CATALYTIC TRANSFORMATIONS OF BIOMASS WITH BRØNSTED AND LEWIS ACID ZEOLITES TO VALUE-ADDED PRODUCTS

by

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ABSTRACT

In this work, Lewis and Brønsted acid zeolites have been applied to transformations of biomass for the synthesis of fuels and chemicals. In the first half of this work, Lewis acid Beta zeolites (Sn-, Zr- and Ti-Beta) were screened for their activity in sugar isomerizations, Meerwein-Ponndorf-Verley (MPV) reduction and etherification. Activity trends of these catalysts varied depending on the chemistry. For isomerization, Sn>Zr~Ti. For MPV reduction, Zr>Sn>Ti. Finally, for etherification, Sn>Zr>Ti. These materials were then studied more in-depth for the MPV reduction of furfural. Hf-Beta, not screened previously, was found to have much higher reaction rates than the other catalysts tested (Zr- and Sn-Beta), despite similar apparent activation energies for the reaction on all three catalysts.

In the next half of this work, a process was developed to make *p*-ethyltoluene, a precursor to *p*-methylstyrene, from bio-derived methylfuran. This process involves three steps. First, acylation of methylfuran with acetic anhydride on Brønsted acid zeolite H-[A1]-Beta to form 2-acetyl-5-ethylfuran (2A5EF). Next, hydrodeoxygenation of 2A5EF with hydrogen on copper chromite to form 2-ethyl-5-methylfuran (2E5MF). Finally, Diels-Alder cycloaddition and dehydration of 2E5MF with ethylene on H-[A1]-Beta to form *p*-ethyltoluene. Overall, this process yields *p*-ethyltoluene in 53.5% yield at excellent isomer selectivity of 99.5% *para*. This methodology was then extended to make *p*-diethylbenzene at 99% *para* selectivity from furan. The first step of this process was studied in more detail on Brønsted and Lewis acid zeolites as it is a Friedel-Crafts acylation that is known to be catalyzed by both types of acids. Brønsted acid aluminum zeolites were found to be more effective than Lewis acid zeolites for the acylation of methylfuran and lower aluminum content was found to result in higher turnover per acid site. Lower apparent energies were found on Lewis acidic Sn catalysts, despite higher rates on the Al catalysts. Kinetic isotope effect experiments indicate a similar mechanism on Brønsted and Lewis zeolites with deprotonation as the rate determining step. In flow experiments, gamma-valerolactone solvent was found to significantly increase the reaction rate.

In summary, several catalytic transformations of biomass have been studied on Brønsted and Lewis acid zeolites in batch and continuous flow reactors for the production of fuels and chemicals. Some of these reactions are exceptionally selective, which was exploited to demonstrate the ability to make *p*-methylstyrene from renewable methylfuran. The activity trends established in this work can be used to choose the best catalyst or sequence of catalysts for transforming renewable biomass feedstocks into valuable products.

Chapter 1

INTRODUCTION

1.1 Fuels and Chemicals from Biomass

The synthesis of fuels and chemicals from renewable feedstocks has been an objective of research in the scientific community for many years. At one point, this work was motivated by increasing oil prices and the notion of peak oil; however, breakthroughs in the oil industry such as shale gas and tight oil have negated these issues. Thus, more recently, concerns about climate change and consumer awareness and demand for "green" products have motivated the replacement of petroleum with renewable feedstocks.^[1] Additionally, shale gas has greatly increased the supply of ethane for ethylene production, which affects the supply of byproducts like aromatics that will not be produced if ethylene is made from cracking ethane instead of naphtha.^[2] Lignocellulosic biomass is non-edible and abundant, making it a very attractive renewable feedstock.^[3] Furfural production from hemicellulose is a mature technology wherein waste feedstocks such as oat hulls, corncobs and sugarcane bagasse is converted to furfural at ~50% yield via acid hydrolysis and dehydration.^[4] The furfural market has continued to increase in recent years due to demand for furfuryl alcohol in metal casting.^[5] Furfural and furfuryl alcohol are the subjects of study in the second and third chapters of this thesis. Furfural can be deoxygenated to methylfuran or decarbonylated to furan, feedstocks that are studied in Chapters 4 and 5. While tetrahydrofuran, a common reaction solvent, can be made from 1,4butanediol, there is no competing petrochemical route for the synthesis of furfural from petroleum.

Hemicellulose is comprised of five carbon sugars, while cellulose is made of six carbon sugars. Hydrolysis of cellulose yields glucose that can be isomerized to fructose then dehydrated to hydroxymethylfurfural (HMF). HMF has been proposed as a versatile platform chemical, and the many value-added chemicals that can be made from HMF have been reviewed.^[6, 7] Examples include oxidation of HMF to 2,5-furandicarboxylic acid (FDCA), a potential replacement for terephthalic acid, and ring-opening and hydrogenation of FDCA to make adipic acid, a monomer used in nylon.^[8] Glucose isomerization is studied in Chapter 2.

Just as in industry, where 90% of all chemical processes employ a catalyst, most of these biomass transformations are catalytic. The hydrolysis of cellulose or hemicellulose to glucose or furfural is acid-catalyzed, usually with a homogeneous acid like sulfuric acid,^[6] although the application of solid catalysts to this reaction is currently being explored.^[9] In practice, solid catalysts are always desired due to their ease of separation from the reactants and products. Thus, many studies, including this work, focus on functionalization or de-functionalization of renewable furanics like HMF or furfural to desired products with solid catalysts. In this thesis, solid acid zeolite catalysts, of both Brønsted and Lewis acid character, have been applied as catalysts to reactions with furanics to produce desired fuel and chemical precursors. The remarkable variety in forms and applications of these zeolite materials is summarized in the next section.

1.2 Zeolites

1.2.1 Brønsted Acid Zeolites

Solid microporous aluminosilicates, or zeolites, have found many applications in commercial catalysis, most prominently in the oil and gas industry for refining crude oil. Their variety can be appreciated by the 232 unique framework types recognized by the International Zeolite Association (IZA).^[10] Each framework is formed from different arrangements of tetrahedral silicon and aluminum atoms. This results in a specific number of unique tetrahedral or "T-sites" that silicon or aluminum occupies. The charge imbalance between trivalent aluminum and tetravalent silicon requires a cation for charge balance which is usually in the form of a proton that corresponds to a Brønsted acid site. These materials have enjoyed much success in the catalysis field due to their ease of separation compared to homogeneous acid catalysts, shape selectivity induced by their microporosity, high thermal stability, and regenerability. Another advantage of these materials is their tunability. Variables affecting activity and selectivity that may be altered include framework type, morphology, Al concentration, and the charge-balancing cation. Effects from framework type originate from restrictions from pore size on what reactants can enter the pore, what reactants can leave the pore and what transition states can form within the pore.^[11] Morphology can also have an affect selectivity, for example, increased product selectivity in larger crystals due to longer diffusion times. Higher selectivity to para-xylene in toluene alkylation and lower selectivity to durene is found on H-ZSM-5 zeolites with larger crystal sizes.^[11] Conversely, morphology that improves diffusion can improve activity and reduce deactivation. For example, mesoporosity introduced by a nanosheet morphology of MFI has been shown to increase activity for reactions

with bulk reactants and decrease increase catalyst lifetime for methanol-to-gasoline compared to conventional MFI.^[12] Aluminum concentration is directly associated with the number of acid sites, but there are instances in which activity has been found to increase with increasing Si/Al. For example, hexane isomerization was found to be maximized at a Si/Al where the Al was isolated without any nearest neighbors.^[13] Finally, the charge-balancing cation can be a proton or it can be a monovalent metal such as sodium or lithium or a divalent metal like zinc. These metal cations can induce Lewis acidity, which will be discussed in the next section.

Another variable is the identity of the trivalent heteroatom in the framework, as other trivalent metals have been incorporated into some frameworks and result in different Brønsted acid site strength compared to aluminum. For example, Fe has been incorporated in the MFI framework for direct hydroxylation reactions,^[14] and Ga substituted into MFI has been used for ethane and propane aromatization.^[15] In some applications, the acidic zeolite is impregnated with metal to create a bifunctional material, usually a noble metal with a hydrogenation function, such as Pt-doped zeolites for hydroisomerization.^[16]

Another option is to substitute higher valency metals into the framework. Silico-alumino-phosphate (SAPO) materials have both trivalent aluminum and pentavalent phosphorous in the framework, reducing the amount of proton (or other cation) needed to charge balance the aluminum. This material has been applied to applications such as methanol-to-olefins on SAPO-34.^[17] Finally, when tetravalent metals are substituted into the framework, there is no cation needed for charge balance and Lewis acidity is induced at the substituted metal site, as detailed in the next section.

1.2.2 Lewis Acid Zeolites

One of the first examples of a Lewis acid zeolite was titanosilicalite (TS-1), a siliceous MFI framework containing Ti atoms, which exhibited superior activity for epoxidation and is used commercially to make propylene oxide from propene and hydrogen peroxide.^[18] Another well-known example of a Lewis acid zeolite is zeolite Beta containing framework Sn (Sn-Beta), which was initially applied to Baeyer-Villiger (BV) oxidations and Meerwein-Ponndorf-Verley (MPV) reductions,^[19, 20] and then later to glucose isomerization.^[21] Beta with Zr in the framework (Zr-Beta) showed slightly less activity than Sn-Beta for BV and MPV reactions with cyclohexanone, while Beta with Ti in the framework (Ti-Beta) showed no activity for these reactions, highlighting the importance that the substituted heteroatom plays in the chemistry.^[22] Additionally, Zr-Beta was found to be more active than Sn-Beta for the MPV reduction of benzaldehyde, highlighting the importance of the Lewis base as well.^[22] Later, when Hf-Beta was also synthesized, it was found to be even more productive than Zr- or Sn-Beta for MPV reduction of methyl levulinate.^[23] These metals have been substituted into other frameworks like MFI and into mesoporous MCM-41,^[21, 24, 25] but Lewis acid zeolites with the Beta framework are the focus of this thesis. In addition to Lewis acidity from framework metals, metal cations, for example Zn^{2+} , can be exchanged with Al zeolites to create Lewis acid sites at the cation. This is a comparatively easier synthesis than making framework Lewis acidic zeolites, but results in a mixture of both Lewis acidity from the metal cation and residual Brønsted acidity from unexchanged framework Al sites.^[26]

1.2.3 Zeolite Beta

Most of the work in this thesis uses zeolites with a Beta framework, so the important properties of this framework will be discussed briefly here. First, it should be noted that Beta is one of the few structures that is partially disordered. Rather than one distinct crystal phase, it is an intergrowth of two phases (Polymorph A and B). This disordered character is denoted by the asterisk before its framework code (*BEA) by the IZA. The channels in Beta are 3-dimensional and comprised of 12 membered rings, resulting in an average pore size of ~6Å.^[27] Beta has 9 unique T-sites that may be occupied by silicon or a heteroatom.

