no mass transfer limitations exist between the gas and liquid phases.
2.1.3. Investigating Intraparticle Diffusion Limitations in the Catalytic System

Figure 2.3 Intraparticle diffusion limitations exist for particle of HBEA that are greater than 0.5 µm in diameter.

Intraparticle diffusion limitations were investigated by running DMF (1 M in n-heptane) to p-xylene reactions at 250 °C and 550 psi ethylene with H-BEA catalysts of known particle size. These reactions were run at a loading of catalyst sufficiently high enough that the reaction was limited by the rate of Diels-Alder cycloaddition. H-BEA catalysts with a Si/Al ratio of 23 and particle sizes of 20 and 200 nm were found to produce products at a rate of 22 mmol/hr. On the other hand, H-BEA with a Si/Al ratio of 30 and particle sizes of 1 and 4.5 µm were found to produce products at a significantly lower rate (14 and 7.5 mmol/hr respectively). Commercial catalysts tested exhibited rates statistically equivalent to the smallest particle sizes.

2.1.4. Reaction Product Characterization

Samples were collected under reaction conditions at high temperature and pressure utilizing a double block sampling system. Characterization of
chemical components within the reaction mixture was performed with an Agilent 6890 gas chromatograph equipped with a G1513A autosampler, HP-Innowax column (to achieve separation of o,m,p-xylene isomers), and a flame ionization detector. The Innowax column used was 30 m long with a 0.32mm diameter and a 0.25μm film thickness. Liquid injection volumes were set at 1 μl and the inlet port was held at a temperature of 280°C and pressure of 11 psi with a split of 75:1. Flow in the column was kept constant at 2.3 ml/min with an average column velocity of 32 cm/sec through the oven ramp cycle. The oven cycle started at 60 °C and held there for 1min before ramping to 90 °C at 5 °C/min, holding for 4 min, and then ramping up to a final temperature of 250 °C at 20 °C/min with a 6 min. hold. Major species were identified by matching retention times with pure standards and all reported data exhibited carbon balance closure greater than or equal to 90 C%.

2.2. Materials and Catalyst Characterization for the Production of p-Xylene

The proton forms of H-Y, H-Beta, and H-ZSM-5 catalysts were provided by Zeolyst and calcined at 550 °C prior to use in reaction testing. H-silica-alumina was prepared by heating silica-alumina (catalyst support grade 135, Aldrich) at 500 °C for 16 hours. Mullite (crystalline aluminum silicate Si/Al=0.27, Aldrich) was calcined at 550°C for 12 hours before use in reaction tests. Siliceous beta and silicalite-1 were prepared using established protocols. The number of Brønsted acid sites was characterized by temperature programmed desorption coupled with thermogravimetric analysis (TPD- TGA) for isopropylamine (IPA) while total acid sites was determined by using ammonia temperature programmed desorption.
(NH3-TPD). Catalyst surface area was determined using N2 sorption isotherms, crystal structures and morphologies of the catalysts were determined by X-ray powder diffraction (X’Pert PRO diffractometer (PANalytical)) and scanning electron microscopy (Magellan 400 (FEI)).

Table 2.1 Catalyst Acid Site and Surface Area Characterization for the Considered Materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al ratio</th>
<th>Bronsted acid sites* (mmol/g)</th>
<th>Total acid sites** (mmol/g)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Y (CBV600)</td>
<td>2.6ᵃ</td>
<td>0.36</td>
<td>0.99</td>
<td>660ᵃ</td>
</tr>
<tr>
<td>H-Y (CBV760)</td>
<td>30ᵃ</td>
<td>0.27</td>
<td>0.64</td>
<td>720ᵃ</td>
</tr>
<tr>
<td>H-Y (CBV780)</td>
<td>40ᵃ</td>
<td>0.12</td>
<td>0.25</td>
<td>780ᵃ</td>
</tr>
<tr>
<td>H-BEA (CP814C)</td>
<td>19ᵃ</td>
<td>0.56</td>
<td>1.21</td>
<td>710ᵃ</td>
</tr>
<tr>
<td>H-ZSM-5 (CBV3024E)</td>
<td>15ᵃ</td>
<td>0.71</td>
<td>1.1</td>
<td>405ᵃ</td>
</tr>
<tr>
<td>H-silica alumina</td>
<td>5ᵇ</td>
<td>0.34ᵇ</td>
<td>0.43ᵇ</td>
<td>585ᵇ</td>
</tr>
<tr>
<td>(amorphous)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Siliceous BEA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>475ᶜ</td>
</tr>
<tr>
<td>Silicalite - 1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>346ᶜ</td>
</tr>
<tr>
<td>Mullite (crystalline)</td>
<td>0.27ᵃ</td>
<td>NA</td>
<td>NA</td>
<td>0.24ᵃ</td>
</tr>
</tbody>
</table>

*Obtained using Isopropylamine-TGA TPD, **Obtained using Ammonia-TPD, aProvided by manufacturer, bWeingarten et. al, cObtained using BET equation within 0.05<P/Pc<0.3

2.3. Variations on the Liquid Phase Reactions for the Study of Different Catalytic Phenomena

2.3.1. Experiments Utilizing Pure DMF

Reactions were carried out in a 100 mL high pressure high temperature Parr bench top reactor (model 4598HTHP with a 4848 temperature controller) using both commercially available and in-house synthesized zeolite catalysts. 2,5-dimethylfuran (99.5+% Alfa Aesar and 99.5+% Acros Organics) was reacted with zeolite catalysts over a temperature range of 200 to 300 °C with a loading of 0.25 g of catalyst to 49 mL of
reactant and 1 mL of n-tridecane as an internal standard (98+% Sigma). The reaction vessel was purged with N2 and stirred at 1000 rpm with a gas entrainment impeller while heating to the reaction conditions. Once reaction temperature was achieved, the vessel was pressurized to 57 bar (825psi) with ethylene gas, which was continuously added during the reaction. Samples were collected immediately after ethylene addition and at later times corresponding to a dimethylfuran conversion of about 10% while the system was at reaction conditions. Products were identified using a gas chromatograph/mass spectrometer and by comparing retention times to those of pure standards. Quantification was performed using a gas chromatograph equipped with a flame ionization detector.

2.3.2. Experiments Investigating Isomerization Inhibition

Reactions to investigate the isomerization of p-xylene were conducted in a 160 ml stirred pressure vessel manufactured by Parr Instruments (model 4566B) with a 4848 controller and gas entrainment stirrer. Temperature was maintained at 300 °C for all experiments, and gas pressure was maintained at 57 bar (800 psi). Nitrogen (Airgas UHP) was used to pressurize all reactions except for the investigation of ethylene (Airgas UHP) as a potential inhibitor of isomerization. Catalyst loading was ~0.42 g (100 ml)-¹ of either H-Y faujasite (Zeolyst CBV 600) or H-BEA (Zeolyst CP814E calcined in flowing air at 550 °C for 12 hrs). A typical reaction mixture consisted of 86 ml n-heptane (Alfa Aesar 99+%), 2 ml tridecane (Sigma-Aldrich 98+%) as an internal standard, varying amounts of p-xylene (Alfa Aesar 99+%), 2,5-dimethylfuran (Alfa Aesar 98+%), and 2,5-hexanedione (Alfa Aesar 98+%), depending on which
reaction component was being tested for inhibition properties. All chemicals were used without further purification.

2.3.3. Experiments for the Determination of Activation Energies and Reaction Orders

Kinetic experiments measured reaction rates for various conditions including catalyst loading, DMF concentration, and ethylene partial pressure to determine activation energies and reaction orders for DMF and ethylene. Reactions investigating the rate of production of Diels-Alder products (p-xylene, alkylated six-carbon ring aromatics, and dimers) shown in Figure 1 utilized 1.4 M DMF in n-heptane with 0.082 M n-tridecane as an internal standard and 200 psi ethylene at either 200 or 250 °C. In these experiments, the mass of catalyst charged to the reactor varied from 0.15 to 0.75 g in 100 ml of reaction solution to yield effective Brønsted acid site concentrations between 1.1 and 5.5 mM. Experiments to determine activation energy (Figure 6.3) were performed at both low (1.3 mM, 0.2 grams) and high (3.2 mM, 0.5 grams) catalyst loading over a temperature range of 200 to 250 °C. Experiments determining reaction orders for DMF and ethylene were conducted at low (1.3 mM) and high (3.2 mM) catalyst loadings with DMF concentrations from 0.46 M to 2.3 M and ethylene pressures from 6.9 to 34.5 bar, as shown in Figure 6.4 and Figure 6.6 respectively.

2.4. Methods for the Analysis of Chemically Bound Species and the Zeolitic Acid Site

2.4.1. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

FTIR analysis was performed with a Bruker Equinox 55 equipped with a
temperature-controlled sample cell and cryogenic MCT detector with 2 \text{cm}^{-1} \text{ resolution. Helium flowed through the sample cell at 20 ml/min, providing an inert atmosphere. A KBr background was collected and subtracted from all samples. H-Y zeolite (Zeolyst CBV-600) was degassed at 550 °C for one hour after a temperature ramp of 5 °C (min)^{-1} from the starting temperature of 120 °C. The degassed zeolite was then saturated with the chemical of interest (DMF, \textit{p}-xylene, or a 1/50th mixture of DMF/\textit{p}-xylene) at 120 °C. Saturation of the catalyst was achieved through the use of a bubble column attached in line with the helium purge that maintained an inert atmosphere over the sample. The sample chamber was then heated to the upper range of reaction temperatures, 300 °C, for one hour to remove any weakly adsorbed chemicals before being cooled back to 120 °C for spectral acquisition.

2.4.2. Thermogravimetric Analysis (TGA)

TGA samples were prepared by loading a ceramic cup with zeolite, heating to 550 °C at a ramp rate of 10 °C (min)^{-1}, and holding for one hour to degas the sample. A constant helium purge of 23 ml (min)^{-1} was passed through the furnace chamber to maintain an inert atmosphere. After the zeolite was degassed and cooled to room temperature, DMF or \textit{p}-xylene was added by redirecting the helium purge stream through a bubble column filled with the chemical of interest. Once the zeolite was saturated, the system was switched back to pure helium flow and any physisorbed species were removed. A temperature ramp of 10 °C (min)^{-1} to 300 °C, with a one hour hold at that temperature, was then used to remove as much adsorbed material as possible at the maximum temperature.
2.4.3. Solid State Nuclear Magnetic Resonance

Solid-state $^{27}$Al MAS NMR was used to investigate the aluminum content in H-Y and H-BEA zeolites before and after reaction. $^{27}$Al MAS NMR spectra were recorded in a fully hydrated state with a Bruker DSX-300 NMR spectrometer at a $^{27}$Al frequency of 78.2 MHz, using a 7 mm MAS probe. The spinning rate was 3 kHz and spectra were acquired with 0.5 s repetition time, 3 μs delay time, and 2000 scans. The chemical shift was referenced to 1.0 M aqueous solution of Al(NO$_3$)$_3$ (0 ppm). The spectra taken prior to reaction was of unused zeolite (H-Y and H-BEA) labeled as “fresh” while the “spent” catalyst was used to produce $p$-xylene from DMF and ethylene at 300 °C in n-heptane solvent.

2.5. Theoretical Calculation Methods for the Acid Catalyzed Conversion of 2,5-Dimethylfuran to $p$-Xylene

All computed thermochemistry and reaction pathway data reported for the initial assessment of $p$-xylene production from H-Y faujasite is based on gas-phase electronic structure calculations; they were performed with Gaussian 09$^{44}$ at the DFT-M062X theory level with the 6-311+G(d,p) basis set. The transition structures correspond to first-order saddle points in the potential energy hypersurface and were verified by frequency (i.e., presence of a single imaginary frequency) as well as internal reaction coordinate (IRC) calculations. The Gibbs thermal energies do not include frequency rescaling. The Brønsted acid catalyzed dehydration reaction of the Diels-Alder cyclo-adduct was modeled by protonation of the cyclo-adduct.

Calculations for solvated $p$-xylene production form dimethylfuran and ethylene were performed in Gaussian 09 (Rev. A.2). The solution phase was modeled with a continuum heptane solvent model (SMD) at the M062X/6-31G(d,p) level. The zeolite H-
Y model (314 tetrahedral atoms, HAlSi313O520) was cut out from the periodic structure of pure faujasite zeolite; the dangling bonds were saturated with hydrogen atoms. The ONIOM method was employed to perform all calculations within the zeolite. The highest layer –comprising the active site and its environment and all adsorbates – was treated at the same level of theory as the solution phase molecules.

The ab initio results were then used to create a microkinetic model which was implemented in Matlab. The kinetic rate constants were calculated using Transition State Theory. To calculate the partition functions first-principles-based energetics and vibrational frequencies were employed: for solution-phase species, translational, rotational and vibrational modes were considered; for adsorbed species only the vibrational motions were used. Adsorption and desorption rate constants were found to be by several orders of magnitude larger than the reaction steps. Thus, adsorption and desorption were assumed to be in equilibrium at all times.
CHAPTER 3

INITIAL PRODUCTION OF P-XYLENE UTILIZING PURE 2,5-DIMETHYLFURAN

Increasing demand for energy and materials has led to an accelerated research effort in the development of renewable chemicals for a sustainable economy.\(^2\) Cellulose and hemicellulose make up as much as 70 wt\% of lignocellulosic biomass and are comprised of five (e.g., xylose) and six-carbon sugars (glucose).\(^{13}\) These sugars, obtained by saccharification of biopolymers (e.g., cellulose, hemicellulose), are considered the primary feedstocks for renewable chemical processes.\(^{14}\)

We investigate here the catalytic conversion of dimethylfuran to p-xylene and demonstrate high yield using zeolite Y catalysts. By reacting liquid dimethylfuran with high-pressure ethylene, we identify (and attempt to minimize through catalyst design) competitive side reactions that reduce p-xylene yield. Additionally, we find that Diels-Alder cycloaddition (the first step in conversion of DMF to p-xylene) does not utilize an active site but is promoted primarily by confinement within zeolites. The second step (dehydration) is catalyzed by Brønsted acid sites, rendering the first reaction step (cycloaddition) rate determining.

3.1. Experimental Examination of the Catalytic System for Pure DMF

Experimental examination of the catalytic cycloaddition of ethylene and dimethylfuran shows that the reaction occurs within a four phase system free of transport limitations (see below). Ethylene gas is absorbed within liquid dimethylfuran containing solid catalyst. A fourth phase, liquid water, was observed to form as the reaction
proceeds. Mass transfer experiments indicate an ethylene mass transfer rate of $k_La=0.066$ sec$^{-1}$ within dimethylfuran resulting from a gas-entrainment impeller. For an H-Y catalyst at 300 °C, the reaction rate constant ($k_{rxn}$) is $4.61 \times 10^{-5}$ sec$^{-1}$. Combined with the mass transfer coefficient ($k_La$), this rate constant gives a Damköhler number ($Da=k_{rxn}/k_La$) of $6.99 \times 10^{-04}$, which indicates that ethylene is transferred into the liquid faster than it reacts.