1.2.4 Zeolite Characterization

Some characterization techniques are used regardless of zeolite acidity (Brønsted, Lewis or non-acidic siliceous). X-ray diffraction (XRD) patterns are used on any type of zeolite to determine crystallinity and framework type. As detailed above, Beta is not a single crystal phase, so XRD can be used to determine the relative abundance of each polymorph. Nitrogen physisorption is used to determine micropore volume. This is often used as another confirmation of zeolite structure as each framework has a typical expected range for volume. For example, Beta materials typically measure ~0.2 cc/g. Solid state ²⁹Si nuclear magnetic resonance (NMR) can be used to study silicon framework defects, and a heteroatom in the framework can also be studied if it is NMR active. Elemental analysis to determine framework metal and cation content can be accomplished via a variety of techniques such as X-ray fluorescence (XRF), energy-dispersive X-ray spectroscopy (EDX), and inductively coupled plasma atomic emission spectroscopy (ICP-AES), the latter of which is the

most sensitive. Scanning electron microscopy (SEM) is used to image the zeolite crystals and determine average crystal size and morphology.

1.2.4.1 Brønsted Acid Zeolites

A variety of zeolite frameworks are available commercially in the Brønsted acid form with aluminum. In addition to Brønsted acidity from Al in the framework, extraframework Al can instill some Lewis acid character to the material as well. The quantity of each of these sites can be probed with pyridine IR. ²⁷Al magic-angle spinning (MAS) NMR is also used to probe Brønsted framework sites, Lewis extraframework sites as well as extraframework alumina that is octahedral rather than tetrahedral.^[28] Computational and experimental work is being conducted to identify the T-sites that aluminum occupies to better understand and model these materials. For example, it has been found that aluminum in T1 and T2 tend to resist dealumination in zeolite Beta.^[29] Recently, extended X-ray adsorption fine structure (EXAFS) was used to examine Al siting in Beta and found very different populations of T-sites in high and low Al concentration samples.^[30] In the EXAFS study, they also found disagreement between experimental results and the thermodynamically most stable Tsites as determined by calculations. This indicates kinetic control of siting during zeolite synthesis and shows the limitations of modeling to determine these sites, making this on-going task even more difficult.

1.2.4.2 Lewis Acid Zeolites

While these materials have been a subject of academic and industrial interest for more than 10 years, their characterization is still rather limited. Part of this is a result of the inconsistency of the synthesis of these materials. For example, recent

work has demonstrated how inconsistent Sn-Beta samples can be, even ones synthesized within the same lab group.^[31] This underscores how important characterization is for these materials, which unfortunately remains very unstandardized compared to the techniques employed for Brønsted acid zeolites. The first limitation for the characterization of these materials is their limited heteroatom incorporation which can make some quantitative analysis challenging due to signal-tonoise ratios. Even techniques like XRF can be unreliable at low incorporation, requiring more expensive techniques like ICP-AES. In this work, for example, it was found that at low incorporation the Si/Metal ratios determined by XRF were often over- or underestimated compared to more reliable ratios determined by ICP-AES.

UV-Vis was commonly applied to detect amorphous metal oxide phases, but this method is not always accurate. For Sn-Beta, for example, adsorption between 200-220 nm corresponds to tetrahedral framework Sn, but adsorption at 240 nm and higher can be either SnO₂ or a hydrated framework Sn atom.^[31] A detection limit of 0.08 wt% was determined for a physical mixture of SnO₂ and zeolite Beta.^[32] Oxide not detected by XRD or UV-Vis may be detected by ¹¹⁹Sn-NMR, in the case of Sn-Beta, or more generally with EXAFS or SEM.^[31, 33-36]

Another issue is that multiple analytical techniques suggest that the already low concentration of heteroatom in the framework is actually comprised of two different types of sites: "open" and "closed". In 2005, Boronat, et al. hypothesized the existence of two different Sn-Beta sites, leading to different frequencies observed in IR of deuterated acetonitrile. The first site was proposed to be a closed site with four bonds to the framework interacting with acetonitrile-d₃ at 2308 cm⁻¹ and and the second site was referred to as an "open" site wherein one bond has been hydrolyzed,

resulting in a stannanol at the Sn atom and a corresponding silanol at the framework. This site was ascribed to the signal observed at 2316 cm⁻¹ and thought to be the stronger Lewis acid site given its interaction with acetonitrile-d₃ at higher temperatures. Boronat then attributed the Baeyer-Villiger oxidation of adamantone to the Sn-Beta open site, as the activity of the catalyst correlated linearly to the intensity of the 2316 cm⁻¹ band.^[37] Later, this same relationship was determined for the MPV reduction of cyclohexanone with 2-butanol on Sn-Beta, and the same dual site was proposed for Zr-Beta.^[38] Recently, molar extinction coefficients were determined for pyridine and acetonitrile-d₃ on Sn-Beta, allowing for quantification of open and closed sites for the first time.^[39] These measurements are not trivial, however, and in work by other groups, the IR peak could not be deconvoluted into two distinct peaks for an open and closed site for Sn-Beta.^[40] A similar interaction with acetonitrile-d₃ was observed for Zr- and Hf-Beta, but unique peaks for open and closed sites could not be distinguished.^[41] One study identified CO adsorption as a technique to distinguish open and closed sites on Zr-Beta and further proposed that acetonitrile-d₃ only interacts with open Zr-Beta sites.^[42] It should be noted that it has been proposed that Ti-Beta synthesized with HF does not form an open site.^[43] In general, quantification of active sites on these materials remains a challenge.

In the case of Sn-Beta, it has been proposed that distinct resonances may be observed for open and closed sites via ¹¹⁹Sn MAS NMR.^[36] This technique is also able to detect changes in the hydration of the site, which has also been demonstrated to play a role on the local environment of the metal atom. ¹¹⁹Sn NMR shows a change in geometry from octahedral to tetrahedral when samples are dehydrated.^[36, 44] These materials rapidly uptake water at ambient lab conditions and even if they are

pretreated to dehydrate the active sites, the site may be re-hydrated by reaction solvents, which are often not water-free. Harris, et al. has suggested that at least the initial activity of Sn-Beta materials is correlated to open site population as determined by acetonitrile-d₃ IR. This work acknowledges, however, that at longer time on stream the environment could be changed, possibly by the hydration phenomena just described. Thus, while great strides have been made in characterizing these materials *ex situ*, understanding the active site under reaction conditions is an even greater challenge.

EXAFS studies on these materials have been extremely limited and may even be limited in their practical application given the heterogeneity of the open and closed sites and that EXAFS is a bulk technique. An EXAFS study by Bare, et al. in 2005 considered a closed site and concluded that the Sn substitutes on opposite sides of the six-membered ring in the framework.^[33] However, now that it is accepted that an open site also exists, it is difficult to know how to interpret this model. More recently Dijkmans, et al. took EXAFS of Sn-Beta made hydrothermally and post-synthetically but again only considered one site, in this case the open one.^[45] EXAFS has also been performed for Ti-Beta, which might be more reliable given the lack of framework hydrolysis to create open sites in this material.^[43]

The lack of knowledge on the populations of these open and closed sites makes it difficult to compare these materials. Throughout this work, the total metal content was used as a best approximation of active site concentration. While this may lead to some false conclusions in trends relating to turnover frequency, in many cases one catalyst is significantly more active than the others even on a per gram basis.

Examples of this include the superior activity of Sn-Beta for sugar isomerization in Chapter 2 and superior activity of Hf-Beta for the reduction of furfural in Chapter 3.

Computational work on these materials has mainly concerned glucose isomerization and MPV reduction.^[22, 38, 46-49] In one computational study for MPV reduction of cyclohexanone with 2-butanol, only the open site was modeled which predicted a lower activation energy on Zr-Beta compared to Sn-Beta. Since greater turnover was found experimentally on Sn-Beta, it was supposed that there was a lower concentration of open sites on Zr.^[38] This study also highlighted an important difference between Sn and Zr. The LUMO for Sn-Beta is its antibonding orbitals for Sn-O, so when it accepts electron density, it is essentially pushing electrons to the neighboring O atoms and making them more basic. The LUMO for Zr, however, is a d orbital of the Zr atom so it can accept electron density directly, without making the neighboring oxygens basic.^[38] Recent modeling on Sn-Beta revealed that the silanol at the Sn open site was more Brønsted acidic than silanol defects, and suggested that coordination with this group rather than the Sn itself may be important.^[50] It is uncertain how Brønsted acidic this site could be, however, given that Sn-Beta does not show signals in pyridine IR that are typically associated with Brønsted acidity.^[39] These computations in parallel with further development of analytical characterization techniques will help to better characterize and quantify active sites in these materials.

1.3 Catalytic transformations of biomass with zeolites

Zeolites have been applied recently to several biomass transformations. Lewis acid zeolites in particular have found several applications relating to biomass transformations as they are able to activate the oxygen groups (ketones, alcohols) prevalent among them, and tend to be more resistive to undesirable oligomerization

reactions compared to Brønsted acid zeolites.^[1] Glucose isomerization is an example of a reaction with renewable sugar feedstocks where Lewis acid zeolites, particularly Sn-Beta, has been found to be very useful. This isomerization is done commercially with enzyme catalysis; however, the use of the solid material is more flexible in terms of separation and operating conditions and exhibits selectivity that is similar to the enzyme.^[21] As described earlier, fructose may be dehydrated to HMF, but Lewis acid zeolites can also catalyze a retro-aldol reaction to make glyceraldehyde from fructose. In fact, it has been shown that methyl lactate can be produced in a one-pot reaction from fructose on Lewis acid Beta zeolites in up 45% yield.^[51] Methyl lactate can then be dehydrated to acrylic acid over sodium exchanged Brønsted acid zeolite Y for a renewable route to acrylic acid.^[52] Brønsted acid zeolites, particularly H-[Al]-Beta, were found to be very selective in the Diels-Alder cycloaddition and dehydration of bio-derived dimethylfuran and ethylene to make para-xylene.^[53] Lewis acid zeolites were found to be more effective than Brønsted acid zeolites for the Diels-Alder cycloaddition of ethylene and oxidized derivatives of HMF for the production of renewable terephthalic acid.^[54, 55] Reduction and etherification of HMF on Lewis acids has been studied in both batch and flow conditions for the synthesis of potential fuel additives.^[56, 57] Thus, these zeolite materials have great potential to be applied in the sustainable and renewable production of commodity chemicals.

1.4 Scope of this thesis

The work in this thesis concerns catalytic reactions of renewable biomass feedstocks to make fuels and chemicals using zeolite catalysts. In Chapter 2 and 3 solely Lewis acid zeolites are studied and in Chapter 4 and 5 both Brønsted and Lewis acid zeolites are studied and compared.

Chapter 2 discusses results of batch reactions with Lewis acid zeolites for three chemistries involved in the transformation of sugars to furanic ethers. First, the isomerization of glucose to fructose and xylose to xylulose. Second, the MPV reduction of furfural (a derivative of xylose/xylulose) to furfuryl alcohol. And finally, the etherification of furfuryl alcohol and isopropanol. Each of these reactions was studied on Sn-, Zr- and Ti-Beta.