In a system with a heterogeneous catalyst, it is important to determine if there are any internal diffusion limitations, which can arise when the reactant size is on the same scale as the pore diameter. The Weisz-Prater Criterion, shown below in Table 3.1, is often used to determine if internal diffusion is limiting the rate of reaction. The Weisz-Prater criterion is defined as $\frac{r_A^{\text{obs}} + \rho_c + R^2}{D_{	ext{eff}} \cdot C_{DMFS}}$ by Fogler. The following data was used to calculate the Weisz-Prater Criterion where the effective diffusivity for dimethylfuran was taken from Roque-Malherbe.

<table>
<thead>
<tr>
<th>Weisz-Prater Criterion</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{wp}$</td>
<td>3.88E-02</td>
<td></td>
</tr>
<tr>
<td>$r_A^{\text{obs}}$</td>
<td>2.53E-05</td>
<td>$\text{mol}<em>{\text{DMF}}/\text{g}</em>{\text{cat}} \cdot \text{s}$</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>2</td>
<td>$\text{g}_{\text{cat}}/\text{cm}^3$</td>
</tr>
<tr>
<td>$R$</td>
<td>1.00E-04</td>
<td>$\text{cm}$</td>
</tr>
<tr>
<td>$D_{\text{eff}}$</td>
<td>1.50E-09</td>
<td>$\text{cm}^2/\text{s}$</td>
</tr>
<tr>
<td>$C_{DMFS}$</td>
<td>8.68E-03</td>
<td>$\text{mol}_{\text{DMF}}/\text{cm}^3$</td>
</tr>
</tbody>
</table>

Since the $CWP << 1$ holds true there should be no diffusion limitations within
the catalyst for this series of experiments.

Initial reaction rates for the cycloaddition and dehydration of dimethylfuran and ethylene were measured for multiple catalysts at low conversion (XDMF-Average = 8.9 ± 1.5%) at 300 °C as shown in Figure 3.1.

![Figure 3.1](image)

Figure 3.1 The initial reaction rate of dimethylfuran conversion (XDMF<10%) and product formation vary for catalyst microstructure and active site. Reaction rates were measured using pure dimethylfuran with the continuous addition of C2H4 (57 bar) at 300 °C. Error bars represent a 90% confidence interval.

The reaction of dimethylfuran and ethylene without a catalyst exhibited a slow reaction rate and resulted in a low conversion (XDMF < 8.5 % after 25 hours of reaction time). The non-catalytic system exhibited the same reaction rates as silicalite-1 (0.03 mol*gc-at^{-1}hr^{-1}) and mullite (nonporous crystalline aluminum silicate without acid sites) (0.04 mol*gc-at^{-1}hr^{-1}). The addition of Brønsted acid sites in H-BEA (0.56 mmol/g) and H-ZSM-5 (0.71 mmol/g) increased the reaction rates (0.48 ± 0.1 mol*gc-at^{-1}hr^{-1}) for both catalysts, which is about an order of magnitude increase over the rate of their siliceous counterparts. Further improvement in catalyst activity was observed with H-Y catalyst, which exhibited a higher reaction rate of about 0.74
mol\*g_{cat}^{-1}\text{hr}^{-1} independent of the Si/Al ratio. H-Y catalysts with Si/Al ratios of 2.6, 30, and 40 all exhibited catalytic performance that was not statistically different. As shown below in Figure 3.2 H-Y catalyst (Si/Al=30) was regenerated for three consecutive trials with no statistically significant loss in activity.

![Graph showing reaction rates](image)

Figure 3.2 XRD and Regeneration of fresh and used H-Y zeolite. (a) Reaction rates with 90\% confidence interval for regenerated H-Y-Si/Al=30 and fresh H-Y Si/Al=2.6 and 40 (b) XRD analysis of H-Y Si/Al=30 before reaction, after reaction in DMF at 300\(^\circ\)C, and after regeneration (in ascending order).

In comparison, an amorphous silica alumina catalyst with Brønsted acid sites (0.34 mmol/g) was more active than H-Y catalyst but exhibited almost no selectivity to \textit{p}-xylene, \(<5\%\). Similar selectivity to major products, \textit{p}-xylene and 2,5-hexanedione, was observed for all microstructured catalysts containing Brønsted acid sites. The average selectivity towards \textit{p}-xylene for the most promising H-Y catalysts was 51.9 \(\pm\) 2.7\% at a conversion of 10.7 \(\pm\) 2.3 \%(90\% confidence interval).

The observed products of the cycloaddition of dimethylfuran and ethylene
are consistent with the proposed furan chemistry of Scheme 3.1. As shown, catalyzed [2+4]- cycloaddition of ethylene to dimethylfuran produces the previously reported bicyclic intermediate, 1,4-dimethyl-7-Oxabicyclo[2,2,1]hept-2-ene.26,47 Subsequent Brønsted-catalyzed dehydration produces p-xylene and water. p-Xylene can be further alkylated to produce products such as 1-ethyl-2,5-dimethylbenzene which are observed in smaller quantities (up to 15% of the converted dimethylfuran is converted to these alkylated products). The formation of water in the dehydration step leads to the hydrolysis of dimethylfuran which produces the ring-opened product, 2,5-hexanedione. This diketone product can further polymerize to form dimers and larger (uncharacterized) oligomers.

Scheme 3.1 Schematic for the conversion of 2,5-dimethylfuran and ethylene to p-xylene and water.

The possibility of xylene isomerization within the Y-zeolite was also investigated within the reaction system. Thermodynamic equilibrium of the xylene
isomers would lead to ~25% o-xylene \(^{48}\) which was not detected in the gas chromatograph indicating that xylene isomerization is not occurring.

A two-step reaction through a bicyclic intermediate is consistent with the measured reaction rates and turnover frequencies based on Brønsted acid sites (H-TOF), as shown in Table 3.2. While low activity is observed for siliceous materials and high activity is observed for Brønsted acid-containing materials, it is also apparent that Brønsted acid catalyzed reactions are not rate-determining in the formation of \(p\)-xylene. H-Y catalysts with significantly different Brønsted acid site density (Si/Al=2.6 and Si/Al=40) exhibit the same catalytic reaction rate (Figure 3.1), while the H-TOF for these two materials are very different (\(5.9 \times 10^{-4}\) s\(^{-1}\) and \(1.7 \times 10^{-3}\) s\(^{-1}\) for Si/Al of 2.6 and 40 respectively). There exists no relationship between catalyst activity and Brønsted site density, which indicates that the rate determining step is the cycloaddition to produce the bicyclic intermediate. Statistically different activities are observed only in zeolites with different microstructures; the cage structure of H-Y zeolite is more active than the channel structure of H-ZSM5 and H-Beta. Consistent with previous literature, the Diels-Alder reaction examined here is enhanced by confinement within pores.\(^{49–51}\) This is supported by the low selectivity to p-xylene of H-silica alumina, an amorphous catalyst with no micropore structure but comparable Brønsted site density to the zeolite catalysts.\(^{52}\)

The need for a Brønsted site that catalyzes the dehydration step is supported by the computed free energy barriers in Figure 3.3.
Figure 3.3 Computed Free Energy Barriers of Dimethylfuran Cycloaddition with Ethylene and Dehydration to p-Xylene at 300 °C. The black line depicts the free energy profile for the uncatalyzed conversion of DMF to p-xylene via Diels-Alder cycloaddition and subsequent dehydration, in the gas phase. The gray line shows the free energy profile for Brønsted acid catalyzed dehydration. For the dehydration reaction, only the highest energy barrier is shown.

The formation of a bicyclic intermediate is not favorable thermodynamically (ΔG_{rxn}=2.28 kcal/mole) at 300 °C, but the product, p-xylene, is overwhelming favorable (ΔG_{rxn}=-38.56 kcal/mole) in accordance with long-time experiments (>24 hours) which achieve conversion exceeding X_{DMF}=90%; all energies refer to the interacting reactant complex. The kinetic barrier for cycloaddition to produce the bicyclic intermediate is 32.89 kcal/mole, while the non-catalyzed dehydration barrier is quite large (57.6 kcal/mole) and qualitatively consistent with low reaction rates of siliceous materials. However, the introduction of Brønsted-acid sites significantly lowers the dehydration barrier to 19.13 kcal/mole, thereby making the first step (cycloaddition) rate determining. This finding is in agreement with the initial catalytic rate experiments (Figure 3.2Figure 3.1) and underscores the necessity of a Brønsted acid catalyst to promote dehydration and ultimately make cycloaddition rate-determining.

The optimum catalyst (H-Y) was investigated at high conversion (X_{DMF}>90%)
to demonstrate the potential of achieving high yield in the considered catalytic system. As shown in Figure 3.4, the competitive rates of $p$-xylene formation and ring-opening/polymerization with H-Y vary with temperature with the best performance occurring at 300 °C. Few uncharacterized oligomers are observed as the experimental carbon balances close at 90±5% for the H-Y catalyst (Si/Al=30) at high conversion for all temperatures. An increase in temperature from 200 to 300 °C reduces the selectivity to 2,5-hexanediol and dimers/oligomers such that selectivity to $p$-xylene is 51±7% for a conversion of 95±4%. The benefit of minimizing the hydrolysis of dimethylfuran was further examined by introducing an aliphatic solvent, n-heptane, as shown in Figure 3. By reacting 25 vol% dimethylfuran in n-heptane at high conversion (XDMF=95%) with H-Y zeolite (Si/Al=30), the formation of 2,5-hexanediol was reduced to only 2.7±3.7%, and the formation of oligomers was almost negligible, thus achieving selectivity to $p$-xylene of 75.7±1.5%.
Figure 3.4 Demonstration of Dimethylfuran Cycloaddition at High Conversion. Increase of reaction temperature from 200 to 300 °C with H-Y zeolite Si/Al=30 and 900 psig C2H4 with pure dimethylfuran exhibits increasing selectivity to p-xylene for high conversion of dimethylfuran, XDMF>90%. Yield of p-xylene further increases by the addition of n-heptane solvent (25 vol% DMF / 75 vol% n-heptane) at 300 °C.

In summary, we have demonstrated that good selectivity (~75%) to p-xylene can be achieved at both low (5-10%) and high (~95%) conversion with H-Y zeolite with the most favorable catalysts containing Brønsted acid sites in microporous materials. p- Xylene formation competes with ring-opening hydrolysis and polymerization; the latter can be significantly reduced by operating at 300 °C and introducing an aliphatic solvent. The rate of p-xylene formation is controlled by the initial cycloaddition step, provided the second dehydration step is Brønsted acid catalyzed. This catalytic system introduces a new chemical pathway to convert biomass-derived furans to high-value aromatic feedstocks.
CHAPTER 4
FORMATION OF OTHER BTX CHEMICALS:
FURAN AND TOLUENE

The need for sustainable production of everyday materials in addition to market volatility of petroleum-based feedstocks has motivated research into the production of renewable aromatic chemicals from biomass.\textsuperscript{2,53-57} Cellulose and hemicellulose comprise a significant fraction of lignocellulosic biomass and provide six-carbon (e.g. glucose) and five-carbon (e.g. xylose) sugars as primary feedstocks for the production of renewable chemicals with six-carbon aromatic ring structures.\textsuperscript{58} Specific chemicals of interest include p-xylene, the feedstock for poly-ethylene terephthalate (PET), and toluene, an important monomer for polyurethane products.\textsuperscript{16,59,60} In this work, we reveal a highly selective method (>90% product selectivity and 90% yield for p-xylene formation at 99% conversion of dimethylfuran) for the production of basic monomers from biomass-derived furan feedstocks by combined catalytic cycloaddition/dehydration reactions using H-BEA zeolite.

We have proposed a renewable method of producing renewable p-xylene by cycloaddition of biomass-derived dimethylfuran (DMF) and ethylene,\textsuperscript{61} which serves as the last step in a complete process for producing p-xylene from cellulose. Glucose, produced by saccharification of cellulose, can be isomerized with Sn-BEA\textsuperscript{28} to fructose, and subsequent acid-catalyzed dehydration produces 5-hydroxymethylfurfural (HMF).\textsuperscript{29,62} Hydrogenolysis of HMF over CuRu/C produces DMF,\textsuperscript{30} and the final step adds ethylene (which can be derived from ethanol dehydration)\textsuperscript{63} to yield p-xylene. Further investigation into the design of this process indicates potential for economic viability, and a sensitivity analysis of the
considered process parameters highlights the need for improved selectivity to \( p \)-xylene in the conversion of DMF.\textsuperscript{64}

4.1. An Improvement in the Conversion of DMF to \( p \)-Xylene Using H-BEA

Our research on the reaction of DMF and ethylene has revealed the fundamental catalytic chemistry, but the optimal catalytic system converted at least 25\% of feedstock carbon into unusable side products at great cost to overall process viability.\textsuperscript{61} The reaction occurs by symmetry-allowed [4 + 2] Diels–Alder cycloaddition of ethylene and subsequent aromatization by acid-catalyzed dehydration in multiple elementary steps to \( p \)-xylene (Scheme 4.1). Addition of ethylene to DMF produces an oxa-norbornene cycloadduct intermediate in a single uncatalyzed step with a barrier of 24.7 kcal mol\(^{-1}\), determined by gas-phase DFT.\textsuperscript{65} In the absence of an acid catalyst, dehydration is inhibited by a large barrier (58.0 kcal mol\(^{-1}\)); however, acid-catalyzed dehydration of 1,4- dimethyl-7-oxabi-cyclo[2.2.1] hept-2-ene occurs readily (19 kcal mol\(^{-1}\)), indicating the necessity of an acid site.


While a previous work has observed the cycloadduct intermediate with GC–MS,\textsuperscript{66}
it was not measured in this work. Elucidation of the reaction pathways by separation of the reaction mixture and characterization by NMR/GC–MS has revealed three competing side reactions\textsuperscript{66} to the main pathway to p-xylene: (1) hydrolysis of DMF to 2,5-hexanedione, (2) secondary addition of DMF to produce dimers, and (3) secondary reactions of ethylene to alkylated aromatics. From this analysis, further improvement of selectivity to p-xylene can be specifically defined as: (a) elimination of the hydrolysis side reaction or (b) reduction of secondary addition of either the dienophile (e.g. ethylene) or the diene (e.g. DMF).

In this work we show that selectivity to p-xylene from DMF and ethylene can be significantly enhanced by using the H-BEA catalyst. As shown in Figure 4.1., initial catalytic reaction rates reveal the activity of several solid-acid catalysts at 250 °C in heptane solvent at low conversion (XDMF, the conversion of DMF, <20%). While previous studies using pure DMF reactant at 300 °C have indicated that Y-zeolite is more active than H-BEA,\textsuperscript{61} the reaction with H-BEA (47 mmol (g-cat h)\textsuperscript{−1}) in the presence of heptane solvent at 250 °C is at least 50% more active than H-Y zeolite. Additionally, several other catalysts including H-ZSM-5, niobic acid, and γ-Al2O3 are nearly an order of magnitude less active than H-BEA under these conditions.

The initial kinetics of solid-acid catalyzed cycloaddition in heptane solvent support the previously proposed mechanism of p-xylene production, and highlight the importance of H-BEA. As shown in Figure 4.1., the initial reaction rate of p-xylene is independent of the Si/Al ratios within given materials such as BEA, which indicates that the overall reaction rate (at low conversion) is independent of the total number of Brønsted acid sites for the considered reaction conditions.
However, it was shown previously that materials require a Brønsted acid site to exceed the rate of cycloaddition/dehydration occurring within the non-catalyzed system. The necessity for a Brønsted acid site for which site-density does not correlate with activity (at high catalyst loading) is consistent with the proposed mechanism of rate-limiting, non-catalyzed Diels–Alder cycloaddition, described previously. \(^{61}\) \(\text{H}^+\) has been shown to exhibit no potential for decrease in the cycloaddition reaction barrier, both experimentally and by DFT. \(^{65}\) With this in mind, the comparison of the activity of H-BEA (RDMF, the initial reaction rate of DMF is equal to 47 ± 3 mmol-pX (g-cat h)\(^{-1}\)) with those of other non-porous materials such as WO\(_x\)–ZrO\(_2\) (RDMF = 50–55 mmol-pX (g-cat h)\(^{-1}\)) shows comparable reaction activities at the same temperature (250 °C). \(^{67}\)
Figure 4.2 Conversion of DMF as a function of time for the reaction of DMF in heptane with ethylene (62 bar) at 250 °C with various catalysts. The Si/Al ratios of catalysts are shown in parentheses.

The potential of H-BEA for combined cycloaddition/dehydration chemistry relative to other materials is further revealed by long-time experiments examining high conversion of DMF. As shown in Figure 4.2, most catalytic materials at 250 °C in heptane solvent exhibit a similar behavior with significant deactivation after ~10 hours. Niobic acid, γ-Al2O3, H-Y zeolite, and H-ZSM-5 all exhibit only ~50–60% conversion after 30 hours. In contrast, H-BEA exhibits a significantly different catalytic behavior and rapidly achieves a high conversion of ~90% in 10 hours under the same conditions.

4.2. The Disappearance of 2,5-Hexanedione at Long Reaction Times

The benefit of the high activity of H-BEA relative to other considered materials is a higher selectivity to p-xylene of ~90% on a carbon basis. As shown in Figure 4.3
selectivity to p-xylene increases with DMF conversion. At XDMF = 20%, selectivity to p-xylene is only 60%, and the hydrolysis product (2,5-hexanediol), alkylated products and oligomers comprise the remaining 40%, within experimental error. However, as XDMF increases to >99%, selectivity to p-xylene exceeds 90%. This counter-intuitive behavior can be partially explained by the concentration of the hydrolysis side-product, 2,5-hexanediol, as revealed in Figure 4.3.a.. For XDMF < 60%, the concentration of all side products increase in step with DMF conversion. However, while no change in concentration is observed for the alkylated products and oligomers after XDMF > 80%, the concentration of 2,5-hexanediol decreases from 0.08 M for XDMF > 60% and reduces to nearly zero concentration for XDMF > 99%. This behavior is consistent with the hydrolysis reaction equilibrium between DMF–water and 2,5-hexanediol; as DMF reacts with ethylene, 2,5-hexanediol reforms DMF to maintain equilibrium. p-Xylene formation is highly favourable thermodynamically, and all reactants including side products in equilibrium will yield p-xylene at high conversion. This was confirmed by a separate experiment shown.
in Figure 4.4., which started with 2,5-hexandione and water in heptane. 2,5-Hexanediol undergoes cyclization to DMF, even with the presence of water, during the heating process (point “RT” to time = 0), and the composition did not change significantly over a 4 hour period. Upon the addition of ethylene, the DMF is converted to p-xylene, which supports the postulation that the decreasing concentration of 2,5-hexanediol seen in Figure 4.3.a is due to the reformation of DMF that then forms p-xylene.

![Figure 4.4 Use of 2,5-hexanediol as the initial feed for p-xylene production. Concentration of products as a function of time for the reaction of 2,5-hexanediol, water, and ethylene (62 bar) over H-BEA (Si/Al = 12.5) at 250 °C.](image)

By the DMF hydrolysis reaction, carbon, which appears lost to the side product 2,5-hexanediol at low conversion, is recovered and results in high selectivity to p-xylene at high conversion of DMF. The superior performance of H-BEA for selective production of p-xylene can therefore be attributed to: (a) its resistance to deactivation,
allowing for high conversion of DMF (Figure 4.2.), (b) its superior activity relative to other solid-acid materials (Figure 4.1.), and (c) its ability to catalyze dehydration of the Diels–Alder cycloadduct without catalyzing important side reactions. p-Xylene, once formed from DMF, does not readily isomerize to o- or m-xylene under the considered reaction conditions, which provides a significant process advantage by eliminating the expensive separation of xylene isomers.

4.3. Utilization of Alternative Feedstocks: Methylfuran and Furan

The high activity of H-BEA is more pronounced for the conversion of DMF to p-xylene than for the reaction of 2-methylfuran (MF)–ethylene to toluene or the reaction of furan–ethylene to benzene. As shown in Figure 4.5.a., the conversion of MF was 93% with H-BEA and 71% with H-Y after 24 hours of reaction under identical conditions to the experiments in Figure 4.2.. Similarly, Figure 4.5.b. depicts the conversion of furan with ethylene which was 54% with H-BEA and 50% with H-Y after 24 hours. Figure 4.6. compares the product selectivities for conversion of DMF and MF at XDMF,MF > 90% and furan at Xfuran > 70% at 250 °C. While 90% selectivity to p-xylene is achieved

![Figure 4.5 Conversion of Methylfuran and Furan over H-BEA and H-Y. (a) Conversion of MF and ethylene and (b) furan and ethylene over H-BEA (Si/Al = 12.5) and H-Y (Si/Al = 2.6) at 250 °C.](image)
Figure 4.6 Product selectivity comparison for different furan feedstocks. Product selectivity to (■) p-xylene, toluene, and benzene; (■) alkylated compounds; and (■) oligomer compounds at high conversion (>99% DMF and MF, 70% furan). Reaction conditions: 1 M furanic feedstock in heptane with ethylene (62 bar) at 250 °C with 0.45 ± 0.05 g of catalyst. Error bars were less than 2% for each compound.

For conversion of DMF, only 46% selectivity to toluene and 35% selectivity to benzene are observed. A significant loss of carbon occurs in the reaction of MF and furan due to increased reactions between the furans forming dimers (e.g. benzofuran) and larger oligomers. The increase in these reactions is likely due to the absence of methyl groups at the furan α-carbon positions, which inhibit these side reactions.

The discovery that H-BEA in heptane exhibits high selectivity with high catalytic reaction rate significantly improves the potential for lignocellulosic biomass to serve as a renewable feedstock for aromatic chemicals. Techno-economic analysis of the process to convert glucose into HMF and eventually p-xylene indicates that the use of H-BEA addresses two of the three most important design parameters for improved economics. First, the high selectivity to p-xylene reduces the loss of feedstock carbon,
which has been identified as the largest process cost. Second, the ability to utilize the side product, 2,5-hexanedione, by dehydration to DMF allows for the recovery of carbon within the process and raises the value of the ring-opened side product. Future research addressing the design of a continuous flow reaction system (based on a standard engineered slurry reactor and separator) which allows for continuous catalyst replacement and separation of $p$-xylene from 2,5-hexanedione–DMF will allow for the hydrolysis side-product to be recycled until it is completely consumed, thus matching the selective performance of the high conversion batch reactor described here.
CHAPTER 5

KINETIC REGIME CHANGE DURING THE FORMATION OF P-XYLENE OVER H-Y FAUJASITE

The work presented in Chapter 3 hinted that the rate at which p-xylene is produced in H-Y could be independent of the number of Brønsted acid sites provided. This observation prompted the hypothesis that the rate-limiting step must be uncatalyzed. This was later supported in a theoretical study by showing that the Brønsted acid cannot catalyze the Diels-Alder reaction which exhibits the highest reaction barrier in the main reaction pathway. In contrast to that, it was more recently observed that the activity towards the formation of p-xylene using WOx–ZrO2 does depend on the how many acid sites were provided, concluding that the rate-controlling formation of the oxa-norbornene intermediate follows a step-wise Brønsted-acid-catalyzed mechanism.

In this work we conduct experiments at a wide range of Brønsted acid site concentrations. We develop a kinetic model based on first-principles calculations to replicate the experiments in silico. Analysis of kinetic parameters, such as reaction orders, determination of the preferred reaction path, and sensitivity analysis of the rate-limiting step has granted insight into the aforementioned apparent contradiction observed in experiments regarding the p-xylene formation activity dependence on the acid site concentration.

5.1. Comparison of Experimental and First Principle Model Kinetics over H-Y Zeolite

We conducted experiments and simulated the reaction of DMF and ethylene in H-Y at 250 °C and monitored the composition in the solution phase over a period of 24 hours
(Figure 5.1). It can be seen that DMF conversion approaches 90% and $p$-xylene is by far the dominant product. For the experimental work the sum of the side products is calculated upon adding the concentrations of 2,5-hexanedione, alkylated products and dimerized products. The first principles calculation only considers 2,5-hexanedione as a side product so that value has been compared to the sum of side products from the experiments. As can be seen below in Figure 5.1 the time-dependent concentration profiles of DMF, $p$-xylene and side products predicted from theory are in excellent agreements with those measured experimentally.

![Figure 5.1](image)

Figure 5.1 Theoretical and experimental solution composition over 24 hours for the major components of the DMF to $p$-xylene reaction. (H-Y, 1.38 M DMF, 250 °C).

We measured the initial $p$-xylene production rate in H-Y at 250°C at different Brønsted acid site concentrations (Figure 5.2), that is the total number of acid sites provided per reaction volume. We find qualitative agreement between experimentally measured (dots) and computed rates (lines). Two distinct regimes become apparent: at low acid site concentration, the rate increases steeply with increasing available acid sites
and it levels at higher loadings. Though not precise, the experiments suggest that a transition between the regimes occurs at around 3.0 mM. It is noticeable that the computational prediction deviates significantly from the experimental measurements at low loadings and that the plateau height at high loadings is slightly overpredicted.

![Figure 5.2](image)

Figure 5.2 Experimental and theory-predicted $p$-xylene production rate at different catalyst loadings at 250 °C. Solid squares represent the experimental measurements (left axis) and the line the corresponding computed rates (right axis).

To understand the origin of the observed rate pattern, we calculated the apparent reaction barriers and reaction orders at Brønsted acid site concentrations corresponding to each regime (Table 5.1). Experiments and simulation results are in good agreement: The reaction order in DMF is around 0.5 at low loadings and approaches 1 at high loadings; the reaction order of ethylene is less affected by the loading; yet, the model predicts a significant increase from 0.62 to 0.81, while a constant reaction order of around 1 was observed in experiments; the apparent activation energy in the high-loading regime is significantly higher than in the low loading regime. We shall return to these observations later to interpret them. Without analysis however, the results suggest that, over the whole
range of catalyst loadings considered, the kinetic properties change significantly hinting at a change in the elementary reaction step that determines the\( p\)-xylene production rate.

Table 5.1 Theoretical and experimental apparent kinetic parameters. Activation energy and pre-exponential were estimated via Arrhenius plot assuming first order reactions in both DMF and ethylene. Low and high catalyst loadings in experiments yielded effective Brønsted acid site concentrations of 1.3 mM and 5.1 mM and in simulations 0.1 mM and 5.1 mM.

<table>
<thead>
<tr>
<th>Kinetic Parameter</th>
<th>Low Catalyst Loading Exp.</th>
<th>High Catalyst Loading Exp.</th>
<th>Low Catalyst Loading Sim.</th>
<th>High Catalyst Loading Sim.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF Reaction Order</td>
<td>0.49 ± 0.08</td>
<td>0.79 ± 0.07</td>
<td>0.46</td>
<td>0.88</td>
</tr>
<tr>
<td>Ethylene Reaction Order</td>
<td>1.01 ± 0.07</td>
<td>0.90 ± 0.13</td>
<td>0.62</td>
<td>0.81</td>
</tr>
<tr>
<td>Activation Energy (kcal/mol)</td>
<td>10.8 ± 2.1</td>
<td>20.1 ± 1.2</td>
<td>16.9</td>
<td>23.9</td>
</tr>
</tbody>
</table>

Since experiments and simulation results are in close agreement in how the\( p\)-xylene production rate depends on the catalyst loading and in the kinetic parameters within the two regimes, we analyze the model to explicate the origin of the two regimes. To do so, we performed a reaction path analysis (Figure 5.3) and a sensitivity analysis (Figure 5.4) at both low and high Brønsted acid site concentrations representing the two regimes. Reaction path analysis reveals that, at both low and high catalyst loadings, the Diels-Alder cycloaddition proceeds uncatalyzed in the homogeneous phase. The cycloadduct then adsorbs at the active site, dehydrates catalyzed by the Brønsted acid before the products desorb back to the homogeneous phase; the preferred route is highlighted within the simplified reaction network in Figure 5.3. Sensitivity analysis reveals that, at low loadings, the rate-limiting step is an elementary step of the H-Y-catalyzed cycloadduct dehydration; at high loadings, the uncatalyzed Diels-Alder reaction in the homogeneous phase limits the\( p\)-xylene production rate (Figure 5.4). We will henceforth refer to the low-loading and high-loading regime as the dehydration-limited and cycloaddition-limited regime, respectively.
Figure 5.3 Reaction path analysis. Simplified reaction network considered, including Diels-Alder reaction and dehydration in homogeneous and heterogeneous phase and hydrolysis. The preferred route is highlighted. Fluxes are given in % at Brønsted acid site concentrations 0.1 mM (low loading, blue) and 5.1 mM (high loading, red).

Figure 5.4 Sensitivity analysis. As catalyst loading decreases the rate of dehydration becomes more important relative to the rate of cycloaddition.

Figure 5.5 shows that the rate at 250 °C is about an order of magnitude greater than at 200 °C for both theoretical calculations and experimental measurements. The relative plateau heights are in excellent agreement between experiment and simulation. While the initial slope at all three temperatures appears to be very similar, the plateau is reached more rapidly at lower rates causing the transition between the two regimes to shift to
lower acid site concentrations for lower temperatures.

Figure 5.5 Rate of p-Xylene production vs acid site concentration at 200 and 250 °C for both theoretical calculations experiments, and at 225 °C for theoretical calculations only.