In Chapter 3, the MPV reduction of furfural to furfuryl alcohol was studied in a continuous flow reactor to determine apparent activation energies under differential conditions on Sn-, Zr- and Hf-Beta. The reaction rate decreased with time on stream for all three catalysts. The origin and mitigation of this decrease in rate was investigated.

In Chapter 4, a three-step process is described that was developed to produce *para*-ethyltoluene (for the production of *para*-methylstyrene) from methylfuran. The first step was Friedel-Crafts acylation of methylfuran with acetic anhydride over H-[Al]-Beta. Next, the acetyl group just added was reduced with hydrogen over copper chromite to make 2-ethyl-5-methylfuran. Finally, this furan was combined with ethylene in a Diels-Alder cycloaddition and dehydration with H-[Al]-Beta to make the *para* aromatic. This chemistry was also extended to a process for the production of *para*-diethylbenzene from furan.

In Chapter 5, Brønsted and Lewis acid Beta zeolites are compared for the first step in the process developed in Chapter 4: Friedel-Crafts acylation of methylfuran with acetic anhydride. Several Brønsted and Lewis acid materials were screened in a batch reactor and then the best Brønsted and Lewis acids were also studied under continuous flow conditions. Again these catalysts exhibited a decrease in rate with

time on stream that was investigated. The mechanism of the acylation was probed with kinetic isotope effect experiments.

In Chapter 6, the results of each of the previous chapters are summarized and recommendations for future work are provided for each of these projects as well as for the application of Brønsted and Lewis acid zeolites to other biomass transformations.

Chapter 2

LEWIS ACID ZEOLITES FOR TRANSFORMATIONS OF BIOMASS-DERIVED MOLECULES

2.1 Introduction

The replacement of conventional petroleum derived fuels and chemicals with renewable raw materials will help reduce the detrimental effects of CO₂ emissions and dependence on foreign oil. Renewable feedstocks derived from lignocellulosic biomass are of particular interest as they are generally inedible, and do not cut into food supply, unlike corn feedstock currently used for bio-ethanol production in the United States.^[3] Microporous silicates (zeolites) with Lewis acid sites are effective catalysts for several reactions useful in the transformation of renewable cellulosic compounds (glucose and xylose) to platform chemicals (such as 5-hydroxymethylfurfural (HMF) and furfural), and to potential diesel replacements (furanic ethers).^[3, 58, 59] Lewis acidity may be introduced to the zeolite when silicon is isomorphously substituted with a metal of the same oxidation state as silicon. Potential metals for such substitution include titanium, zirconium, hafnium, and tin. The substituted metal sites in the framework act as Lewis acids that accept Lewis base electron pairs from organic molecules adsorbed in the zeolite pores.

Isomorphous substitution of zeolite Beta has been achieved with several tetravalent metals.^[43, 57, 60, 61] In contrast to typical metal chloride or alkoxide Lewis acid catalysts, which are homogeneous and generally sensitive to water, these solid Lewis acids provide the advantages of heterogeneous catalysis and are water-

tolerant.^[62] Zeolite Beta with framework tin (Sn-Beta) has been found to be highly effective in the isomerization of sugars in water.^[21, 63] Zirconium-Beta (Zr-Beta) has shown superior performance to Sn-Beta in some reactions, including several Meerwein-Ponndorf-Verley (MPV) reductions.^[22, 64, 65] Titanium-substituted zeolite Beta (Ti-Beta) is comparatively easier to prepare than Sn-Beta or Zr-Beta, and since Ti(IV) is closer to Si(IV) in size, higher metal incorporation has been achieved for Ti compared to the other metals.^[43] These Ti materials are excellent catalysts for epoxidation of alkenes with hydrogen peroxide.^[66]

Each of these catalysts demonstrates Lewis acidic properties, but Lewis acid strength is a rather difficult property to define as it presents differently in different reactions.^[67] Boronat et al. investigated Sn-, Zr- and Ti-Beta for several reactions including Baeyer-Villiger (BV) oxidations, MPV reductions, and epoxidation of octene.^[22] The activity trends for the two former reactions were correlated to the increase in positive charge (polarization) of the carbon of the reactant carbonyl after adsorption to the metal site, as determined from computational modeling. Depending on the reactant, this increase was sometimes larger for Sn-Beta and sometimes larger for Zr-Beta. However, this correlation breaks down for epoxidation, where only Ti-Beta was found to be active. For this reaction, activity was instead correlated to differences in the lowest LUMO energy and was therefore described as the strongest Lewis acid based on this parameter.^[22]

The specific reactions of bio-derived compounds for which an array of Lewis acid zeolite Beta catalysts were tested are shown in Figure 2.1. First was the isomerization of glucose to fructose. Cellulose is comprised of D-glucose units, but
the isomer of this molecule, fructose, is more easily dehydrated to HMF, a platform chemical from which many fuel additives and chemicals may be prepared.^[3, 68] HMF can be obtained in 70% yield from fructose.^[69] Hemicellulose is comprised of five-carbon sugars and can be used to produce furfural, another platform chemical.^[63] This process typically uses agricultural waste feedstocks such as corn cobs, oat hulls and bagasse. The yield of furfural is not as high (~50%) but it is an industrial process and the production capacity is increasing in places like China where there is demand for furfuryl alcohol in the metal casting industry.^[4] Alternatively, xylose derived from hemicellulose could undergo an analogous pathway as glucose where xylose is isomerized to xylulose and then dehydrated to furfural. This pathway may lead to higher yields of furfural compared to the industrial process, and thus xylose isomerization is a reaction investigated in this chapter. Lewis acid catalyzed sugar isomerization occurs via an intramolecular hydride transfer from C2 to C1.^[21, 63]

The Lewis acid materials discussed here are also active for MPV reduction via *intermolecular* hydride transfer from a donor alcohol This chemistry was probed with the reduction of furfural using isopropanol to make furfuryl alcohol, shown in Figure 2.1.

Finally, these Lewis acid zeolites have been found to catalyze the etherification of alcohols,^[56, 57] so the etherification of furfuryl alcohol and isopropanol was also studied (Figure 2.1). The product of this is a furanic ether that may be blended with, or serve as a replacement for, diesel fuel.^[59]



Figure 2.1: Lewis acid catalyzed reactions of biomass-derived compounds

2.2 Experimental

2.2.1 Materials

Synthesis of Sn-, Zr-, and Ti-substituted Beta zeolites was carried out in aqueous solution containing tetraethylorthosilicate (Sigma-Aldrich, 98%) as a silica source, tetraethylammonium hydroxide (TEAOH) (Alfa Aesar, 35%) as a structuredirecting agent (SDA), and a metal source. Metal sources were SnCl₄·5H₂O (Sigma-Aldrich, 98%), ZrO₂Cl·8H₂O (Sigma-Aldrich, 98%) and titanium isopropoxide (Sigma-Aldrich, 97%), respectively. The solution was transferred to a 23mLTeflon liner (A280AC, Parr), and then hydrofluoric acid (HF) (Acros, 48%) was added and mixed manually with a spatula until a stiff gel was obtained. In the case of Sn- and Zr-Beta, siliceous zeolite Beta seeds were also added to gel. This siliceous Beta was synthesized according to the method described by Camblor, et al.^[70] Gels were placed in Teflon autoclaves held in stainless steel mantles and heated in an oven at 413 K. Sn-Beta was rotated at 50 rpm, while the other two zeolite gels were heated under static conditions. The gel composition molar ratios and heating time for each zeolite are reported in Table 2.1 (MO₂ represents the substituted-metal oxide content).

Zeolite	SiO ₂	ТЕАОН	HF	H ₂ O	MO ₂	Days in autoclave
Sn-Beta	1	0.56	0.56	7.5	0.008	11
Zr-Beta	1	0.56	0.56	7.5	0.01	20
Ti-Beta	1	0.54	0.53	6.6	0.021	20

Table 2.1: Zeolite synthesis gel molar ratios and heating times

After synthesis, samples were washed with deionized water, filtered and dried overnight at 353 K. Samples were calcined at 853 K in air for three hours to remove the organic SDA material. The structure and crystallinity of the various Beta samples was confirmed with X-Ray Diffraction (XRD) patterns obtained using a Phillips X'Pert X-ray diffractometer and a CuK α radiation source ($\lambda = 1.542$ Å). UV-Visible spectra of each sample were taken with a Jasco V-550 spectrophotometer with a diffuse-reflectance attachment.

2.2.2 Methods

Isomerization reactions were conducted in 10 mL glass vials loaded with reactant, catalyst and a magnetic stir bar, and sealed with crimp seal septum (Chemglass, CG-4920-10). The vials were then placed in a reactor block filled with oil on a stirring hot plate (Chemglass, CG-1991-04) for the desired reaction length and quenched by placing the vial on ice. 1.5 g solutions of 10 wt% glucose (Sigma, \geq 99.5%) or xylose (Sigma-Aldrich, \geq 99%) in water were combined with the appropriate amount of catalyst for a 1:50 molar ratio of metal to reactant. The metal content of the catalyst was assumed to be the same as that in the synthesis gel. The product was separated from the catalyst by filtration, and the liquid products were analyzed with high-pressure liquid chromatography (HPLC) on an Aminex HPX-87C column. Conversion and yield were defined as follows:

$$Conversion = \frac{C_{reactant,t=0} - C_{reactant}}{C_{reactant,t=0}} \times 100$$

$$Yield = \frac{C_{isomer}}{C_{reactant,t=0}} \times 100$$

Reduction and etherification reactions were performed in a 45mL Parr reactor (model 4714). 0.2 g of either furfural (Sigma-Aldrich, 99%) or furfuryl alcohol (Alfa Aesar, 98%) was combined with 20 mL of isopropyl alcohol (Fisher, 99.9%) and the appropriate amount of catalyst for a 1:200 molar ratio of metal to reactant. The reactor was purged three times with nitrogen and then pressurized with nitrogen to 200 psi. The reactor was held under stirring in an oil bath for the desired reaction time, then quenched in a room temperature water bath. Product was separated from the catalyst by filtration and the liquid product was analyzed with gas chromatography (Agilent 7890A) equipped with a flame ionization detector. An HP-Innowax column (Agilent) was used with the following method: hold at 313K for 4 min, 10K/min ramp to 523K and a final hold for 5 min.

2.3 Results and Discussion

2.3.1 Catalyst Characterization

XRD patterns for the Lewis acid zeolites are shown in Figure 2.2. The pattern of a commercial Al-Beta sample is shown for reference and the Lewis acid materials have spectra consistent with the Beta framework. The UV-Vis spectra of each Lewis acid zeolite and its corresponding metal oxide are shown in Figures 2.3-2.5. As the adsorption of the zeolites is distinct and at lower wavelengths than the oxides, it is

clear that the materials do not have a significant oxide content. However, as noted in the Chapter 1, the limited sensitivity of this method is makes it unreliable for small amount of impurities and other characterization techniques like EXFAS or SEM would be needed to know if these materials have trace amounts of amorphous oxide phase. It should be noted that the metal content was not confirmed with any elemental analysis techniques and was assumed to be the same as the amount included in the synthesis gel. In subsequent chapters, the final metal content of the catalyst was always confirmed with elemental analysis, either by inductively coupled plasma atomic emission spectroscopy (ICP-AES) or X-ray fluorescence (XRF). In all of the following experiments, the amount of catalyst included in the reaction was determined by the specified ratio of Lewis acid metal to reactant so turnover frequency normalized by the amount of metal would follow the same trend as conversion and yield data. The metal incorporation was based on the metal content of the synthesis gel, and since it is known that the final metal content can differ from that in the synthesis gel, there is some uncertainty in the comparisons between catalysts. There is additional uncertainty in accurate accounting of the number of active sites due to the existence of open and closed sites. So the metal content in the synthesis gel is an acceptable estimate of active sites for these screening reactions.



Figure 2.2: XRD patterns of Lewis acid zeolites



Figure 2.3: UV-Vis spectra of Sn-Beta and SnO₂



Figure 2.4: UV-Vis spectra of Zr-Beta and ZrO₂



Figure 2.5: UV-Vis spectra of Ti-Beta and TiO₂

2.3.2 Isomerization

Sugar isomerization was used to investigate the catalysts' properties for intramolecular hydride transfer. Table 2.2 shows reaction condition, glucose

conversion, and fructose yield for each catalyst for isomerization of glucose to fructose. Conversion of glucose and yield of fructose was highest on Sn-Beta and similar for Ti-Beta and Zr-Beta. This is consistent with previous results from Moliner et al.,^[21] who reported lower activity for glucose isomerization on Ti-Beta compared to Sn-Beta. In that study, 32% yield of fructose was reported at 55% glucose conversion after 30 minutes of reaction at 383 K on Sn-Beta; the same values were found for Sn-Beta in this work. For Ti-Beta, 26% conversion of glucose and 14% yield of fructose was reported by Moliner after 90 minutes of reaction on Ti-Beta at 383 K,^[21] but at the same conditions only 14% conversion and 6% yield was observed here, which may be caused by a lower incorporation of titanium in the sample synthesized in this work.

Catalyst	Temperature [K]	Time [minutes]	Glucose Conversion [%]	Fructose Yield [%]	Fructose Selectivity [%]
Sn-Beta	383	30	55	32	58
Sn-Beta	413	10	57	30	53
Ti-Beta	383	30	9	3	33
Ti-Beta	383	90	14	6	43
Ti-Beta	413	30	23	10	43
Zr-Beta	383	30	9	1	11
Zr-Beta	413	30	14	10	71

Table 2.2: Glucose isomerization with Lewis acid zeolites

The trend among catalysts was similar for xylose isomerization to xylulose, with xylose conversion and xylulose yield reported in Table 2.3. Sn-Beta was more effective leading to higher conversion and yield in a shorter reaction time than Ti-Beta and Zr-Beta at the same temperature. As with glucose isomerization, Ti- and Zr-Beta exhibited similar conversion and product yield for xylose isomerization. The results for Sn-Beta are consistent with results available in the literature, where a previous study for xylose isomerization on Sn-Beta reported approximately 22% yield of xylulose at 80% conversion on Sn-Beta at 383 K in 30 minutes, which is similar to 23% yield at 73% conversion found in this study at the same conditions.^[63] Glucose isomerization was more selective than xylose isomerization. Comparing results at 383 K, the selectivity to fructose was 58% and the selectivity to xylose only 32%.

Catalyst	Temperature	Time	Xylose	Xylulose Yield
Catalyst	[K]	[minutes]	Conversion [%]	[%]
Sn-Beta	383	30	73	23
Sn-Beta	413	30	90	23
Ti-Beta	383	60	9	4
Ti-Beta	413	30	22	14
Zr-Beta	383	30	8	3
Zr-Beta	413	30	20	17

Table 2.3: Xylose isomerization with Lewis acid zeolites

2.3.3 Meerwein-Ponndorf-Verley Reduction

The MPV reduction of furfural to furfuryl alcohol proceeds via a transfer hydrogenation from isopropanol to the accepting aldehyde group of furfural was used to test for catalytic activity for *intermolecular* hydride transfer. Furfuryl alcohol yields over each catalyst for reduction experiments at various temperatures are shown in Figure 2.6. Zr-Beta and Sn-Beta were both active for reduction, with significantly higher activity on Zr-Beta. Ti-Beta did not display catalytic activity for this reduction chemistry, even at temperatures as high as 368 K. Much lower activity for MPV reduction on Ti-Beta, compared to Zr-Beta and Sn-Beta, has also been reported for reduction of cyclohexanone and benzaldehyde,^[22] HMF,^[57] and methyl levulinate.^[23] While it was acknowledged in section 2.3.1 that the lack of reliable composition information of the samples could lead to uncertainty about the observed trends, this is not the case for this reaction as the same trend was also observed in the next chapter, where the chemical composition was well characterized for all samples.



Figure 2.6: Yield of furfural alcohol on Zr-Beta and Sn-Beta. Conditions: 0.2 g furfural in 20 mL of isopropanol, 200 psi, 1 hour

2.3.4 Etherification

The reaction of furfuryl alcohol with isopropanol to form 5isoproxymethylfuran, was tested to compare the catalysts properties for etherification. Here the activity is based on conversion of furfuryl alcohol, as a standard for the etherification product was not available. As shown in Figure 2.7, Sn-Beta was much more active for this reaction than Zr-Beta (92% conversion compared to 35% at 428 K), while Ti-Beta barely catalyzed the etherification (<0.1% conversion) up to 418 K. The etherification of Lewis acids has only been studied in cascade reactions of reduction and etherification so there are no studies to directly compare the etherification experiments done here, however high etherification activity for Sn-Beta was evident in a study for the reduction and etherification of HMF by Lewis et al.^[57] In that report, an etherification side product, in which the alcohol HMF undergoes etherification but the aldehyde remains intact, was only significant on Sn-Beta compared to Zr- and Ti-Beta, indicating the lower activity for reduction and higher activity for etherification that is observed here. Additionally, the major product observed on Ti-Beta was an acetal^[57] which is in agreement with the low activity of Ti-Beta for both reduction and etherification that is observed here.



Figure 2.7: Etherification of furfuryl alcohol and isopropanol on Zr-Beta and Sn-Beta. Conditions: 0.2g furfuryl alcohol in 20 mL isopropanol, 200 psi, 2 hours

2.4 Conclusions

The varying trends in conversion and reactivity for each of the reactions investigated in this chapter is at once interesting and confounding. Sn-Beta shows high activity in all reactions, while Ti-Beta shows relatively little or no activity in all reactions. Ti-Beta has the lowest LUMO energy and could be considered the strongest Lewis acid in this respect, but it is unclear why the strongest Lewis acid would be less productive (in the case of isomerization) or essentially inactive (in the case of reduction and etherification) than the other Lewis acid materials. On the other hand, compared to other substituted Beta materials, Ti-Beta was found to have the weakest interaction with pyridine as studied by ¹⁵N MAS NMR^[71], and could thus be considered the weakest Lewis acid in the series. In this work, Mulliken electronegativity was found to scale with the observed pyridine shift and may be a better descriptor of acidity.^[71] However, based on this parameter, the expected trend in activity based on Lewis acidity would be Sn>Zr>Ti and this trend clearly does not hold for all the reactions studied here. This highlights the difficulty in quantifying and characterizing Lewis acidity and thus the inability to predict the activity of these materials based on a single descriptor.

Another interesting finding is that Ti-Beta is catalytically active for intramolecular hydride transfer in isomerization but not intermolecular hydride transfer in MPV reduction. As Ti-Beta is considered to be four-coordinated to the framework (not forming an open site),^[43] in contrast to Sn- and Zr-, this difference might be explained by a favorable geometry of the open active site to coordinate not only to adjacent functional groups on the same molecule (as in isomerization) but also to activate a bimolecular mechanism (as in MPV reduction). Isotopic labeling experiments have established that Sn-Beta and Ti-Beta follow the same C1-C2 hydride

shift mechanism to make fructose, eliminating the possibility that Ti-Beta is active for this chemistry via a distinct mechanism.^[36, 72]

Zr-Beta is distinct as well due to its varying activity across the reactions; where is it more active than Sn only for MPV reduction. Previous work has shown higher turnover for MPV reduction of benzaldehyde and lower turnover for MPV reduction of cyclohexanone on Zr-Beta compared to Sn-Beta.^[22] Given this result and the higher turnover on Zr-Beta for furfural reduction here, it is tempting to suggest that Zr-Beta is more effective in the reduction of aldehydes, but since glucose isomerization involves the activation of an aldehyde and adjacent alcohol, so this generalization does not hold and the origin of higher activity on Zr-Beta remains unknown.

In summary, this chapter has shown that the prediction of Lewis acid activity is quite difficult and seems to depend on the Lewis base. It is clear that Ti-Beta is not an effective catalyst for MPV reduction or etherification. Sn-Beta is a superior catalyst for etherification and intramolecular hydride transfer in sugar isomerization. Based on these investigations and previous results found in literature, the best catalyst for the intermolecular hydride transfer in MPV reduction depends on the Lewis base and in the case of furfural reduction, Zr-Beta is a better catalyst than Sn-Beta.

Chapter 3

LEWIS ACIDIC ZEOLITE BETA FOR THE MEERWEIN-PONNDORF-VERLEY REDUCTION OF FURFURAL

3.1 Introduction

The large-scale use of biomass-derived fuels will reduce dependency on fossil fuels and will help mitigate anthropogenic CO₂ emissions and climate change.^[73] Lewis acid zeolites have been shown to catalyze a number of reactions for converting biomass-derived feedstocks, such as glucose and xylose, into fuels and chemicals. Aluminosilicate zeolites are traditionally associated with Brønsted acidity but zeolites with Lewis acidic properties can be obtained by the substitution of tetravalent metals (Ti^{IV}, Sn^{IV}, Zr^{IV}, etc.) into the framework of siliceous zeolites. Titanium in the framework of siliceous MFI-type zeolites (i.e., TS-1), for example, catalyzes partial oxidation of alkanes and epoxidation of alkenes and is used commercially for propene epoxidation.^[74, 75] After the discovery of TS-1, titanosilicate zeolite Beta (Ti-Beta) was investigated for the oxidation of larger molecules,^[66, 76, 77] and zeolite Beta with framework Sn (Sn-Beta) was shown to catalyze reactions such as the Baeyer-Villiger oxidation.^[19] Additionally, zeolite Beta catalysts with framework titanium, tin, and zirconium have been shown to catalyze the Meerwein-Ponndorf-Verley (MPV)