5.2. Selectivity Changes with Respect to Kinetic Regime and Varying Reactant Concentration for H-Y Zeolite

In an effort to understand how changing kinetic regimes might alter product selectivity and potentially improve product yields, the selectivities of the various reaction products were measured for changing initial DMF concentration and ethylene pressure in each regime. The selectivities presented here are based on the selectivity of each product that goes through a Diels-Alder pathway as compared with the total formation of Diels-Alder products. The side product 2,5-hexanedione has been left out of these selectivity calculations because at high DMF conversion the diketone will cyclize and dehydrate to form reactant DMF which goes on to form the Diels-Alder pathway products shown above. As shown in Table 5.2, increasing DMF concentration from 0.46 to 2.3 M decreases selectivity towards p-xylene from about 65 to 35 % and increases selectivity towards polymerized products from about 30 to 60 % in both kinetic regimes. In contrast,
changing ethylene pressure from 6.9 to 34 bar (100 to 500 psi) does not provide a significant change in selectivity to any of the products in any regime. Figures detailing the change in Diels-Alder product selectivities at all studied DMF concentrations and ethylene pressures can be found in the SI. The trends here showing increased selectivity towards p-xylene and decreasing polymer selectivity with decreasing DMF concentration correlates well with previous literature.\textsuperscript{61,70} The fact that increasing ethylene pressure does not have a significant effect on the product selectivity but does increase reaction rate (the reaction order with respect to ethylene is about one) suggests that higher ethylene pressures are optimal.

Table 5.2 Selectivity for Diels-Alder products with changing kinetic regimes and varying reactant concentrations.

<table>
<thead>
<tr>
<th>Kinetic Regime (Compound Selectivity %)</th>
<th>0.46 M DMF</th>
<th>2.3 M DMF</th>
<th>1.38 M DMF</th>
<th>1.38 M DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14 bar Ethylene</td>
<td>14 bar Ethylene</td>
<td>6.9 bar Ethylene</td>
<td>34.5 bar Ethylene</td>
</tr>
<tr>
<td>Dehy. Limited</td>
<td>68 ± 4.2</td>
<td>36 ± 4.2</td>
<td>56 ± 8.6</td>
<td>55 ± 8.6</td>
</tr>
<tr>
<td>p-Xylene Select.</td>
<td>32 ± 4.7</td>
<td>61 ± 4.7</td>
<td>44 ± 8.4</td>
<td>38 ± 8.4</td>
</tr>
<tr>
<td>Dehy. Limited</td>
<td>0.0 ± 1.3</td>
<td>2.7 ± 1.3</td>
<td>0.0 ± 1.1</td>
<td>6.9 ± 1.1</td>
</tr>
<tr>
<td>Polymer Select.</td>
<td>63 ± 11</td>
<td>37 ± 11</td>
<td>51 ± 8.1</td>
<td>53 ± 8.1</td>
</tr>
<tr>
<td>Dehy. Limited</td>
<td>27 ± 11</td>
<td>55 ± 11</td>
<td>49 ± 8.6</td>
<td>44 ± 8.6</td>
</tr>
<tr>
<td>Alkylated Select.</td>
<td>9.7 ± 2.2</td>
<td>8.3 ± 2.2</td>
<td>0.0 ± 0.6</td>
<td>2.9 ± 0.6</td>
</tr>
</tbody>
</table>

As seen in Figure 5.1 two distinct kinetic regimes exist for the p-xylene formation: starting at low loadings, the rate increases with increasing acid site concentration until it plateaus at higher loadings. At low loadings the rate strongly depends on the effective acid site concentration because the rate-limiting acid-catalyzed dehydration requires active acid sites (dehydration-limited regime). We show that the rate
plateaus at higher loadings when the uncatalyzed Diels-Alder cycloaddition controls the rate; that is because the rate may not change upon increasing the catalytically active acid site concentration when this uncatalyzed reaction is rate-limiting (cycloaddition-limited regime).

The apparent kinetic parameters we observed in the two regimes further corroborates the notion of two regimes with different kinetic limitations: (a) The apparent reaction barrier at high loadings, of about 20 - 24 kcal/mol (Table 5.1) substantiates the predictions about the uncatalyzed Diels-Alder reaction being rate-controlling as Diels-Alder reactions are known to occur within the range 20 kcal/mol;\textsuperscript{71} this is also consistent with the apparent reaction orders in DMF and ethylene being close to 1, since one would expect integral reaction orders for this uncatalyzed reaction. (b) The HY-catalyzed dehydration, on the other hand, is faster and must be preceded by an adsorption step; consistent with that are the lower apparent activation energy (10-17 kcal/mol) and partial reaction orders at lower loadings.

The activation energy of the Diels-Alder reaction exceeds that of the dehydration significantly. It may thus appear counterintuitive that – when the dehydration is rate-controlling at low loadings – the overall p-xylene formation rate is lower than in the high loading regime. This phenomenon however is easily understood when one considers that the rate not only depends on the rate constant but also on the concentrations of the reactants, and that, at low loadings, the effect of the small number of available active sites is more dominant than the effect of the associated reaction barrier.

The existence of two regimes indicates that an ideal catalyst at the transition point would maximize reaction rate without using excess catalyst. In addition to saving
material costs, avoiding an excess of the catalyst may also limit unwanted side reactions that would otherwise occur on the Brønsted acid sites not participating in cycloadduct dehydration. The transition point increases from about 1.7 mM to 3 mM within the temperature range of 200 to 250 °C.

5.3. A Contradiction in Results from Previous Work Brought to a Conclusion

The regimes we observed offer an explanation for an apparent contradiction in experimental observations regarding the dependence of the p-xylene production on the active site concentration. In previous work, Williams et al. observed no dependence of the rate on active site concentration when they varied the Si/Al ratio of their catalyst. Operating at 300 °C, and in pure DMF, their catalyst loading (1.7 mM to 3.2 mM) was around the regime transition point. The observed constant kinetic rates however indicate that the reaction was controlled by the uncatalyzed Diels-Alder reaction and thus independent from the acid site concentration. On the other hand, Wang et al. conducted their experiments at 250 °C at significantly lower loadings, around 0.2 mM, clearly lower than the transition point. They found that the activity towards forming p-xylene depended on how many acid sites were available and how acidic they were, and concluded rate-limiting Brønsted acid-catalyzed formation of the cycloadduct. Yet, according to Woodward and Hoffmann Brønsted acid catalysis for this reaction is highly unlikely. In view of our results presented above, the reason why the experiments of Wang et al. appeared to be limited by an acid-catalyzed reaction is because they operated at a very low acid loading (smaller than the transition point) and thus in the dehydration-limited regime. They further observed a partial reaction order of 0.19 in DMF, which – according to our results above – clearly must be in the dehydration-limited regime. The
two experimental studies were therefore conducted at two different ends of the kinetic curve which – without the knowledge of the two regimes – caused the respective research groups to come to contradicting observations and diverging conclusions.

In conclusion, there exist two different reaction regimes based upon the loading of H-Y faujasite during the formation of $p$-xylene from DMF and ethylene. As catalyst loading increases, past an acid site concentration in solution of 3 mM (at $250\, ^\circ\text{C}$), the production of $p$-xylene becomes limited by the rate of formation of the cycloadduct. Below this critical acid site loading the rate is controlled by dehydration of the cycloadduct. It has also been shown that lowering the initial concentration of DMF will increase selectivity towards $p$-xylene and increasing the ethylene pressure increases reaction rate but does not change product selectivity in both the cycloaddition and dehydration limited regimes.

In our results discussion we hypothesize how two experimental studies came to contradicting observations by explaining that they were operating in two different kinetic regimes of the same kinetic curve. While available acid sites and site acidity may influence the slope of the curve in the dehydration regime they will likely not affect the plateau height in the regime limited by the uncatalyzed cycloaddition. In other words, at least the cycloaddition-limited regime is universal for all (Brønsted acid) catalysts. Since we recommend operating at the regime transition or in the cycloaddition-limited regime to obtain the highest-possible reaction rates, the logical next step to optimize the entire process is to develop methods to accelerate the Diels-Alder reaction.
CHAPTER 6

A CHANGE IN REACTION ORDER DURING THE FORMATION OF P-XYLENE OVER H-BEA

Diels-Alder reactions of biomass-derived furans have recently demonstrated potential for producing renewable six-carbon aromatic chemicals including p-xylene and PTA. In the first step, a furan diene, 5-hydroxymethylfurfural (HMF), is produced by isomerization of glucose to fructose, performed using either base catalysts\textsuperscript{27,72} or heterogeneous Lewis acid catalysts such as Sn-BEA.\textsuperscript{28} Subsequent dehydration of fructose produces HMF, with yields as high as 80\%,\textsuperscript{33,73,74} and HMF is currently being manufactured at a scale of 20 tons per year.\textsuperscript{75} It has recently been proposed that oxidized variants of HMF can undergo Diels-Alder (DA) addition of ethylene, producing six- carbon ring aromatic chemicals with 1,4-substitution. For example, oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) and subsequent DA addition of ethylene can produce TPA; however, this reaction is slowed by the carboxylic acid groups of FDCA resulting in only low yields of TPA.\textsuperscript{76,77} More recently, the DA reaction of ethylene with other oxidized variants has been reported but with only limited yield of six-carbon aromatic ring products.\textsuperscript{78}

A more selective route to p-xylene and PTA first reduces HMF to 2,5-dimethylfuran (DMF).\textsuperscript{30,79,80} As shown in Scheme 1.1, the reaction of DMF and ethylene (itself produced from ethanol dehydration\textsuperscript{26,61,67} ) undergoes cascade reactions of Diels-Alder cycloaddition to X, followed by dehydration to p-xylene in a single reactor.\textsuperscript{26} p-Xylene can then be integrated within the existing chemical process where it is oxidized to TPA.

Conversion of DMF and ethylene to p-xylene has been demonstrated using H-Y and H-BEA zeolites at yields of 75 and 90\%, respectively, in the presence of n-heptane
In competition with the pathway to p-xylene are three side reactions: (a) hydrolysis of dimethylfuran, (b) multiple addition of ethylene to form alkylated aromatic chemicals, and (c) dimerization of the furan feedstock and/or aromatic products. Gas-phase DFT studies have highlighted the benefit of strong acids for promoting the main pathway and facilitating high yield to p-xylene. Dehydration of the DA cycloadduct of DMF/C2H4 occurs in three steps, the first of which is prohibitive (Ea ~ 60 kcal/mol) at moderate reaction conditions (T < 300 °C). Strong Bronsted acids have been predicted to dramatically lower the cycloadduct dehydration barrier (Ea ~ 17 kcal/mol) providing a low-energy pathway to p-xylene. However, strong Bronsted acids have been predicted to have negligible impact on rate of Diels-Alder cycloaddition of DMF and ethylene.

Lewis acids such as Lithium can lower the dimethylfuran DA reaction from the uncatalyzed barrier of 59 kcal/mol to as low as 29 kcal/mol.

Despite proof-of-concept results and cursory knowledge of the reaction mechanism, little is known about the cascade kinetics of the reaction of DMF and ethylene and the role of catalysts on the combined chemistries of DA addition and dehydration. Moreover, reports of measured kinetics of the reaction of DMF and ethylene have reported different behavior; we have previously reported zero-order kinetics in H-Y catalysts, while Dumesic and co-workers have reported a reaction order with respect to DMF of 0.19 using tungstated zirconia. In this work, we will evaluate the kinetics of the reaction of DMF and ethylene, resolve the differences in reported rate expressions, and provide a kinetic model based on catalyst surface coverage that can be used for design of improved multifunctional zeolite catalysts.
6.1. Ensuring the HBEA Catalytic System is not Transport Limited

Kinetics of $p$-xylene production from DMF and ethylene with H-BEA zeolite (Si/Al 12.5) catalyst have been investigated using semi-batch Parr pressure vessels and analyzed with gas chromatography. Experimental data reveal the existence of two kinetic reaction regimes that coincide with two reactions controlling the rate of formation of $p$-xylene from DMF and ethylene: (i) Diels-Alder cycloaddition and (ii) dehydration. Insight into both the cycloaddition limited regime and the dehydration limited regime has been obtained through the determination of activation energies and reaction orders of the DMF and ethylene in each regime.

Ethylene gas-liquid mass transfer experiments were conducted to eliminate the potential for interphase mass transfer limitations. Experiments depicted in Figure 6.1A were performed by adding 60-100 mL of n-heptane to the reaction vessel and rapidly pressurizing to 800 psi with ethylene. Once pressurized, the gas dispersion impeller was initiated at 1000 rpm; the system pressure was then monitored with 1/24th of a second precision. A least squares fit of the data provided a gas-liquid mass transfer coefficient of $k_{La}=0.066$ sec$^{-1}$. The Damköhler number was calculated from $Da = k_{rxn}/k_{La}$ resulting in values of the order $10^{-4}$ to $10^{-3}$, providing quantitative support that no ethylene uptake limitation exists at any of the considered experimental conditions.
Figure 6.1 Characterization of Reactor Transport. A. Ethylene Interphase Mass Transfer
Ethylene gas pressure in the headspace of the batch reactor containing heptane at 25 °C measured as a function of time is fit to determine $k_{La} = 0.066$ sec$^{-1}$. This rate is orders of magnitude faster than DMF consumption, which occurs on the order of hours. The DaII of the system was determined to be 0.0006 $<< 0.1$ indicating that there is no transport limitation between the gas and liquid phases. B. Intraparticle Mass Transfer. Rate of production of Diels-Alder products (mM hr$^{-1}$) relative to H-BEA particle size, using 1.38M DMF at 250 °C and 550 psi ethylene.

Additional experiments were conducted to measure the rate of reaction of DMF and ethylene as a function of particle size of H-BEA zeolite. As shown in Figure 6.1B, the overall reaction rate was determined at 1.38 M DMF in n-heptane, 250 C, and 550 psi ethylene for four particle sizes of H-BEA: (i) 20 nm, (ii) 200 nm, (iii) 1 µm, and (iv) 4.5µm. The two smallest particles achieved the same overall reaction rate, indicating that intraparticle diffusion limitations were not rate determining at the considered reaction conditions. All kinetic experiments used to determine reaction rates, activation energies, and reaction orders utilized a commercial H-BEA containing mesopores; this commercial catalyst exhibited identical reaction rate to the smallest synthesized zeolites indicating that no intraparticle diffusion limitations exist for the considered experimental conditions.
6.2. Activation Energies and Reaction Orders for DMF and Ethylene in HBEA

The reaction of DMF and ethylene by cascade reactions of Diels-Alder cycloaddition and dehydration exhibit two distinct kinetic regimes for the production of p-xylene and total Diels-Alder products (p-xylene, alkylated C6-aromatic chemicals, and dimers containing C6-aromatic chemicals). As shown in Figure 6.2, the DA product rate as a function of total Bronsted acid sites exhibits first order behavior (linear). As Bronsted acid concentration increases, the reaction rate eventually achieves a maximum rate. At 250 °C (solid black squares, left hand axis) the maximum rate of production of Diels-Alder compounds is 13 mM/hr^{-1}, while at 200 °C (open squares, right hand axis) the maximum reaction rate is 1.6 mM/hr^{-1}. The transition between the two regimes occurs at a Bronsted acid site concentration between 2.0 and 2.5 mM, which corresponds to a catalyst loading of approximately 0.35 g H-BEA (Si/Al 12.5) in 100 mL of reaction solution. The same trend is observed at both 200 and 250 °C, even though the overall reaction rate increases by nearly an order of magnitude.
Figure 6.2 Rate of formation of Diels-Alder (DA) products with respect to Brønsted acid density. Low strong acid site concentrations correspond to first order rate of formation of Diels-Alder products, consistent with the rate of dehydration. High acid site concentrations result in constant rate of formation of Diels-Alder products, consistent with the Diels-Alder cycloaddition reaction. Conditions: PEthylene=13.6 atm and 200 °C (□) right axis or 250 °C (■) left axis.