A renewed interest in Lewis acidic zeolites was prompted by the discovery that Sn-Beta is a highly selective catalyst for the isomerization of glucose to fructose, a reaction that involves an intramolecular hydride transfer.^[21] MPV reduction can be used to reduce the carbonyl group on hydroxymethylfurfural and furfural (made from the dehydration of sugars) over these microporous Lewis acids.^[56, 57, 78-82] In addition, etherification of alcohols can be catalyzed by solid Lewis acids,^[56, 57] and thus one may envision a reaction cascade in which an abundant biomass feedstock, like glucose, may be isomerized, dehydrated and then converted via reduction and etherification to more valuable and stable chemicals using these catalysts. These Lewis acidic materials catalyze several additional reactions, such as Diels-Alder cycloaddition and dehydration, aldol and retro-aldol reactions, and carbonyl-ene reactions.^[1, 41, 54, 55, 83] The variety of applications, as well as their tolerance to water (in contrast to conventional Lewis acids), give these materials great potential for the production of valuable products from biomass feedstocks.^[84]

For the reactions described above, metal(IV)-substituted framework materials display faster reaction rates than the corresponding metal oxide and the metal oxide doped on the siliceous zeolite.^[21, 40, 57, 64] Roy et al. compared the Lewis acidic properties of framework Sn-Beta and an extra-framework Sn-Beta (SnO₂ impregnated on siliceous Beta) using adsorption/FTIR of deuterated acetonitrile; the experiments show a distinct absorption peak in the FTIR spectra that is absent on the extra-framework form of Sn-Beta, and this peak has been assigned to acetonitrile coordinated to the Lewis acid site.^[40] A nearly 1:1 complex of tin sites with diethyl ether was also observed, while the extra-framework sample had a coverage about half as much as its tin concentration.^[40] The same 1:1 coordination has recently been observed for Zr- and Hf-Beta samples as well.^[41] Despite these investigations and the potential practical value of these catalysts, important aspects of their chemistry are still not understood. For instance, Sn-Beta shows the fastest turnover frequency for glucose

isomerization,^[84] but zirconium and hafnium Beta (Zr- and Hf-Beta) have higher rates for many MPV-type reactions,^[57, 64, 65] even though it is postulated that both reactions proceed via an "open" active site, a site in which a M-O-Si bond has been hydrolyzed forming a hydroxyl group on the metal atom and a neighboring silanol on the zeolite framework (see Figure 3.1).^[38, 85] The MPV reaction is believed to proceed via the coordination of the carbonyl on the "open" metal site, polarizing the carbonyl bond. Meanwhile, the alcohol also interacts with the metal site and is deprotonated by the neighboring silanol. A six-membered ring transition state is then formed when a hydride is transferred from the alcohol to the carbonyl (Figure 3.1).^[23, 38] This results in the formation and desorption of the new alcohol and carbonyl products.



Figure 3.1: Closed and open Lewis acid site and MPV reduction transition state with furfural and isopropanol

In this chapter, kinetic studies are described that were conducted using a laboratory-scale microreactor on M(IV)-framework zeolite Beta (M=Sn, Zr and Hf) for the MPV reduction of furfural to furfuryl alcohol, to compare turnover frequencies for the different metal atoms and understand the difference in observed reaction rates on structurally similar catalysts. A much higher rate of reaction was observed on Hf-

Beta compared to Sn- and Zr-Beta. The apparent activation energy on all three catalysts was very similar. Deactivation with time on stream was observed on all the catalysts (T = 328-358 K), but activity could be recovered upon calcination of spent catalyst and deactivation rate could be greatly reduced by operation at higher temperatures (T = 408 K).

3.2 Experimental

3.2.1 Catalyst Synthesis

Sn-Beta was synthesized following a protocol described in ref^[60] with two modifications. First, siliceous zeolite Beta was used instead of dealuminated Beta seeds. Second, the synthesis was heated for 14 days rather than 11. Zr-Beta was synthesized according to literature (Si/Zr=100, 20 days),^[64] but with siliceous zeolite Beta seeds instead of dealuminated Beta. Synthesis of the siliceous zeolite Beta was based on the method of Camblor et al.,^[70] but allowing four days for crystallization rather than two. Hf-Beta was synthesized using the same protocol as used for Zr-Beta but with a hafnium precursor. Specifically, 8.1 g tetraethylammonium hydroxide (Sigma Aldrich, 35%) was mixed with 7 g tetraethylorthosilicate (Sigma Aldrich, 98%) and allowed to hydrolyze for 1.5 hours. Then 0.143 g of hafnium oxychloride octahydrate (Alfa Aesar, 98+%) and 0.64 g deionized water were added to the mixture and allowed to stir at room temperature for several hours until all the ethanol formed and 0.95 g water were evaporated. The solution was transferred to a 23mLTeflon liner (A280AC, Parr) and then 0.8 g hydrofluoric acid (Acros, 48%) was added and mixed with a spatula, forming a clear gel. A suspension of 0.084 g of previously synthesized siliceous zeolite Beta in 0.41 g deionized water was also added and mixed into the gel. The composition of the final gel was: 1 SiO₂: 0.01 HfO₂:0.56 TEAOH:7.5 H₂O:0.56 HF. The Teflon liner was placed in the corresponding stainless steel autoclave (4749, Parr) and heated statically in a convection oven at 413K for 20 days. After this time, catalysts were filtered over a fine frit ceramic filter (CG-8590-60F, Chemglass), washed three times with deionized water, and dried in air in a drying oven at 353K overnight. The samples were then calcined in air by heating stepwise to 393K at a rate of 1K/min and holding for 2 hours, then heating to 853K at 3K/min and holding for 6 hours. The temperature ramp down was 40K/min.

Na-exchanged Hf-Beta and Sn-Beta were prepared following a procedure adapted from literature.^[85] Specifically, 300 mg of M-Beta was mixed with 45 mL of 1 M NaNO₃ (Sigma-Aldrich, \geq 99%) in distilled water for 24 hours at room temperature. The sample was recovered by filtration over a ceramic filter (Chemglass, CG-1402-16) and washed 3 times with 1 M NaNO₃ (50 mL solution for each wash). Then the material was calcined at 853 K for 5 hours (5 K/min ramp). The ratio of Na/Hf after exchange determined by X-Ray fluorescence with a Rigaku Supermini200 was 0.71. Na/Sn determined by X-Ray fluorescence was 14. Because this value was so high, the sample was sent to ICP-AES, which should be a more accurate analysis and Na/Sn was reported to be 8.2.

3.2.2 Catalyst Characterization

X-ray diffraction patterns were collected using a Bruker D8 diffractometer with Cu Kα radiation. The pattern was collected for 2 seconds at each increment of 0.02 degrees between 5 and 50 degrees. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analysis was performed by Galbraith Laboratories (Knoxville, TN) to determine metal content of the final samples. The UV/Vis spectra

of the samples was measured using a Jasco V-550 UV-Vis spectrometer with a diffuse reflectance cell. Nitrogen physisorption was performed in a Micromeritics 3Flex system to determine the micropore volume of each catalyst. Samples were degassed overnight at 523K and backfilled with nitrogen prior to analysis. Scanning electron microscopy images were recorded on a JEOL JSM 7400F at 10µA.

Sn-Beta was first evaluated under the same reaction conditions as recommended in the literature (10 wt% glucose in water, 1:50 metal:glucose molar ratio, 413K, 12 minutes) and similar yields of glucose and fructose, 49% and 28% respectively, were observed compared to those reported (46% and 30%).^[21] This test ascertains that our samples are similar to the ones reported by Moliner et al.

Thermogravimetric analysis (TGA) on spent catalysts was collected on a Mettler Toledo TGA/DSC Thermal Gravimetric Analyzer with STARe software. Samples were heated at a rate of 5K/min under 80 mL/min of air flow. The first derivative (dTGA) of the TGA curves was calculated numerically using Origin. The derivative curves were smoothed with an FFT filter with the number of points specified as 100.

Extraction of retained organics on spent catalysts was performed as previously described in ref^[86]: 30 mg of spent catalyst was dissolved in 1 g HF (Acros, 48%) and 2.6 g DI water and allowed to sit for 1 hour. The organics were extracted with methylene chloride and analyzed with a GC/MS (Shimadzu QP2010 Plus).

3.2.3 Reaction Kinetics

Reactions were conducted under continuous flow in a stainless steel reactor heated by an oil bath (see Figure 3.2 for process flow diagram). A U-shape configuration was used so that approximately 9 inches of a 1/8 inch line of tubing

 $(1/8" \text{ OD}, 0.028" \text{ wall}, 316 \text{ Stainless}, Swagelok) heated the reactant before going in an up flow configuration to a <math>^{1}/_{4}$ inch tube (1/4" OD, 0.035" wall, 316 Stainless,Swagelok) that held the catalyst bed. The $^{1}/_{4}$ inch reaction section was equipped on either side with VCR fittings holding 10 µm stainless steel filters (Swagelok) to ensure no movement of catalyst particles out of the bed. The catalyst was stabilized by the filter on one side and glass wool was placed between the catalyst and the other filter. Distilled (less than 2 hours before the start of experiment) furfural diluted in isopropanol was supplied to the reactor by an HPLC pump (Alltech, 301 HPLC pump). The reactor contents were held under 14 bar pressure using an ultra-low flow precision back-pressure regulator (Equilibar, EB1ULF1). At each sample time, 1 mL of effluent was collected at the outlet and analyzed offline. Liquid samples were analyzed by gas chromatography (Agilent 7890A) equipped with a flame ionization detector. An HP-Innowax column (Agilent) was used with the following method: hold at 313K for 4 min, 10K/min ramp to 523K and a final hold for 5 min.



Figure 3.2: Process flow diagram of reaction setup

The equation for the plug flow reactor is:

$$r = \frac{dF}{dW_{cat}}$$

where *F* is the reactant molar flow rate and W_{cat} is the weight of the catalyst bed. Under the differential conditions (<20% conversion) used here, this may be simplified to:

$$r = \frac{F_0 - F}{W_{cat}}$$

where F_0 is the initial molar flow rate of reactant and F is the molar flow rate at the reactor outlet. The flow rate term can be separated into volumetric flow rate and concentration, resulting in the following equation:

$$r=\frac{v(C_0-C)}{W_{cat}}$$

Reaction rates reported here were calculated based on the amount of furfuryl alcohol (FA) product detected, rather than change in reactant concentration:

$$r = \frac{v \cdot C_{FA}}{mol \ metal}$$

where v is the reactant flow rate in L/min, C_{FA} is the concentration of furfuryl alcohol in mol/L in the reaction effluent, and *mol metal* is the moles of metal atom in the catalyst bed as determined by ICP-AES. When more than one measurement was conducted for a data point, the average is reported with the standard deviation or plotted with an error bar. No more than three measurements were used for a data point, but most data is reported based off of a single experimental run.

Deactivation was observed in all experiments. We have used the initial-rates method (extrapolated to time $t_0 = 0$ s) to estimate the initial activity of the catalysts.

Liquid samples were collected every 30 minutes for 4 hours after an initial 60 minute startup period. An exponential curve was then fit to the data to determine the rate at t₀. Conversion was kept below 20% in all cases except for the highest temperature (358 K) used to determine the activation energy on Zr-Beta and Sn-Beta, where space velocity was not adjusted and conversion reached 28% and 24%, respectively. Additionally, experiments at 408 K had higher conversion (>50%). Carbon balances for the tests between 328-358 K were between 96%-102% on Sn- and Zr-Beta, while on Hf-Beta the range was 97%-106%.

Due to the high activity of Hf-Beta, a much smaller amount of catalyst (30 mg) was needed to achieve similar conversion to Zr-Beta and Sn-Beta. In runs with Hf-Beta, 30 mg of α -Al₂O₃ (Alfa Aesar, 99.98%) was mixed with the catalyst in order for the bed to be a practical length in the reactor tubing. The alumina was tested for inertness at 358 K and did not result in any conversion of furfural.

In regeneration experiments, fresh samples were compared to a different sample that had been spent and calcined because the reactor is not equipped for calcination of the catalyst bed *in situ*. Specifically, in regeneration experiments with Hf-Beta, a sample of 60 mg was spent at the same conditions as the kinetic experiments, then the bed was removed and calcined at the same conditions described above in catalyst synthesis. 30 mg of this regenerated sampled was then run (mixed with α -Al₂O₃) and compared to a fresh sample at the same conditions.

3.2.4 Kinetic isotope effect experiments

For kinetic isotope effect experiments, furfural and isopropanol or isopropanold₈ (Sigma-Aldrich, 99.5 atom% D) were diluted in toluene (Fisher, 99.9%) and tested in the flow reactor as described at 348 K. Different amount of catalysts and different

feed concentrations were used in order to obtain appreciable conversion. For Zr-Beta, 60 mg of catalyst and a feed of 0.028 mol/L furfural and 0.2 mol/L isopropanol or isopropanol-d₈ was used. For Sn-Beta, 85 mg of catalyst and a feed of 0.05 mol/L furfural and 0.5 mol/L isopropanol or isopropanol-d₈ was used. Finally, 30 mg Hf-Beta and a feed of 0.05 mol/L furfural and 0.3 mol/L isopropanol or isopropanol-d₈ was used. Since the k_H/k_D determined from comparing rates at 60 minutes time on stream was found to be very close to the ratio determined from comparing rates extrapolated to t₀ from time on stream data for Hf-Beta, the k_H/k_D measurements for Zr- and Sn-Beta were taken from the rates at 60 minutes time on stream.

3.2.5 Batch Testing

Some samples were tested for the MPV reaction for one hour in a batch system, at the same conditions but higher concentration than the continuous flow experiments. Specifically, 0.2 g of furfural in 20 mL isopropanol (100 mmol/L) was loaded into a 45 mL 4714 Parr reactor with the specified amount of catalyst and a magnetic stir bar for mixing. The reactor was pressurized with nitrogen to 200 psi, placed in an oil bath at the desired temperature, and quenched with an ice bath after 1 hour reaction time. The reaction product was filtered from the catalyst with a 0.2 micron syringe filter (Corning) and analyzed with the same GC analysis as the flow experiments. Siliceous Beta (Si-Beta) and ZrO₂ were tested at 348K with 65 mg of catalyst and no reaction of furfural was observed in either case. Hf-Beta, Sn-Beta and Na-exchanged Hf-Beta and Sn-Beta were tested at 338 K with 25 mg of Hf catalysts and 50 mg of Sn catalysts.

3.3 Results and Discussion

3.3.1 Catalyst Characterization

XRD patterns for the zeolites samples were consistent with the diffraction patterns of zeolite Beta (Figure 3.3), with no detectable impurities or an amorphous phase observed in the patterns. The micropore volume of all catalysts was 0.20 cc/g or greater, similar to the typical value for Beta (Table 3.1).

Table 3.1: Si:Metal ratios for M-Beta synthesis gel and final sample, and micropore volumes determined by nitrogen physisorption. *as determined by ICP spectroscopy.

Catalyst	Gel Si:M Ratio	Product Si:M Ratio [*]	M Weight %	Micropore Volume (cc/g)
Sn-Beta	125	136	1.43	0.20
Zr-Beta	100	199	0.76	0.21
Hf-Beta	100	167	1.74	0.22



Figure 3.3: Metal-Beta X-Ray Diffraction Patterns. (a) Hf-Beta, (b) Sn-Beta, (c) Zr-Beta, (d) H-Al-Beta (Zeolyst, CP814E)

The diffuse reflectance UV/vis spectra of the catalysts (Figure 3.4) do not indicate metal oxide in any of the samples and are comparable to those reported in the literature.^[23, 40, 57] The amount of metal included in the zeolite synthesis gel and the final amount incorporated in the sample, as determined by ICP-AES, are summarized in Table 3.1. For the Zr and Hf samples, the ratio is nearly two times higher than the value in the synthesis gel. Since the other analytical techniques do not reveal the presence of a significant amount of metal oxide in the samples, it is possible that the metal not incorporated into the framework remains soluble in the supernatant fluid, perhaps as a metal fluoride, and is removed during washing and filtration, but the fluid was not analyzed to confirm this. SEM images of catalyst samples reveal particles with square bipyramidal crystals with sizes of about 5 micron for all the catalysts

(Figure 3.5). Some small particles can be observed on the surface of the crystals, particularly Sn-Beta. These might be a small amount of metal oxide, but the amount is sufficiently small that there is not enough to be detected by other analytical methods (or to affect isomerization activity in the case of Sn-Beta). These particles could be due to secondary nucleation as well.



Figure 3.4: UV-Vis Spectra of Hf-, Zr-, Sn-Beta



Figure 3.5: SEM of a) Sn-Beta, b) Zr-Beta and c) Hf-Beta

3.3.2 MPV Reaction Rates

The MPV reduction of furfural with isopropanol produces furfuryl alcohol and acetone. Of the three catalysts investigated, Hf-Beta exhibited the highest rate of furfuryl alcohol production, followed by Zr-Beta and Sn-Beta (Figure 3.6). Comparing rates at 60 minutes of time on stream for runs at 348 K, Hf-Beta had a rate of 4.0 mol furfuryl alcohol produced/min/mol metal (min⁻¹). Zr-Beta was less than half this value (1.6 min⁻¹) and Sn-Beta was an order of magnitude less reactive than Hf-Beta (only 0.4 min⁻¹).



Figure 3.6: Rate of furfuryl alcohol production with time on stream. Reaction Conditions: 348 K, 14 bar, [Furfural]₀=52 mmol/L in isopropyl alcohol. WHSV [mol Furfural/mol metal/min]=Hf: 34.4, Zr: 11.3, Sn: 5.5

Apparent activation energy was determined in the temperature range of 328-358K (Table 3.2). Plots of furfuryl alcohol production on each catalysts at each temperature point are shown in Appendix A.1. Hf-Beta has the lowest activation energy (49.6 kJ/mol), while the activation energies of Zr-Beta and Sn-Beta are nearly identical (60.7 and 60.4 kJ/mol, respectively). These values are similar to those reported by Luo et al. for the MPV reduction of methyl levulinate with 2-butanol on the same catalysts (Hf-,Zr-,Sn-Beta) in which all three had an apparent activation energy between 52.5 and 51.7 kJ/mol.^[23] Despite little difference in activation energy among catalysts, that study also reported the same trend in reactions rates (Hf-Beta > Zr-Beta > Sn-Beta) that is reported here. It cannot be definitively stated whether the similar activation energies are due to a coincidental agreement of the sums of different heats of adsorption and different true activation energies for each catalyst, or if those values are all similar among the catalysts. Heats of adsorption on each catalyst could be probed with microcalorimetry but the results would be difficult to interpret given the heterogeneity caused by open and closed sites in these materials. Despite the similar ionic radii of Zr and Hf (0.73Å and 0.72Å), Zr has an activation energy closer to Sn, which is smaller (0.69Å). A computational study of hafnium and zirconium oxides found larger electron affinity for hafnium oxide compared to zirconium oxide despite these materials being nearly identical both vibrationally and structurally.^[87] The differences in Hf and Zr observed here may be caused by larger electron affinity of Hf, causing stronger binding to reactants and translating into a lower apparent activation energy.

Table 3.2: Pre-exponential factor and apparent activation energy. Confidence intervals are based on a two-tailed t-distribution with α=0.1 and n-2 degrees of freedom. Units of A: (mol alcohol*L)/(mol metal*s*mol furfural) Reaction Conditions: 328-358 K, 14 bar, [Furfural]₀=52 mmol/L in isopropyl alcohol. WHSV [mol Furfural/mol metal/min]=Zr: 11.3, Hf: 35 at 328-348K and 55 at 358K, Sn: 5.5.

Catalyst	ln(A)	E _{a,app} [kJ/mol]
Zr-Beta	20.3±4.7	60.7±13.5
Sn-Beta	18.9±2.4	60.4±6.9
Hf-Beta	17.4±4.6	49.6±13.1

3.3.3 Active Site Characterization

Since the open site has been hypothesized as the true active and here the rates are normalized by total metal content, it is prudent to consider the true number of these active centers in each sample, which may be different from the number of metal atoms in the sample. Hf-Beta and Sn-Beta were exchanged with sodium in the same manner as Bermejo-Deval, et al. in order to probe the nature of the active site.^[36] Sodium should exchange with the hydroxyl group at the open site and alter its reactivity, while the closed site will be undisturbed. Results from batch MPV reduction reactions with Na exchanged and unexchanged Hf- and Sn-Beta are shown in Table 3.3. The yield of furfuryl alcohol was reduced from 15.9% for un-exchanged Hf-Beta to 0.8% yield for Na-exchanged Hf-Beta indicating the importance of the open site. Similarly, the yield of furfuryl alcohol for Sn-Beta was 9.9% and reduced to 0.4% for Na-exchanged Sn-Beta. Although this establishes the activity of the open and

closed site are difficult to quantify, particularly under reaction conditions,^[39] so in this work the total metal content was used as an estimate of active site concentration to compare reaction rates on each catalyst.

Table 3.3: Effect of Na-exchange on Lewis acid zeolites for MPV reduction of furfural. Conditions: 0.2 g furfural in 15.92 g isopropanol, 338 K, 1 hour, 200 psi.

	Si:M	Na:M	Catalyst weight [g]	Furfuryl Alcohol Yield [%]
Hf-Beta	147	n/a	25	15.9
Na-Hf-Beta	147	0.7	25	0.8
Sn-Beta	106	n/a	50	9.9
Na-Sn-Beta	106	8.2	50	0.4

3.3.4 Kinetic isotope effect experiments

Kinetic isotope effect studies using perdeuterated isopropanol while keeping the ratio of furfural to isopropanol high (>5) were conducted. A primary, normal kinetic isotope effect ($k_H > k_D$) was exhibited for all catalysts (Table 3.4). This type of kinetic isotope effect is indicative of a hydrogen bond breaking in the rate-determining step. This result is consistent with a proposed mechanism, initially articulated by Corma et al., that the hydride shift is the rate-determining step for MPV.^[38] Thus, the rate-determining step is the same for each of the M-Beta catalysts, which is consistent with their very similar apparent activation energies.

Table 3.4: Kinetic isotope effect of MPV reduction of furfural with isopropanol and isopropanol-d₈. Reaction conditions in section 3.2.3.1.