Arrhenius plots were generated at conditions consistent with each kinetic regime identified in Figure 6.2 to evaluate the rate-limiting chemistry. Figure 6.3A depicts an Arrhenius plot generated at the experimental conditions of Figure 6.2 with an acid site concentration of 1.3 mM and variation in the temperature between 200 and 250 °C. Linear least squares fit reveals an activation energy of $E_a = 11.7 \pm 3.5$ kcal/mol for the conditions exhibiting first order dependence on Bronsted acid concentration. Figure 6.3B depicts an Arrhenius plot generated at the experimental conditions of Figure 6.2 with an acid site concentration of 3.2 mM and variation in the temperature between 200 and 250°C.
Figure 6.3 Barriers for the energy of activation in each kinetic regime. A. Dehydration and B. Diels-Alder cycloaddition

The high activation energy kinetic regime was further characterized for its dependence on the DMF and ethylene reactant concentrations. Figure 6.4 depicts the reaction rate dependence for Diels-Alder products at a Bronsted acid site concentration of 3.2 mM and temperature of 200 °C. As shown in Figure 6.4A, variation of the initial concentration of DMF from 0.4 to 2.1 M indicates a reaction close to first order (1.13 ± 0.06). Similarly, Figure 6.4B shows reaction rate dependence for ethylene as close to first order (1.17 ± 0.12) at a DMF concentration of 1.38 M (18 wt%) in n-heptane with ethylene partial pressure varying from 6.9 to 34.5 bar. Ethylene concentration in Figure 6.4B was estimated using data from Zhuze and co-workers.86
Figure 6.4 Reaction orders measured in the Diels-Alder cycloaddition limited regime.
A. Dimethylfuran B. Ethylene

Selectivity to products in the high activation energy kinetic regime exhibit dependence on the DMF and ethylene reactant concentrations as depicted in Figure 6.5. As shown in Figure 6.5A, increasing initial DMF concentration decreases selectivity towards p-xylene from 85 to 45% and increases selectivity towards dimer products from 15 to 55%. Negligible change in selectivity to alkylated species was detected. In contrast, as illustrated in Figure 6.5B, variation in initial ethylene pressure from 6.9 to 34.5 bar (100 to 500 psi) does not have a statistically significant effect on selectivity to p-xylene or other products.
Figure 6.5 Selectivity to products from dimethylfuran and ethylene in the cycloaddition limited kinetic regime, H-BEA (Si/Al 12.5). A. Variable initial DMF concentration, $C_{DMF}$. Conditions: $T=200^\circ$C, $P_{Ethylene}=13.6$ atm. Increasing DMF concentration decreases selectivity to $p$-xylene. B. Variable initial ethylene concentration, $C_{Ethylene}$. $T=200^\circ$C, $C_{DMF}=1.38$ M. Increasing concentration of ethylene has minimal impact on selectivity to major products.

Reaction rate orders of DMF and ethylene with H-BEA (Si/Al 12.5) were also determined in the low activation energy kinetic regime with Bronsted acid concentration of 1.3 mM and 200 °C, as depicted in Figure 6.6. As shown in Figure 6.6A varying DMF concentration from 0.4 to 2.1 M indicates a reaction close to first first order ($1.09 \pm 0.08$). Variation in ethylene concentration with fixed DMF concentration of 1.38 M (18 wt%) shown in Figure 6.6B exhibited first order behavior, with ethylene rate dependence of $1.04 \pm 0.05$. 
Figure 6.6 Reaction orders measured in the dehydration limited regime.

A. Dimethylfuran  B. Ethylene

The effect of variation in initial DMF concentration or ethylene pressure on selectivity to Diels-Alder products in the low activation energy kinetic regime is illustrated in Figure 6.7. Increasing initial DMF concentration decreases selectivity to p-xylene from 80% to 55% and increases selectivity towards alkylated products from 2.5 to 27%; dimer products remain relatively constant at 22% as shown in Figure 6.7A. Variation in initial ethylene pressure from 6.9 to 34 bar (100 to 500 psi) resulted in no statistically significant difference in selectivity to any of the major products as shown in Figure 6.7B.
Figure 6.7 Selectivity to products from dimethylfuran and ethylene in the dehydration limited kinetic regime, H-BEA (Si/Al 12.5). A. Variable initial DMF concentration, C_{DMF}. Conditions: T=200 °C, P_Ethylene=13.6 atm. Increasing DMF concentration decreases selectivity to p-xylene. B. Variable initial ethylene concentration, C_{Ethylene}. T=200 °C, C_{DMF}=1.38 M. Increasing concentration of ethylene has minimal impact on selectivity to major products.

6.3. A Simplified Kinetic Model For HBEA

The kinetics of p-xylene formation over HBEA can be fit to the following reaction scheme where the reactant DMF binds strongly to the Brønsted acid active site. This MDF remains bound to the active site and inhibits xylenes isomerization as detail later in Chapter 7. The homogeneously formed Diels-Alder cycloadduct then abstracts a proton for the protonated (and bound) DMF. Once the cycloadduct has abstracted the proton three possible pathways can occur: dehydration to p-xylene, dehydration/alkylation, and dehydration/polymerization.
Reaction Scheme:

1) DMF Adsorption     \[ \text{DMF} + S \rightarrow \text{DMF-S} \]
2) Cycloaddition      \[ \text{DMF} + \text{Eth} \leftrightarrow \text{CA} \]
3) Dehydration        \[ \text{CA} + \text{DMF-S} \rightarrow \text{pXy} + \text{DMF-S} \]
4) Alkylation         \[ \text{CA} + \text{DMF-S} + E \rightarrow \text{Alk} + \text{DMF-S} \]
5) Polymerization     \[ \text{CA} + \text{DMF-S} + \text{DMF} \rightarrow \text{Poly} + \text{DMF-S} \]

If DMF binds strongly and irreversibly to the Brønsted acid site and then essentially functions as a proton donor to the cycloadduct for dehydration DMF-S and S can be replaced by BA (total Brønsted acid sites) to give the following simplified reaction scheme.

Simplified Reaction Scheme:

1) Cycloaddition     \[ \text{DMF} + \text{Eth} \leftrightarrow \text{CA} \]
2) Dehydration        \[ \text{CA} + \text{BA} \rightarrow \text{pXy} + \text{H}_2\text{O} + \text{BA} \]
3) Alkylation         \[ \text{CA} + E + \text{BA} \rightarrow \text{Alk} + \text{BA} \]
4) Dimerization       \[ \text{CA} + \text{DMF} + \text{BA} \rightarrow \text{Ply} + \text{BA} \]

The various reaction components in the reaction process are defined below.

DMF = 2,5-Dimethylfuran
Eth = Ethylene
CA = Diels-Alder Cycloadduct
pXy = \text{p-Xylene}
Alk = Alkylated Products (like 1-methyl-4-propylbenzene)
Ply = Dimers of DMF and p-xylene or two xylenes
DAP = Diels-Alder Products (sum of p-xylene, alkylated, and polymerized products)
S = Open Brønsted Acid Site (-S is bound to the site)
\(\Theta\) = Total Number of Acid Sites
BA = Brønsted Acid Site

The detailed species balances and calculation of equilibrium constants from Gibbs free energies of reaction allow the remaining rate constants to be fit in Excel.
Species Balances

\[
\frac{dC_{DMF}}{dt} = -k_1 C_{DMF} C_{Eth} + k_{-1} C_{CA} - k_4 C_{DMF} C_{CA} C_{BA}
\]

\[
\frac{dC_{Eth}}{dt} = -k_1 C_{DMF} C_{Eth} + k_{-1} C_{CA} - k_3 C_{Eth} C_{CA} C_{BA}
\]

\[
\frac{dC_{pXY}}{dt} = k_2 C_{CA} C_{BA}
\]

\[
\frac{dC_{Alk}}{dt} = k_3 C_{Eth} C_{CA} C_{BA}
\]

\[
\frac{dC_{ply}}{dt} = k_4 C_{DMF} C_{CA} C_{BA}
\]

\[
\frac{dC_{CA}}{dt} = k_1 C_{DMF} C_{Eth} - k_{-1} C_{CA} - k_2 C_{CA} C_{BA} - k_3 C_{Eth} C_{CA} C_{BA} - k_4 C_{DMF} C_{CA} C_{BA}
\]

Apply the steady state assumption \(\frac{dC_{CA}}{dt} = 0\) and solve for \(C_{CA}\)

\[
C_{CA} = \frac{k_1 C_{DMF} C_{Eth}}{k_{-1} + k_2 C_{BA} + k_3 C_{Eth} C_{BA} + k_4 C_{DMF} C_{BA}}
\]

Substitute \(C_{CA}\) into the DAP balance and divide by \(C_{BA}\)

\[
\frac{dC_{DAP}}{dt} = \frac{k_1 C_{DMF} C_{Eth} (k_2 + k_3 C_{Eth} + k_4 C_{DMF})}{\frac{k_{-1}}{C_{BA}} + (k_2 + k_3 C_{Eth} + k_4 C_{DMF})}
\]

Take the limit of \(\frac{dC_{DAP}}{dt}\) as \(C_{BA}\) approaches \(\infty\)

\[
\frac{dC_{DAP}}{dt} = k_1 C_{DMF} C_{Eth}
\]

Solve for \(k_1\) from the data then use \(\Delta G = -RT \ln(K_{eq})\) to solve for \(k_{-1}\)

Substitute \(C_{CA}\) into the species balances for \(p\)-xylene, alkylated and polymerized products.
\[
\frac{dC_{pXY}}{dt} = \frac{k_2 C_{BA} k_1 C_{DMF} C_{Eth}}{k_{-1} + k_2 C_{BA} + k_3 C_{Eth} C_{BA} + k_4 C_{DMF} C_{BA}}
\]
\[
\frac{dC_{Alk}}{dt} = \frac{k_3 C_{Eth} C_{BA} k_1 C_{DMF} C_{Eth}}{k_{-1} + k_2 C_{BA} + k_3 C_{Eth} C_{BA} + k_4 C_{DMF} C_{BA}}
\]
\[
\frac{dC_{PLY}}{dt} = \frac{k_4 C_{DMF} C_{BA} k_1 C_{DMF} C_{Eth}}{k_{-1} + k_2 C_{BA} + k_3 C_{Eth} C_{BA} + k_4 C_{DMF} C_{BA}}
\]

Data for the evolution of the species above can be fit, and the error minimized, to solve for \(k_2, k_3, \text{ and } k_4\).

Figure 6.8 below shows the model fit for the initial rate of formation of all the Diels-Alder products and the individual components: p-xylene, alkylated products, and polymerized products where the experimental data is displayed in points and the corresponding model fit is a solid line.

Figure 6.8 Initial reaction rate as a function of effective Brønsted acid site concentration. All Diels-Alder products experimental (■) and model (▬), p-xylene experimental (●) and model (▬), polymer products experimental (♦) and model (▬), alkylated products experimental (▲) and model (▬)
The corresponding rate constants for the data fit above is shown below in Table 6.1.

Table 6.1: Rate constants determined from the simplified kinetic model fit to data for the formation of Diels-Alder products, p-xylene, alkylated products, and polymer products.

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>7.23E-06</td>
</tr>
<tr>
<td>$k_{-1}$</td>
<td>8.89E-07</td>
</tr>
<tr>
<td>$k_2$</td>
<td>1.30E-03</td>
</tr>
<tr>
<td>$k_3$</td>
<td>2.22E-03</td>
</tr>
<tr>
<td>$k_4$</td>
<td>2.00E-05</td>
</tr>
</tbody>
</table>

The simplified kinetic model fit well with the measured reaction orders in that the reaction order for both DMF and ethylene is on in the cycloaddition limited regime (as the Brønsted acid site concentration approaches infinity). The reaction orders of one in the dehydration limited regime make sense as long as $k_{-1}$ is small relative to $k_{2,3,4}$, which appears to be true given the values in Table 6.1.