Catalyst	kh/kd
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Zr-Beta	2.7
Sn-Beta	1.5
Hf-Beta	3.6±1.2

3.3.5 Catalyst Deactivation

All three catalysts deactivated with time on stream, the more severe deactivation being observed on Sn- and Zr-beta catalysts. Because of this deactivation, the conversion data collected every 30 min from 1 hour to 4 hours was fitted to an exponential function and the intercept at t₀ was taken was the "initial" rate (Table 3.5). The fit to these curves was very good for Zr-Beta (r^2 =0.97-0.99) and for Hf-Beta (r^2 = 0.85-1) and fair for Sn-Beta (r^2 = 0.8-0.99). Based on these fits, the exponential decay was also used to estimate the catalyst half-life (Table 3.5). Hf-Beta had the longest half-life of 6.6 h, followed by Zr-Beta (4.9 h) and Sn-Beta (3.5 h). Rate and half-life data at the other temperature points on each catalyst are reported in Appendix A.2.

Table 3.5: Initial rates of furfuryl alcohol and furfural diisopropyl ace	tal formation and
catalyst half-life at 348 K. See Figure 3.6 for conditions.	[†] Run with 10
mmol/L furfuryl alcohol supplied in the feed. *Units:[mo	ol
product/min/mol metal] *Units:[hours]	

Initial Reaction Rate	Sn-I	Beta	Zr-Beta		Hf-Beta	
	Rate [*]	Half-life*	Rate [*]	Half-life [*]	Rate [*]	Half- life [*]
Furfuryl alcohol	0.51	3.5	1.83±0.21	4.9±0.8	4.60	6.6
Furfural acetal	0.35	4.0	0.19±0.03	4.9±2.9	0.34	4.9

Furfuryl 0.16±0.06 4.3±0.9 1.10 4.5 2.96 5.5
--

In addition to furfuryl alcohol, furfural diisopropyl acetal (also formed from furfural and isopropanol) is observed in the product mixture in small amounts (Figure 3.7). It was identified by GC/MS, on the basis of having a fragmentation pattern consistent with an acetal of furfural and isopropanol. Two sources were identified for the formation of this acetal: first, it forms homogeneously in the reactant reservoir. Furfural can be easily oxidized by light and air, which leads to the formation of acidic species that can catalyze other reactions.^[88, 89] This is likely what causes the homogeneous formation of acetal in the feed reservoir. Because of this homogeneous formation, the FID response factor was estimated by allowing 0.058 mol/L furfural to age in isopropanol at room temperature for 4 hours and assuming all furfural lost (0.6%) was converted to acetal. In a blank run with no catalyst at 348K, acetal formation was not observed to increase beyond what was already formed in the reservoir. Acetals are known to form from carbonyls on Lewis acids as well, and the acetal is also formed on these M(IV)-Beta catalysts in parallel to the MPV reaction.



Figure 3.7: Furfural and isopropanol reaction pathways

Figure 3.8 shows the rate of acetal formation with time on stream over each catalyst at a temperature of 348 K. It exhibits the same decrease in rate with time on stream as observed for furfuryl alcohol. Although the rate of production of acetal is similar on all the catalysts, it is nearly as high as the rate of furfuryl alcohol production on Sn-Beta, and consequently this catalyst is the least selective towards the desired MPV reduction. On Hf-Beta and Zr-Beta the rate of acetal formation is small such that acetal selectivity is only as high as 20% at the lowest temperature tested (328 K). Initial rates and decay constants from exponential fits for furfuryl alcohol and acetal production are included in Table 3.4. The mechanism of acetal formation is expected to be similar to that of MPV, in that the furfural carbonyl bond is activated by coordination with the Lewis acid metal, but instead of the isopropanol also coordinating with the metal, the alcohol oxygen directly attacks the electrophilic carbonyl carbon.^[90]



Figure 3.8: Rate of furfural diisopropyl acetal production with time on stream. Reaction Conditions: 348 K, 14 bar, [Furfural]₀=52 mmol/L in isopropyl alcohol. WHSV [mol Furfural/mol metal/min]=Hf: 34.4, Zr: 11.3, Sn: 5.5

In their as-prepared form, all the catalysts are white powders, but after reaction there is a clear change to various colors (teal, blue, grey) in all cases (see Appendix A.3 for examples), most likely due to the retention of organic material within the micropores of the catalysts. Thermogravimetric analysis (TGA) of the spent catalysts (Figure 3.9) show that the weight loss in the catalyst pores is approximately the same for all three catalysts (13.4-14.0%). There are, however, clear differences in the shape of the TGA traces. The trace of Sn-Beta, in particular, indicates that the spent catalyst has carbon species that are thermally more stable and combust at higher temperatures than the other two catalysts. This sample also exhibits weight loss at temperatures as high as 1000 K although this may be due, in part, to the collapse of the zeolite framework. The TGA traces for both Hf-Beta and Zr-Beta plateau after 800 K and the initial weight loss peaks at 386 K compared to 318 K for Sn-Beta. Sn-Beta exhibits an additional weight loss peak closer to Hf and Zr at 410 K.



Figure 3.9: Thermogravimetric analysis of spent M-Beta catalysts. Analysis was performed in air at a heat rate of 5 K/min. Inset is first derivative of TGA curve.

Competitive adsorption of reaction products has been observed for low temperature, liquid phase reactions on zeolites^[91-93] and can cause significant reductions in reaction rates. To investigate this possibility in the furfural-isopropanol reaction system, the effect of furfuryl alcohol on reaction rate in all the catalysts was measured. When 10 mmol/L furfuryl alcohol is supplied in the feed with the same amount of furfural used in previous runs (52 mmol/L), a decrease in reaction rate was observed on all the catalysts (Table 3.2, line 3). The rate decreased the most on Sn-Beta with a nearly 70% decrease in initial rate compared to the measurement with no furfuryl alcohol in the feed. The effect on Hf-Beta and Zr-Beta was less pronounced, with reductions of 36% and 40%, respectively. Although these catalysts are known to be active for the aldol condensation of aldehyde with acetone in this temperature range,^[94] no change in reaction rate was observed when acetone, the co-product of this MPV reaction, was supplied in the feed at a 1:1 molar ratio acetone:furfural on Zr-Beta (Figure A.4). These results confirm that these catalysts suffer from product inhibition of the furfuryl alcohol, reducing the overall rate at the investigated temperatures.

Another possible mode of deactivation is the formation and retention of large reaction products. Both furfural and furfuryl alcohol oligomerize,^[89, 95, 96] and it is possible that under reaction conditions one or both oligomerize within the zeolite pores leading to blocking of the active sites and reduced catalytic activity. To test for the presence of oligomers in the samples, the species occluded in a sample of spent Hf-Beta were analyzed by dissolving the zeolite in an HF solution as described in the methods section.^[86] Furfuryl alcohol and difurfuryl ether (a dimer of furfuryl alcohol) were identified in the extracted product along with higher molecular weight species, indicating that formation and occlusion of large organic species. Pore blocking by these large molecules is likely one of the deactivation mechanisms. The unidentified higher molecular weight species present in the spent catalyst have similar fragmentation patterns and a discrete distribution of residence times by GC/MS, which strongly suggests oligomer formation and oligomerization reactions of furfuryl
alcohol is similar to the findings of Jae et al., who observed greater deactivation for the etherification of 2,5-bis(hydroxymethyl)furfural (BHMF) with isopropanol on Sn-Beta than the MPV reduction and etherification of hydroxymethyl furfural (HMF) with isopropanol on Sn-Beta. These authors also noted the likelihood of selfetherification of the BHMF inside the catalyst as a cause of more severe deactivation compared to HMF.^[56] Considering weight loss at higher temperatures observed by TGA on Sn-Beta, it is likely that higher molecular weight oligomers (with higher boiling points) from either furfuryl alcohol or furfural form on Sn-Beta than in the other two catalysts.

3.3.6 Catalyst Regeneration

After calcination of spent catalysts at the same conditions used for the removal of the structure-director (853 K in air), the initial catalyst activity is regained (Figure 3.10) and the catalyst color returns to white (see Figure A.4). The small decrease in activity observed for "spent and calcined sample 1" is within the error of experiment and not due to irreversible deactivation. A second sample was spent and calcined (sample 2) and resulted in nearly identical rates to the fresh sample. This result confirms that deactivation is primarily caused by retention of organic species in the zeolite pores, and that within the timescale used for these tests, there is no significant loss of active sites from the zeolite framework.



Figure 3.10: Rate of furfuryl alcohol production with time on stream on fresh Hf-Beta (open symbols) and spent and calcined Hf-Beta (closed symbols). "Hf-Beta spent and calcined sample 2" is a separate bed and not a second regeneration cycle. Reaction Conditions: Same as Figure 3.6.

Catalyst deactivation can be mitigated, to some extent, by operating the reaction at higher temperatures as indicated by the change over time of reaction rate at 408K (Figure 3.11). At this temperature, a subsequent reaction of the furfuryl alcohol may occur with the excess isopropanol to form a furfuryl isopropyl ether (Figure 3.7). On Hf- and Zr-Beta, only a very small amount (<2.5% yield) is produced, but on Sn-Beta the ether production is significant (initially ~20% selectivity). For Hf-Beta, the half-life at 408 K is three times (20.6 h) its half-life at 348 K. Deactivation on Zr-Beta at 408 K is not well described by an exponential fit, due to the increase in rate at the initial reaction time points. Loss of activity between the first and last time points is only 10%, compared to an average of 35% in the runs at 348 K. Sn-Beta shows the

greatest stability for furfuryl alcohol production at 408 K with a near constant rate over the sampling time. However, the rates of acetal and ether production (initially ~30% combined selectivity at this temperature) do fall with time on stream, so the furfural conversion on Sn-Beta is not stable. The initial rate of furfural conversion is 3.76 mol furfural/min/mol metal, and the half-life based on furfural conversion (instead of furfuryl alcohol production) is 13.1 h. For comparison, the half-life of Sn-Beta at 348 K based on furfural conversion is 5.2 h. The carbon balance is stable during this run, so it is not clear why the furfuryl alcohol rate does not increase correspondingly with the decrease in the secondary ether product. Nonetheless, despite a stable rate of alcohol production, the Sn-Beta still exhibits deactivation like the other catalysts at this temperature. The increased stability obtained from increasing temperature is likely due to more favorable desorption of alcohol product, preventing it from further reacting to large oligomers.