In conclusion, there exists two different reaction regimes based upon the loading of H-BEA catalyst for the formation of $p$-xylene from DMF and ethylene. At low catalyst loadings the reaction is limited by the rate of dehydration of the Diels-Alder cycloadduct. As catalyst loading increases past an acid site concentration in solution of 2.5 mM, the formation of $p$-xylene becomes limited by the rate of formation of the Diels-Alder cycloadduct. It has also been shown that lowering the initial concentration of DMF will increase the selectivity towards $p$-xylene by decreasing the formation of polymerized and alkylated products. Increasing the pressure of the reactant ethylene serves to increase the production of Diels-Alder compounds in both the cycloaddition and dehydration limited regimes without having a statistically significant effect on product selectivity. Therefore, based on this kinetic study on the formation of $p$-xylene from DMF and ethylene, it is recommended to operate at higher temperatures, lower
DMF concentrations, higher ethylene pressures, and an effective Brønsted acid site concentration above 2.5 mM to achieve maximum reaction rates and high product selectivity.
CHAPTER 7

INHIBITION OF XYLENE ISOMERIZATION FOR ULTRA PURE
PRODUCT YIELDS

Production of biorenewable fuels and chemicals has gained interest due to an increased demand for energy independence and the need for a sustainable products and materials.\textsuperscript{3,4} Initial approaches to renewable fuels and chemicals have focused on enzymatic or hybrid enzymatic/thermochemical processing of biomass for renewable fuels and chemicals.\textsuperscript{6} A hybrid process combines the benefits of high selectivity provided by enzymes and the speed of thermochemical processes. A third option utilizes highly selective catalysts for a thermochemical process to produce furans and other basic chemicals from biomass-derived sugars.\textsuperscript{13,14} One renewable chemical of interest is \textit{p}-xylene, which can be directly integrated into modern chemical platforms for the production of PET, a material used in multiple consumer products such as plastic bottles.\textsuperscript{16,18} In addition, consumption of benzene/toluene/xylenes (BTX) continues to aggressively grow and could be offset with biomass sources.\textsuperscript{12}

Thermochemical production of \textit{p}-xylene from sugars benefits from a limited number of reactions, each of which can be independently optimized to high selectivity for an overall process with viable yield. Isomerization of glucose to fructose occurs using biological (i.e., enzymes) or thermochemical catalysts, including base catalysts\textsuperscript{27} and Lewis acid heterogeneous catalysts such as Sn-Beta.\textsuperscript{28} Fructose then dehydrates to hydroxymethylfurfural,\textsuperscript{29} which is further hydrodeoxygenated to produce 2,5-dimethylfuran (DMF).\textsuperscript{30} The last step produces \textit{p}-xylene from DMF and ethylene (itself produced by dehydration of ethanol), which completes the transformation of renewable biomass feedstock to aromatic chemicals which can be integrated within existing refinery
Initial studies of the final step of this process to convert furans to aromatic chemicals with six-carbon rings has demonstrated high yield (75-90%) of \( p \)-xylene from DMF using H-Y and H-BEA zeolites\(^{61,70} \) and has stimulated further research on the process chemistry, kinetics and catalytic mechanisms. Experimental examination of the reaction pathways of the cycloaddition of ethylene/dimethylfuran identified three competing reactions: (a) hydrolysis of dimethylfuran, (b) multiple addition of ethylene to alkylated aromatic chemicals, and (c) dimerization of furans.\(^{66} \) Additionally, gas-phase DFT has evaluated the series mechanism of Diels-Alder cycloaddition of ethylene/dimethylfuran combined with dehydration to produce \( p \)-xylene.\(^{65} \) These studies highlighted a necessity for Brønsted acidity to catalyze the dehydration of the oxa-norborene intermediate, the overall rate limiting reaction absent catalysts. Further calculations have identified the beneficial role of Lewis acids like lithium, which can lower the energy barrier of cycloaddition (when Bronsted acids are already present) and increase the overall reaction rate.\(^{65} \)

### 7.1. The Question of Xylene Isomerization over H+ form Zeolites

Despite progress on development of thermochemical conversion of DMF to \( p \)-xylene, there remain several important aspects of the reaction that are not well understood. One of the main benefits of this process is its high yield to xylenes as well as its extremely high selectivity (99%) to the para-isomer of xylenes; this particular attribute nearly eliminates the need for expensive xylene separation.\(^{82} \) It is well known that \textit{ortho-}, \textit{meta-} and \textit{para-}xylenes readily isomerize in the presence of solid acid catalysts, such as H-Y and H-BEA zeolite, under the reaction temperatures of 240 to 300 °C.\(^{48,83–86} \)
However, isomerization has not been observed during the production of \( p \)-xylene from DMF using H-Y or other solid acid catalysts; once formed, \( p \)-xylene remains intact.\(^{61,67}\)

Isomerization of xylenes occurs through both intramolecular and intermolecular pathways in zeolite catalysts. The unimolecular mechanism proceeds through a 1,2-methylshift, allowing for reactions such as a shift of \( p \)-xylene to meta-xylene. Alternatively, the bimolecular mechanism can occur through transalkylation, requiring two adjacent acid sites, to form toluene and trimethylbenzenes (TMB) from \( p \)-xylene.\(^{87}\)

The favored isomerization mechanism depends on reaction conditions and catalyst properties including temperature, catalyst microstructure, acid site density and acid site strength. The bimolecular mechanism is more favored in zeolites than in catalysts like silica-alumina\(^{87}\) as well as at higher temperatures, as it requires 3-4 kcal/mol more energy than the unimolecular mechanism.\(^{88}\)

The bimolecular pathway, associated with disproportionation on adjacent acid sites, is favored in zeolites as the Si/Al ratio decreases (greater Brønsted acid site density), and the pore size of the zeolite increases.\(^{85-88}\)

Considerations of reaction temperature, and the greater acid site density in zeolites, indicates that the bimolecular mechanism, which produces toluene and trimethylbenzene, should occur when producing \( p \)-xylene from DMF using H-Y and H-BEA zeolite.

The role of strong acid sites in H-Y and H-BEA for catalyzing dehydration, while not promoting isomerization, is of primary interest. Much characterization of zeolite structure and acid sites, and in some cases elucidation of species bound to them, has been achieved through FT-IR.\(^{89-91}\)

Dealuminated H-Y faujasite contains a characteristic peak associated with the external silanols located at 3743 cm\(^{-1}\). Additionally, characteristic peaks for the tetrahedrally-coordinated strong acid sites in the
supercages and sodalite cages are located at 3627 cm\(^{-1}\) and 3563 cm\(^{-1}\) respectively.\(^{92}\) Characterization of these acid sites has been complemented by \(^{27}\)Al MAS NMR, which monitors type and relative ratio in faujasite and beta.\(^{89,93,94}\) In the case of dealuminated H-Y zeolite, tetrahedrally coordinated aluminum, denoted by a frequency shift of ca. 60 ppm, represents strong Brønsted acid sites. Octahedrally coordinated aluminum denotes extraframework aluminum, represented by a peak at ca. 0 ppm, which is slightly Lewis acidic.\(^{89}\) In the case of dealuminated H-Y, there also exists a peak shoulder at ca. 32 ppm, which has been previously attributed to distorted tetrahedrally coordinated aluminum.\(^{95}\) \(^{27}\)Al-NMR of H-BEA shows a similar spectrum to that of H-Y and has tetrahedrally coordinated Al at 60 ppm and Octahedrally coordinated Al at 0 ppm.

In this paper, we investigate the mechanism leading to inhibition of \(p\) xylene isomerization in H-Y and H-BEA zeolite during the cycloaddition of dimethylfuran and ethylene. Inhibition is studied by considering xylene isomerization in the presence of the most prevalent components in the reaction of DMF/C\(_2\)H\(_4\). The interaction of chemical adsorbates with active sites was examined by diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) to establish the preferential adsorption of DMF versus \(p\)-xylene on strong Brønsted acid sites. Acid sites were quantitatively characterized before and after use using isopropylamine TPD; additional characterization utilized \(^{27}\)Al-NMR to determine the extent of structural transformation of zeolite acid sites during and after reaction. Finally, thermogravimetric analysis (TGA) provided insight into the degree of cationic polymerization of DMF present on the strong acid sites present in the H-Y faujasite.\(^{96,97}\) This investigation will lead to a better understanding, and through that
understanding further improvement, of a reaction system for the production of renewable aromatic chemical building blocks.

7.2. Investigation of Xylene Isomerization Inhibition

Inhibition of \( p \)-xylene isomerization was investigated, primarily through the addition of different reaction components in a stirred pressure vessel in the presence of H-Y and H-BEA zeolites. Analytical techniques including DRIFTS, TGA, and \(^{27}\text{Al-NMR} \) provided insight on the key species bound to Brønsted acid sites, which are responsible for the inhibition of \( p \)-xylene isomerization.

7.2.1. Isomerization Inhibition by the Principal Reaction Components

In production of \( p \)-xylene from DMF and ethylene, it has been noted that negligible \( o/lm \)-xylene isomers are produced, despite the existence of acidic active sites capable of promoting isomerization of \( p \)-xylene.\(^{61,67} \) To investigate this phenomenon, the isomerization of \( p \)-xylene was evaluated at conditions relevant to its production from DMF (i.e. at 300 \( ^\circ \)C in \( n \)-heptane solvent using H-Y zeolite (CBV-600)). As shown in Figure 7.1, a reaction mixture of \( p \)-xylene in \( n \)-heptane with zeolite exhibits the expected behavior of rapid xylene isomerization; a significant portion of the \( p \)-xylene disproportionates and isomerizes before reaching an asymptotic value of 55% conversion. Rearrangement of \( p \)-xylene produces numerous products, including \textit{meta} and \textit{ortho} xylenes as well as toluene, trimethylbenzene, and heavier alkylation products. Deactivation of the catalyst with time prevents the system from achieving equilibrium, which typically produces \textit{meta} xylene at a 2:1 ratio to \textit{ortho} and \textit{para} xylene.\(^{48} \) Catalyst
deactivation was confirmed by performing a second experiment with increased catalyst loading, which led to increased conversion of \( p \)-xylene, as seen in Figure 7.1B. The increase in extent of reaction to 75\%, as compared to Figure 7.1A, indicates that the system does not reach equilibrium before the catalyst fully deactivates.

![Figure 7.1 Isomerization of \( p \)-Xylene.](image)

(A) Isomerization of \( p \)-xylene readily occurs at conditions relevant to production from DMF and ethylene. (B) The extent of isomerization is demonstrated to be dependent upon the catalyst loading, suggesting catalyst deactivation which results in non-equilibrated products of \( p \)-xylene (■), \( o,m \)-xylene (□), toluene and trimethylbenzene (○), and alkylated products (Δ). Reaction Conditions: 300 °C, 800 psi \( N_2 \), 86 ml Heptane, 12 ml \( p \)-xylene, 2 ml Tridecane, (A) 0.42 g H-Y Si/Al=2.6, (B) 1.41 g H-Y Si/Al=2.6

To determine the source of xylene isomerization inhibition, the principal reaction components were tested individually for their impact on isomerization chemistry. The examined compounds included: the reactants DMF and ethylene, as well as the most prevalent side products, 2,5-hexanedione and water.

DMF was shown to strongly inhibit isomerization of \( p \)-xylene as shown in Figure 7.2A. In a mixture that contained initial concentrations of 0.2 M DMF and 1 M \( p \)-xylene, no conversion of \( p \)-xylene was observed within experimental error. In a second experiment, reducing the initial DMF concentration by an order of magnitude, to 0.02M
DMF, limited the isomerization of \( p \)-xylene to less than 5\%, as shown in Figure 7.2B. The conditions in Figure 7.2B represent ten dimethylfuran molecules per Brønsted acid site for H-Y (Si/Al 2.6). This indicates that inhibition of xylene isomerization will occur even when the \( p \)-xylene is present at concentrations fifty times greater than the DMF. For comparison with the original process of Williams et. al., this condition (\( p \)-xylene concentration being fifty times DMF concentration) is the equivalent to 98\% conversion of the dimethylfuran with 100\% selectivity towards \( p \)-xylene. It can also be seen in Figure 7.2 C,D that DMF will inhibit isomerization in the presence of H-BEA with results that are indistinguishable from those obtained for H-Y for both high and low DMF loadings. However, it should be noted that in both of these cases there is also 2,5-hexanedione, probably formed from hydrolysis of DMF with water adsorbed on the catalyst surface during heating, present in solution at amounts anywhere from one to two hexanedione per Brønsted acid site.
Inhibition of $p$-Xylene Isomerization by Dimethylfuran (A) 2,5-Dimethylfuran inhibits the isomerization of $p$-xylene at $1/5$th the xylene concentration in the presence of H-Y zeolite, Si/Al 2.6. (B) 2,5-Dimethylfuran inhibits the isomerization of $p$-xylene at $1/50$th of the xylene concentration with H-Y zeolite, Si/Al 2.6. (C) 2,5-Dimethylfuran inhibits the isomerization of $p$-xylene at $1/5$th the xylene concentration in the presence of H-BEA zeolite. (D) 2,5-Dimethylfuran inhibits the isomerization of $p$-xylene at $1/50$th of the xylene concentration with H-BEA zeolite, Si/Al 12.5. Legend. $p$-xylene (■), DMF (●), $o,m$-xylene (□), toluene and trimethylbenzene (○), heavy alkylation products (Δ). Reaction Conditions: 300 °C, 800 psi N2, 86 ml Heptane, 2 ml Tridecane, 0.41 g H-Y Si/Al=2.6 , (A) 10 ml $p$-xylene, 2 ml DMF, (B) 12 ml $p$-xylene, 0.2 ml DMF.

The second chemical examined for inhibition of $p$-xylene isomerization was 2,5-hexanedione, the hydrolysis product of dimethylfuran. As shown in Figure 7.3A-B, isomerization of $p$-xylene was strongly inhibited by the presence of 2,5-hexanedione exhibiting negligible $p$-xylene conversion, within experimental error. Figure 7.3A shows inhibition of $p$-xylene isomerization under conditions where the hexanedione
concentration was set at one-fifth that of the p-xylene (2 ml of 2,5-hexanedione and 10 ml of p-xylene to 88 ml of heptane solvent). Figure 7.3B depicts a reduction of hexanodione concentration by an order of magnitude to one fiftieth that of the p-xylene; in this case, there were approximately ten DMF per Brønsted acids and conversion of p-xylene was still below 5%. This set of experiments shows that the conversion of the xylene will be inhibited to the same degree, for the considered conditions, with both hexanedione and DMF. During the experiments of Figure 7.3A-B, it was observed that DMF and water were formed through acid-catalyzed cyclization of 2,5-hexanedione. The presence of DMF in the reaction mixture is particularly visible in Figure 7.3A, where the concentration of DMF is far greater than hexanedione. This acid catalyzed cyclization has been observed to take place in high Al content H-ZSM5 at yields above 95%,68 which is consistent with our observations. Due to the cyclization reaction, the role of 2,5-hexanodione on p-xylene isomerization chemistry cannot be independently determined. However, it is apparent that the presence of 2,5-hexanodione will readily form DMF, which appears to inhibit the isomerization reactions of p-xylene.
Figure 7.3 Inhibition of \(p\)-Xylene Isomerization by 2,5-Hexanedione. The presence of 2,5-Hexanedione inhibits isomerization at both (A) \(1/5\)th xylene concentration and (B) \(1/50\)th the xylene concentration. Identified chemical species include: \(p\)-xylene (■), DMF (●), hexanedione (▲), \(o,m\)-xylene (□), toluene and TMB (○), heavy alkylated products (Δ). Reaction Conditions: 300 °C, 800 psi N\(_2\), 86 ml Heptane, 2 ml Tridecane, 0.41 g H-Y Si/Al=2.6 , (A) 10 ml \(p\)-xylene, 2 ml 2,5-Hexanedione, (B) 12 ml \(p\)-xylene, 0.2 ml Hexanedione

The final two components examined were ethylene, the dienophile in the Diels-Alder cycloaddition reaction with DMF, and water, the product of cycloadduct dehydration. Neither ethylene nor water was observed to have any inhibitory effect on xylene isomerization. In the experiment shown in Figure 7.4A, \(p\)-xylene (12 mL) in heptane (86 mL) was reacted at 300 °C in a reactor with 200 psi partial pressure ethylene (800 psig total, balance heptane and DMF vapor pressure). It is shown in Figure 7.4A that the addition of ethylene resulted in an increase in the number of heavily alkylated products and showed no effect towards inhibiting isomerization of \(p\)-xylene. These heavily alkylated species constitute a wide array of products, the precise identification of which is outside the scope of this work. Addition of water also had no effect on \(p\)-xylene isomerization chemistry. As shown in Figure 7.4B, the reaction of 10 mL of \(p\)-xylene, 2 mL of water, and 86 mL of heptane was examined at 300 °C in the presence of H-Y
zeolite. In both cases, p-xylene conversion of 60% and the formation of toluene and trimethylbenzene were observed as the dominant products at 60% selectivity.

Figure 7.4 p-Xylene Isomerization in the Presence of Ethylene or Water. (A) Ethylene promotes formation of heavy alkylated products in the presence of p-xylene in addition to isomerization and (B) Water does not inhibit the isomerization. Identified chemicals include: p-xylene (■), o,m-xylene (□), toluene and TMB (○), heavy alkylated products(Δ). Reaction Conditions: 300 °C, 86 ml Heptane, 2 ml Tridecane, 0.42 g H-Y Si/Al=2.6. (A) 800 psi Ethylene, 12 ml p-xylene, (B) 800 psi N2, 10 ml p-xylene, 2 ml water.

7.2.2. Investigation of Brønsted Acid Sites

Figure 7.5A shows the $^{27}$Al MAS NMR spectra of fresh and spent H-Y catalyst. Fresh catalyst was used as received. ‘Spent’ catalyst was used in the reaction of DMF (15 wt%) and ethylene in heptane solvent at 300 °C. From the spectra of fresh H-Y catalyst, there exists a small amount of non-framework, pentacoordinated aluminum (32 ppm) in addition to framework tetrahedrally coordinated aluminum (60 ppm) and extraframework octahedrally coordinated Al (0 ppm). In comparison, the spectrum of spent catalyst does not exhibit the shoulder at 32 ppm. Additionally, the ratio of tetrahedral to octahedral coordinated aluminum has markedly decreased, indicating that a partial loss of part of the Brønsted acidity with reaction may occur. Despite these
changes, framework aluminum which produces Brønsted acid sites exists in the examined H-Y zeolite both before and after reaction. Figure 7.5B illustrate the $^{27}$Al MAS NMR spectra of H-BEA which shows a similar loss in Brønsted acidity upon reaction. Interestingly the Octahedrally coordinated Al at 0 ppm nearly disappears after reaction and the intensity of the tetrahedrally coordinated Al (50 ppm) is greatly reduced.

Figure 7.5 $^{27}$Al-NMR of H-Y and H-BEA Zeolite. (A) H-Y zeolite (CBV-600, Si/Al 2.6) catalyst that has been used to produce p-xylene from DMF and ethylene and not regenerated by coke burnoff (spent) shows reduced tetrahedrally-coordinated aluminum (ca. 60ppm) relative to octahedrally-coordinated aluminum (ca. 0 ppm) as compared to unused catalyst (fresh). (B) H-BEA zeolite (CP814E, Si/Al 12.5) exhibit a trend similar to H-Y in that the tetrahedrally coordinated Al peak at 60 ppm loses intensity after reaction.

Binding of reactant species to Brønsted acid sites in H-Y zeolite was examined using Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS). As shown in Figure 7.6, the IR spectra of degassed H-Y zeolite identifies initial -OH bonds, including: (a) the external silanols on H-Y faujasite at 3743 cm$^{-1}$, and (b) the tetrahedrally coordinated aluminum corresponding to the -OH stretching bands from
the acid sites located in the super and sodalite cages at 3628 cm\(^{-1}\) and 3565 cm\(^{-1}\), respectively.\(^9\) It is shown in Figure 7.6 that acid sites (3628 cm\(^{-1}\) and 3565 cm\(^{-1}\)) are completely covered at a moderate temperature of 120 °C by adsorbing DMF, \(p\)-xylene, or a pre-mixed solution of the two (1:50 DMF to \(p\)-xylene by concentration). After heating to 300 °C, the strong acid sites at 3628 cm\(^{-1}\) and 3565 cm\(^{-1}\) are not regenerated by desorption of the DMF or the DMF/\(p\)-xylene mixture. However, when the zeolite saturated with \(p\)-xylene is heated to 300 °C, the peaks associated with Brønsted acid sites are completely recovered. The loss of the OH stretching bands associated with the strong acid sites, even after heating the dilute DMF in \(p\)-xylene mixture, strongly indicates that the DMF is the chemical species bound to those sites.

![Figure 7.6 DRIFTS of DMF/\(p\)-Xylene on H-Y Zeolite.](image)

(i) Degassed zeolite H-Y (Si/Al 2.6) exhibits –OH stretches associated with external silanols (3740 cm\(^{-1}\)) and Bronsted acid sites in supercages (3628 cm\(^{-1}\)) and sodalite cages (3565 cm\(^{-1}\)). (ii-iv) Adsorption at 120 °C of DMF (ii), \(p\)-Xylene (iii), and a 1/50 mixture of DMF/\(p\)-Xylene (iv) shows absence of free Bronsted acid sites. (v-vii) Increasing the temperature to 300 °C recovers Bronsted acids previously occupied by \(p\)-xylene (vi), while DMF adsorbed on Bronsted acid sites associated within super- and sodalite cages remain adsorbed at 300°C.
TGA was performed on H-Y and H-BEA zeolites with adsorbed DMF or \( p \)-xylene to characterize desorption of these components in the temperature range of 100-300 °C, as shown in Figure 7.7. Vaporized chemicals were adsorbed on zeolites at 120 °C and then heated to 300 °C with an inert atmosphere. DMF remains adsorbed on H-Y and H-BEA at temperatures as high as 300 °C, as shown in Figure 7.7A-B. The \( y \)-axis indicating the number of adsorbed DMF species per active site was calculated by dividing the moles of reactant adsorbed by the previously measured Brønsted acid site concentration, for the fresh catalyst, provided in Table 7.1. DMF initially adsorbs at a ratio of about 4:1 with Brønsted acid sites on dealuminated H-Y zeolite (Figure 7.7A), while it only adsorbs with a ratio of 2:1 for H-BEA (Figure 7.7B). As the temperature is increased from 120 °C to 300 °C, only 40% of the adsorbed DMF will desorb for H-Y, leaving a ratio of two DMF molecules per Brønsted acid site at reaction temperatures (Figure 7.7A). For H-BEA, only 30% of adsorbed DMF molecules will desorb, leaving a final ratio of one DMF per acid site under reaction conditions (Figure 7.7B). In comparison, \( p \)-xylene binds at a ratio of about 3:2 to Brønsted acid sites of both H-Y and H-BEA, as shown in Figure 7.7C and D, respectively. However, at a temperature of 120 °C under flowing helium, more than 50% of \( p \)-xylene will desorb from both zeolites. Upon heating to 300 °C, all of the \( p \)-xylene desorbs from both H-Y and H-BEA (Figure 7.7C and D). TGA analysis was also performed on \( \gamma \)-alumina, a surrogate for the octahedrally coordinated Al in the zeolites, to gain an understanding of how DMF would desorb from Lewis acid sites. The data, presented in supporting information, shows that DMF readily desorbs from \( \gamma \)-alumina at a temperature of only 160 °C.
Thermogravimetric analysis of 2,5-dimethylfuran (DMF) on H-Y (A) and H-BEA (B) exhibits incomplete desorption. In comparison, TGA of p-xylene on H-Y (C) and H-BEA (D) exhibits complete desorption at 300 °C.

7.2.3. Dehydration of Cyclohexanol

The capability of H-Y and H-BEA zeolites for catalyzing dehydration was further studied using the chemical surrogate cyclohexanol. Cyclohexanol was selected for size
(kinetic diameter of 6 Å)\textsuperscript{98} and functionality (single hydroxyl group). As shown in Figure 7.8A, a mixture of cyclohexanol (5 mL), heptane (52 mL), and 0.3 g H-BEA zeolite was reacted at 200 °C for 60 minutes and rapidly produced cyclohexene at 80% yield. A second experiment, depicted in Figure 7.8B, considered a similar experiment with the addition of DMF (2 mL); dehydration of cyclohexanol was observed to occur at the same rate with almost 100% yield of cyclohexene. Despite the presence of strongly-adsorbing DMF, cyclohexanol readily dehydrates in the presence of H-BEA zeolite.

![Figure 7.8 Dehydration of Cyclohexanol on H-BEA and H-BEA/DMF Complexes. (A) Dehydration of 11 wt% cyclohexanol (■) in heptane on H-BEA (Si/Al 12.5) at 200 °C rapidly forms cyclohexene, which further dimerizes to secondary products. (B) Dehydration of 11 wt% cyclohexanol (■) in the presence of 4 wt% DMF in heptane with H-BEA (Si/Al 12.5) at 200 °C rapidly forms stoichiometric quantities of cyclohexene.](image)

7.3. A Consideration of the Isomerization Inhibition Experiments

Figure 7.1 illustrates that, as expected, \textit{p}-xylene readily isomerizes in the presence of H-Y and H-BEA for the conditions that are required to produce it from DMF and ethylene (>200 °C). The existence of twice as much toluene and trimethylbenzene in the products as compared to \textit{ortho}- and \textit{meta}-xylene indicates that the predominant isomerization mechanisms are bimolecular in nature. Prevalence of the bimolecular
reaction path is likely due to the high density of acid sites present in the considered zeolites.

While isomerization of \( p \)-xylene occurs with fresh zeolites, a first consideration for the mechanism leading to inhibition of \( p \)-xylene isomerization in the reaction of DMF and ethylene must consider that strong Bronsted acid sites are eliminated during reaction. Water produced in the production of \( p \)-xylene from DMF has the potential for converting strong acid sites in both H-Y and H-BEA to extraframework Lewis acid sites.\(^{96} \) However, characterization of H-Y and H-BEA shown in Table 7.1 reveals that strong acid sites exist both before and after reaction.

Table 7.1 Characterization of Zeolite Materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation Method</th>
<th>Brønsted acid sites (mmol/g)(^{A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Y (CBV600)</td>
<td>Fresh</td>
<td>0.34 ± 0.04</td>
</tr>
<tr>
<td>H-Y (CBV600)</td>
<td>Post-Reaction, Calcined in Air at 550 °C(^{b} )</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>H-Y (CBV600)</td>
<td>DMF-Adsorbed(^{c} )</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td>H-BEA (CP814E)</td>
<td>Fresh</td>
<td>0.70</td>
</tr>
<tr>
<td>H-BEA (CP814E)</td>
<td>Post-Reaction, Calcined in Air at 550 °C(^{b} )</td>
<td>0.39 ± 0.01</td>
</tr>
<tr>
<td>H-BEA (CP814E)</td>
<td>DMF-Adsorbed(^{c} )</td>
<td>0.42 ± 0.00</td>
</tr>
</tbody>
</table>

\(^{A}\)Obtained using Isopropylamine-TGATPD
\(^{b}\)Obtained following reaction of DMF+C H at 300 °C. Calcined in air at 550 °C.
\(^{c}\)Adsorbed with DMF at 120 °C and then heated to 300 °C for one hour before using standard Isopropylamine-TGATPD

Additionally, from the \(^{27}\)Al MAS NMR of Figure 7.5, the spectra of fresh and spent H-Y and H-BEA both indicate the presence of tetrahedrally-coordinated aluminum that comprises Brønsted sites at 60 and 50 ppm respectively. The extraframework tetrahedrally coordinated aluminum acid sites associated with the peak at 32 ppm disappears for H-Y, but it has been previously noted that the
extraframework Al associated with this peak is less stable and does not play a strong role in acidity. Given the weak role in acidity of the peak at 32 ppm, it seems unlikely that the loss of this peak after reaction will greatly affect overall catalyst activity. Further evidence that strong acid site concentration is not significantly altered comes from previous work that shows identical activity for production of \( p \)-xylene from DMF for H-Y catalysts regenerated in flowing air at 550 °C.\(^{61,67}\) It can be concluded that Brønsted acid sites remain in the zeolite catalysts before, after, and during reaction.

The absence of \( p \)-xylene isomerization in the reaction of DMF and ethylene indicates that a reactant (or intermediate/product) occupies the Brønsted acid sites necessary for isomerization chemistry to occur. When DMF is added to the reaction mixture, isomerization of \( p \)-xylene over the considered zeolites completely stops (Figure 7.2). This effect is particularly strong, as it occurs at low concentrations relative to \( p \)-xylene (1/50) as shown in Figure 7.2B. The inhibition effect also occurs with 2,5-hexanediol, a hydrolysis product of DMF; however it should be noted that DMF rapidly reforms through cyclization of 2,5-hexanediol as the favored equilibrium chemical species in the presence of strong acid sites. In contrast, water and ethylene had no impact on the isomerization chemistry. These results indicate that DMF or 2,5-hexanediol adsorption on Brønsted acid sites is the key interaction of the inhibition mechanism.

Adsorption of DMF on strong acid sites was further studied through the use of DRIFTS, shown in Figure 7.6, allowing for monitoring of the Brønsted acid sites located in the super and sodalite cages (peaks at 3628 cm\(^{-1}\) and 3565 cm\(^{-1}\), respectively). From this data, it is clear that DMF remains adsorbed to strong acid sites at reaction temperatures (200-300 °C), while \( p \)-xylene will be completely removed upon
heating. This effect is strong, as a mixture of 1/50\textsuperscript{th} DMF\textit{/}p-xylene exhibits the same results as a saturated sample of pure DMF, providing strong evidence that DMF binds preferentially to Brønsted acid sites and blocks competing chemistries.

TGA data provided in Figure 7.7A,B supports the stronger binding of DMF to the Brønsted acid sites of H-Y and H-BEA zeolite, thereby inhibiting isomerization of the \textit{p}-xylene. DMF inside H-BEA zeolite can be estimated at one molecule under reaction conditions and two molecules per Brønsted acid site for H-Y. It can also be seen from Figure 7.7C,D that the majority of the bound \textit{p}-xylene can be removed by flowing helium while holding at 120 °C before being completely desorbed upon heating to reaction conditions.

While adsorption of DMF on Brønsted acid sites serves to inhibit xylene isomerization, the inhibition mechanism must also be consistent with the reaction mechanism leading to production of \textit{p}-xylene. Specifically, blocking of xylene isomerization by DMF adsorption to Brønsted acid sites must still allow for dehydration of oxanorbornene intermediates to six-carbon aromatic species such as \textit{p}-xylene. Three possible reaction mechanisms for \textit{p}-xylene formation are considered as shown in Figure 7.9, all of which depend on the adsorption strength of DMF.
Figure 7.9 Proposed Catalytic Cycles Converting DMF to \( p \)-Xylene. This catalytic cycle is illustrated with DMF. However, it is possible that a similar scheme could exist where 2,5-hexanediol replaces DMF in the scheme above.

It has previously been shown, by use of a thermochemical cycle, that heats of adsorption on Brønsted acid sites exhibit a correlation with proton affinities,\textsuperscript{97,99} thus allowing for relative differences in adsorption strengths of adsorbate mixtures to be speculated at from tabulated values of proton affinity (PA). From a list of proton affinities in Table 7.2, it is apparent that molecules like DMF (PA 865.9 kJ/mol) and 2,5-hexanediol (PA 892.0 kJ/mol) likely adsorb more strongly, and preferentially occupies Brønsted acid sites, relative to other molecules in the reaction mixture such as \( p \)-xylene (PA 794.4 kJ/mol), water (PA 691.0 kJ/mol) or ethylene (PA 680.5 kJ/mol).
Because the proton affinity of DMF greatly exceeds that of NH$_3$ (PA 853.6 kJ/mol), DMF adsorption likely results in proton transfer from the zeolite to the aromatic ring at one of three places: (i) the $\alpha$-carbon, (ii) the $\beta$-carbon, or (iii) the oxygen atom.$^{100,101}$ Gibbs free energies for proton transfer from H-Y to the DMF $\alpha$-C and $\beta$-C, as computed and tabulated in Table 7.3: Proton Transfer Enthalpies and Free Energies, demonstrate that proton transfer to the $\alpha$-C is thermodynamically favorable (-2.9 kcal/mol). Moreover, kinetic barriers associated with proton transfer to DMF are sufficiently low (6-8 kcal/mol), that DMF with a protonated $\alpha$-C is likely the dominant surface species, as the reaction is initiated.

Table 7.2 Proton Affinities of Reactant Chemicals

<table>
<thead>
<tr>
<th>Compound</th>
<th>Proton Affinity (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-Hexanедione</td>
<td>892.0$^a$</td>
</tr>
<tr>
<td>Dimethylfuran (DMF)</td>
<td>865.9$^a$</td>
</tr>
<tr>
<td>Dimethylfuran $\alpha$-C</td>
<td>864.4$^b$</td>
</tr>
<tr>
<td>DMF-Ethylene Cycloadduct</td>
<td>862.8$^b$</td>
</tr>
<tr>
<td>Ammonia</td>
<td>853.6$^a$</td>
</tr>
<tr>
<td>Dimethylfuran $\beta$-C</td>
<td>841.0$^b$</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>810.0$^b$</td>
</tr>
<tr>
<td>$p$-Xylene</td>
<td>794.4$^a$</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>784.5$^a$</td>
</tr>
<tr>
<td>Water</td>
<td>691.0$^a$</td>
</tr>
<tr>
<td>Ethylene</td>
<td>680.5$^a$</td>
</tr>
</tbody>
</table>

$^a$National Institute of Standards and Technology.
$^b$Computed using the methods of Chapter 2.
Three mechanisms are considered for conversion of adsorbed DMF-complex on Bronsted acid sites to \( p \)-xylene. Ethylene within the zeolite/cage pore could react directly with adsorbed DMF (green pathway of Figure 7.9), resulting in adsorbed oxa-norbornene intermediate. The loss of one of the two C-C \( \pi \)-bonds in DMF upon adsorption eliminates the possibility for Diels-Alder chemistry, and this reaction would need to occur by stepwise addition of ethylene, as has been proposed for other reactions of furan.\(^{102} \) However, stepwise addition of ethylene has been computed to be energetically unfavorable.\(^{65} \) Moreover, attempts to conduct step-wise addition of ethylene to adsorbed DMF have not produced six-carbon-ring products such as \( p \)-xylene. These experiments entailed adsorbing DMF in heptanes solution onto \(~2\)g of HY zeolite and filtering out the DMF adsorbed zeolite before rinsing it with heptanes. The DMF adsorbed catalyst was then added to a heptanes solution and heated to 250 °C before adding ethylene. The reaction progress was monitored with time and no products were formed.

A second mechanism considers homogenous reaction of DMF and ethylene to
form the DA cycloadduct, which can competitively adsorb with DMF for Bronsted acid sites. As shown in Table 7.2, the PA of DMF (865.9 kJ/mol) and the DMF-C2H4 cycloadduct (862.8 kJ/mol) are nearly the same, indicating that they should exhibit similar adsorption energies. Once formed either in the reactant liquid or zeolite pore/cage, it should compete with DMF for active sites; once DMF desorbs, the Brønsted acid site can be occupied by the DA cycloadduct. At this point, the reaction can proceed through C-O bond cleavage and a series of two proton transfers as described in previous literature.65

While mechanism two is consistent with the experimentally observed catalyzed formation of p-xylene and the inhibition of p-xylene isomerization, the mechanism cannot fully explain the dehydration capability of adsorbed DMF-complexes in H-BEA and H-Y. As shown in Figure 7.8, dehydration of cyclohexanol with H-BEA in the presence of DMF readily forms cyclohexene; it was anticipated that dehydration of cyclohexanol (PA = 810 kJ/mol) should be inhibited by high surface coverage of DMF (Figure 7.8B) due to the strong adsorption (PA of DMF, 865.9 kJ/mol). Therefore, it seems possible, that zeolites retain Brønsted acidity even after adsorption of DMF. Experiments were also performed that investigated the possibility of cyclohexanol dehydration on the extra-framework octahedrally coordinated Al through the surrogate γ-alumina as shown in supporting information. These experiments showed no cyclohexanol dehydration under our reaction conditions.

A proposed third mechanism to form adsorbed oxanorbornene proposes that the DMF-Bronsted acid site complex forms a new, weaker Bronsted acid site. As drawn in Figure 7.9, proton transfer from the H-Y zeolite Bronsted acid site to DMF can occur to the α-C, creating a DMF complex with an acidic furan α-carbon. A second proton
transfer can then occur from the protonated $\alpha$-carbon to the $\beta$-carbon of the adsorbed furan. DFT calculations, listed in Table 7.3, supports this proton transfer which is energetically favorable ($\Delta G = -3.3$ kcal/mol) and can occur with low kinetic energy barriers ($E_a = 16.2$ kcal/mol). The acidic $\beta$-C proton of the DMF complex is then abstracted by the ether oxygen of oxanorbornene and dehydration can occur along the pathway illustrated in Figure 7.10.

![Graph showing energy changes in the reaction]

**Figure 7.10** Proton transfer from adsorbed DMF to the cycloadduct.

At the same time, proton transfer of the acidic H of the adsorbed DMF complex to $p$-xylene is neither energetically favorable ($\Delta G = +27.6$ kcal/mol) and has a significant energy barrier ($E_a = +26.6$ kcal/mol). Once the proton on the $\beta$-C of the DMF complex is abstracted, the previously adsorbed DMF molecule becomes electronically neutral, and it is likely to be displaced at the active site by the newly protonated (and positively charged) oxanorbornene. The mechanism can then proceed as proposed in the pathway.
illustrated in Figure 7.10. The third mechanism, whereby the acid site is the DMF-zeolite complex, indicates the formation of a new Bronsted acid site which is sufficiently strong to protonate oxanorbornene and dehydrate cyclohexanol but sufficiently weak so as not to promote \( p \)-xylene isomerization.

A combination of stirred pressure vessel experiments, spectroscopic investigations, and thermogravimetric analysis has been used to elucidate the reason for \( p \)-xylene isomerization inhibition during production by the cycloaddition/dehydration of DMF and ethylene. Inhibition of \( p \)-xylene isomerization over H-Y and H-BEA zeolites is shown to result from adsorption of DMF (or the DMF hydrolysis product 2,5-hexanedione) on Brønsted acid sites. Inhibition will occur at DMF concentrations as low as \( 1/50^{th} \) that of \( p \)-xylene. It was also shown that 2,5-hexanedione will cyclize to DMF at reaction conditions relevant to \( p \)-xylene production and, consequently, isomerization will be inhibited. In addition water has no effect on \( p \)-xylene isomerization, while ethylene promotes the formation of heavy alkylated aromatics while still allowing isomerization of \( p \)-xylene.

Use of \(^{27}\)Al-NMR and isopropanolamine TGA has revealed that Bronsted acid sites exist in H-Y and H-BEA zeolites throughout the course of the reaction. In addition, preferential binding of DMF over \( p \)-xylene to the strong acid sites in the super and sodalite cages of H-Y under reaction temperatures has been shown through the use of DRIFTS. Finally, a greater amount of DMF bound to H-Y and H-BEA zeolite acid sites than \( p \)-xylene was revealed through TGA.

Finally, a mechanism by which adsorbed DMF could transfer a proton and effectively catalyze dehydration reactions has been proposed. It should be noted that this
is only one possible pathway and that, by the proton affinity argument presented earlier, the side product 2,5-hexanedione could also be binding to the acid site and preventing isomerization, in addition to acting as a proton transfer medium to the cycloadduct.
CHAPTER 8

FUTURE CHALLENGES TO THE PRODUCTION OF SUSTAINABLE AROMATICS FROM BIORENEWABLE FURANS

8.1. Lessons Learned from the Production of p-Xylene from DMF and Ethylene

The production of renewable aromatic chemicals from biomass shows increased potential, especially since the advent of shale gas can effectively replace many of the smaller molecular weight commodity chemicals which lack aromatic structure. The novel research presented in this thesis on the production of p-xylene form potentially biomass derived 2,5-dimethylfuran and ethylene is one just one example of biorenewable chemical production. During the study of p-xylene production from DMF many lessons have been learned that could be applied to the formation of similar chemicals. These lessons ranged from the minimization of side reactions, to strategies for maximizing the reaction rate with minimum catalyst, and even to the creation of a novel type of modified type of Brønsted acid site that can promote dehydration chemistries but inhibit xylene isomerization.

The greatest knowledge gained from this research is arguably the greater understanding of side reactions and how they can be minimized. Polymerization side reactions to form dimers and trimers played a major role in reducing product selectivity when using pure DMF. Utilization of n-heptane solvent greatly reduced these side reactions and experiments investigating DMF reaction order showed that the lower the initial DMF concentration the greater the p-xylene selectivity. These polymerization reactions became even more important when methylfuran and furan were used as reactants as discussed in Chapter 4. The unprotected α-carbon on these two reactants
leads to a greater number of polymerized side products; and in the case of furan it was even shown that the Diels-Alder cycloaddition was not the favored pathway.\textsuperscript{102}

Reaction rate could be maximized by increasing temperature, which also served to increase xylene selectivity, as well as by increasing the concentration of ethylene in solution. The existence of two regimes also indicates that an optimal loading of catalyst would put one just into the cycloaddition limited regime without using excess catalyst that could serve to produce coke in long term continuous experiments.

While the elucidation of side reactions allowed for the greatest increase in xylene selectivity the most novel aspect of this work is the discovery of a partially poisoned zeolitic acid site that is capable of promoting dehydration chemistry but inhibit xylene isomerization. The preferential adsorption of DMF over p-xylene to the Brønsted acid site present in the zeolite discussed in Chapter 7 provides a potential way to modify zeolite acidity in complex reaction systems. The computational support for a proton transfer pathway from the zeolite to the DMF $\alpha$-carbon, followed by transfer to the $\beta$-carbon, with a final proton shift to the homogeneously formed cycloadduct represents one potential reaction sequence. It should be noted that a similar reaction sequence could exist from the hexanedione side product to the cycloadduct that we have yet to observe through infrared experiments. Regardless of how the pathway occurs the result is the same: dehydration is promoted while isomerization is inhibited. One potential benefit of this discovery can be seen in the selective dehydration of cyclohexanol by a zeolite with adsorbed DMF as shown in Figure 7.8.

In summary, the reduction of polymerization side reactions with an aliphatic solvent, optimization of reaction rate with increased temperature and ethylene pressure,
and the modification of zeolite acidity by preferential adsorption of reactant DMF are all lessons that should be carried over to the study of other systems producing renewable aromatics from biomass derived furans.

8.2. New Pathways to Renewable Chemicals and their Potential Pitfalls

Chapter 4 of this thesis briefly touched on the conversion of ethylene and methylfuran/furan to toluene/benzene at yields of 46 and 35% respectively. The pitfall of these reactants has been discussed in the previous section with regards to the unprotected α-carbon. Figure 8.1 below serves to illustrate how the production of the aromatics covered in this thesis is just the tip of the iceberg in terms of what could be manufactured using cascade reactions of Diels-Alder cycloaddition followed by dehydration.

Figure 8.1 There is an almost infinite variety of aromatics with the potential to be produced from biomass derived furans.

It should be noted that in the Figure 8.1 that many of the new reaction utilized a dienophile other than ethylene. This could be one of the most beneficial aspects to these
alternative pathways given that ethylene is a poor dienophile leading to more difficult Diels-Alder chemistry and faster retro-DA reactions. In fact, the pathway to product phthalic anhydride has been done with yields of 80%.\textsuperscript{103}

Another aspect of this reaction system that could be improved is the catalyst activity with respect to the Diels-Alder reaction. Currently, there seems to be no confinement catalysis of the DA reaction in the zeolite pores like other Diels-Alder chemistries,\textsuperscript{38,49} otherwise we would theoretically see a difference in reaction rate between the various zeolites). Additionally, the Brønsted acid catalyst does not serve to catalyze the DA reaction; however a Lewis acid catalyst could reduce the energy barrier of cycloaddition.\textsuperscript{65}

In summary, the production of renewable aromatics from biomass derived furans could benefit from the addition of Lewis acid sites to the catalytic system to reduce the energy barrier of the DA cycloaddition. Careful selection of the furanic diene will also be essential as those with unprotected \(\alpha\)-carbons have a much greater tendency to polymerize than those that are protected with unreactive methyl groups. The third and final point involves selection of the dienophile. It could be possible to add functionality with a dienophile like acetaldehyde as proposed in Figure 8.1 or acrolein as done in other work.\textsuperscript{34} These new dienophiles would benefit the most if they are able to stabilize the cycloadduct and lower the energy barrier for cycloaddition.
APPENDIX: SEM IMAGES OF CONSIDERED CATALYSTS

The morphologies of the samples were investigated on Magellan 400 (FEI). The samples were spread on conductive carbon tape and coated by platinum. Nitrogen sorption isotherms of siliceous beta and silicalite-1 were collected on Autosorb iQ (Quantachrome) automated gas sorption system. The samples were degassed at 200°C. The surface area was calculated by using BET method with relative pressure ranging from 0.05 to 0.3. The phases of lab-made siliceous zeolites were confirmed by using X’Pert PRO diffractometer (PANalytical) with Cu Kα radiation. The diffraction patterns were collected at an operating voltage of 45 KV and a current of 40 mA in the range of 2θ=4°-40°.
Figure S1. Representative SEM micrographs of interested commercial catalysts (a) CBV600; (b) CBV760; (c) CBV780; (d) CP814C; (e) CBV3024E; (f) H-silica-alumina. Note that the scale bar is different for CP814C.
**Figure S2.** Representative SEM micrographs of interested siliceous zeolites (a) silicalite-1 and (b) siliceous beta.

The SEM image above illustrates the varied particle size for the investigation of diffusion limitation within the HBEA catalyst.
BIBLIOGRAPHY


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