Figure 3.11: Rate of furfuryl alcohol production with time on stream at 408K. Reaction Conditions: 14 bar, [Furfural]₀=52 mmol/L in isopropyl alcohol. WHSV [mol Furfural/mol metal/min]=Hf:9.4, Zr: 11.3, Sn: 5.5

3.4 Conclusions

Zeolite Beta catalysts with framework tin, zirconium or hafnium were investigated in the MPV reduction of furfural with isopropanol, a model reaction system to understand hydrogen transfer processes relevant to the upgrading of biomass feedstocks and to the production of valuable chemicals. Hf-Beta was found to have the highest reaction rate for this reaction, as well as the lowest activation energy. Despite the similar size of Zr and Hf, higher rates were observed on Hf-Beta, however the accurate accounting of the open active site is difficult and normalizing rate by total metal content may lead to incorrect trend observations. Assuming that open and closed site populations are constant in the temperature ranges investigated, the apparent activation energy will not be affected by this normalization and very similar apparent activation energies were found on the materials, indicating a similar mechanism, which is supported by the observation of a primary kinetic isotope effect on all catalysts. Interestingly, the standout activity of Hf-Beta has been reported for MPV reduction of methyl levulinate with 2-butanol,^[23] but Hf- and Zr-Beta have exhibited similar rates for other chemistries such as aldol condensation.^[94]

Oligomerization of the product (and possibly the reactant) has a detrimental, although reversible, effect on reaction rate via the blockage of pores, as evidenced by TGA and analysis of occluded catalyst species. Low rates on Sn-Beta seem to be linked to a high degree of polymerization that may quickly block access to active sites. However, for a similar reaction in which no deactivation was observed (reduction of methyl levulinate with 2-butanol), the rate on Sn-Beta was also the lowest, suggesting that Sn-Beta has inherently lower activity for intramolecular hydride transfer in addition to being the most susceptible to deactivation with furfural reduction.^[23] Adsorption plays a fundamental role in the reaction as demonstrated by the mitigation of deactivation upon increase in reaction temperature. These findings will be instructive in applying these catalysts in the upgrading of biomass derivatives such as glucose and fructose. The continuous flow operation used in this study is relevant to how these catalysts would be employed industrially. This type of setup is also very valuable in observing deactivation phenomena that would likely go undetected in batch mode reactor studies.

Chapter 4

PRODUCTION OF PARA-METHYLSTYRENE AND PARA-DIVINYLBENZENE FROM FURANIC COMPOUNDS

4.1 Introduction

Processes to prepare commodity chemicals from bio-derived feedstocks are needed to reduce dependence on fossil fuels, reduce anthropogenic greenhouse gas emissions and foster sustainable technology.^[97, 98] Bio-based processes can also compensate for supply reductions of specific chemicals resulting from the large increase in shale gas production in the United States and other countries.^[2] For example, the recent increased supply and price reduction of ethane has increased investment in ethane cracking units for the production of ethylene.^[99] The loss of aromatic byproducts resulting from switching cracking unit feedstocks from naphtha to ethane creates an opportunity to meet aromatics demand with aromatic chemicals made from renewable sources.^[2] Furans derived from the dehydration of glucose and xylose, the building blocks of cellulose and hemicellulose, have been proposed as starting materials for numerous bio-based processes to produce fuels and chemicals.^[97, 100] In this chapter, we show that furans can also be used to produce *para*-ethyltoluene and *para*-diethylbenzene, two precursors to important engineering polymers.

The use of furans as dienes in Diels-Alder reactions over zeolite catalysts has been described in a number of recent reports.^[41, 54, 55, 101-105] Selective production of *para*-xylene from dimethylfuran and ethylene with zeolite Beta catalyst was developed by Chang and co-workers.^[53] The selectivity to the *para* isomer is high in

this chemistry because when ethylene is added in a cycloaddition to a 2,5-disubstituted furan, as dimethylfuran is, the resulting aromatic is 1,4-substituted, i.e., parasubstituted. There may be subsequent isomerization, but *para*-selectivity will be high since it is the first isomer formed. Here, we used similar chemistry to prepare precursors to *p*-methylstyrene and *p*-divinylbenzene. Poly-*p*-methylstyrene exhibits superior properties relative to polystyrene or poly-vinyltoluene (typically a 35:65 mixture of *p*-methylstyrene to *meta*-methylstyrene), such as lower density and higher glass transition temperature.^[106, 107] Divinylbenzene is a crosslinking agent often used in the manufacture of polystyrene resins. While ethylbenzene, the precursor of styrene, is made from the alkylation of benzene with ethylene,^[108] the use of this approach to make *p*-ethyltoluene (and subsequently *p*-methylstyrene) is complicated by the formation of multiple isomers with similar physical properties.^[109] The shape selectivity of zeolites has been employed to minimize the production of the ortho isomer, but at low conversion and with excess toluene to avoid polyalkylation. While this technique is successful in eliminating the ortho isomer in the product, it does not eliminate the *meta* isomer.^[107] It is also possible to make ethyltoluene by acylating toluene directly and reducing the acetyl group to ethyl, but this also results in a mixture of isomers, even if zeolites are employed.^[110-114] Moreover, the production of toluene from bio-derived methylfuran is considerably less selective than the production of *p*-xylene from dimethylfuran.^[101, 103] We have investigated the formation of *p*-ethyltoluene by first acylating methylfuran at the C5 position, then reducing the acetyl group to ethyl and finally combining 2-ethyl-5-methylfuran with ethylene in a tandem Diels-Alder cycloaddition and dehydration reaction to produce the *para* aromatic product.

Friedel-Crafts acylation traditionally involves acetic anhydride or acetyl chloride over Lewis acid catalysts like aluminum chloride. In the 1980s, solid acids began to be investigated for the acylation of aromatics and were found to be active and selective but not stable, suffering from rapid deactivation.^[115, 116] This deactivation is due to a number of processes including coke formation, entrapment of over-acylated product in the zeolite pore, and retention of the more polar reaction product at the active site.^[92, 111, 112, 117, 118] Adsorption of acetic anhydride on H-ZSM-5 has been shown to form acetic acid and an acetyl-zeolite surface species.^[119] This suggests a mechanism that parallels the homogeneous-acid catalyzed mechanism involving the formation and attack of an acylium ion. That is, acetic anhydride reacts with the Brønsted acid site, forming acetic acid and leaving an acylium ion at the site. The aromatic species then attacks this surface acyl cation via electrophilic substitution. The aromatic species donates a proton to regenerate the Brønsted acid site. Investigations of anisole acylation with isotopically-labelled acetic anhydride were consistent with an acylium ion intermediate and ruled out ketene (formed from deprotonated acylium) as an intermediate in liquid phase aromatic acylation.^[120] Though it was determined that ketene was not an intermediate towards the product, ketene formation and oligomerization was suggested to be a possible mechanism of deactivation.

In this chapter, the Friedel-Crafts acylation of methylfuran has been employed as the first step in the preparation of *p*-ethyltoluene. Methylfuran can be obtained renewably from the deoxygenation of furfural, which is obtained from hemicellulosic waste feedstocks like corn stover and oat hulls.^[4] To achieve high selectivity to the *para* isomer of ethyltoluene, we have exploited the inherent *para* selectivity of aromatics formed from the Diels-Alder cycloaddition of 2,5 substituted furans and

ethylene. First, the desired ethyl functional group was added via acylation of methylfuran followed by reduction of the resulting ketone by hydrodeoxygenation. Finally, the corresponding aromatic product of *p*-ethyltoluene was formed by Diels-Alder cycloaddition with ethylene and dehydration of the oxanorbornene intermediate (Figure 4.1). The chemistry used to make styrene from ethylbenzene over iron and chromium oxide catalyst promoted with potassium could then be applied to make *p*-methylstyrene from *p*-ethyltoluene.^[109] This methodology has also been applied to the formation of diethylbenzene, a precursor to divinylbenzene (Figure 4.2). Ethyltoluene and diethylbenzene were produced in high overall yield (>67%) and greater than 99% *para* isomer selectivity using H-Beta as catalyst for the acylation reaction, copper chromite for the hydrodeoxygenation, and again H-Beta for the Diels-Alder reaction.



Figure 4.1: Process to produce *para*-methylstyrene from 2-methylfuran



Figure 4.2: Process to produce *para*-divinylbenzene from furan

4.2 Experimental

4.2.1 Materials

The ammonium forms of zeolite Beta (Zeolyst, CP814E) and ZSM-5 (Zeolyst, CBV 2314) were purchased from Zeolyst and calcined as follows: ramp 5 K min⁻¹ to 393 K, hold 2 hours, ramp 5 K min⁻¹ to 853 K, hold 4 hours. The hydrogen form of Zeolite Y was used (Zeolyst, CBV720) as received. Si-Beta and Zr-Beta catalysts were synthesized as described previously.^[121] Sn-Beta catalyst characterized in Chapter 2 was used for the combined acylation and Diels-Alder experiment in section 4.3.1.4. Si/Al ratios of the commercial zeolites were confirmed by X-Ray fluorescence with a Rigaku Supermini200. For Zr-Beta, Si/Zr ratio was determined by ICP-AES performed by Galbraith Laboratories (Knoxville, TN). Micropore volume was determined with nitrogen physisorption in a Micromeritics 3Flex system. Samples were degassed overnight at 523 K and backfilled with nitrogen prior to analysis. X-ray diffraction patterns were collected using a Bruker D8 diffractometer with Cu K α radiation. Each pattern was collected for 0.5 seconds at each increment of 0.02 degrees

between 5 and 50 degrees. SEM images were recorded on a JEOL JSM 7400F at 10 $\ensuremath{\mu A}.$

4.2.2 Acylation Reactions

5 mL of reactant (furan (Acros, 99+%), 2-methylfuran (Acros, 99%, stabilized), or 2-ethylfuran (Sigma Aldrich, \geq 99%)) and 15 mL of acetic anhydride (Sigma-Aldrich, \geq 99%) were loaded into a 4714 45 mL Parr reactor with 0.1 g of catalyst and a magnetic stir bar for mixing. The reactor was pressurized with nitrogen to 200 psi and then placed in an oil bath at a temperature of 453 K for the desired amount of time, and finally quenched with an ice bath. To test the catalyst regenerability for this reaction, spent H-Beta was collected from two completed experiments (where fresh catalyst was used at the beginning of both experiments), calcined at 823 K for 6 hours, and then tested at the same conditions.

When 2-ethylfuran was used as starting reagent, the product 2-acetyl-5ethylfuran, which is not available commercially, was isolated using a microdistillation unit (Ace Glass 6563). It was obtained at 95% purity on a carbon basis as determined by gas chromatography (Agilent 7980A GC-FID) using a Polyarc methanizer. The NMR spectrum of the isolated product is shown in Appendix B.1.

4.2.3 Hydrodeoxygenation Reactions

4.2.3.1 Small-Scale

For hydrodeoxygenation of the acylated furans, 16 mL total of 0.11-0.12 g mL⁻¹ reactant (2-acetyl-5-methylfuran (Sigma-Aldrich, \geq 98%) or 2-acetyl-5-ethylfuran) in tetrahydrofuran (Fisher) was combined with 0.1 g of copper chromite catalyst (Sigma-Aldrich) in a 4790 50 mL Parr reactor with a magnetic stir bar. In the case of 2-

acetylfuran (Aldrich, 99%), a much higher ratio of catalyst to reactant was required; and 15 mL of 0.065 g mL⁻¹ of 2-acetylfuran in tetrahydrofuran was combined with 0.5 g copper chromite. The reactor was sealed and purged with nitrogen gas, and then filled with 400 psi hydrogen gas. The reactor was heated to 503 K with a ceramic band heater for 5 hours (not including a 30 minute ramp time). The reactor was quenched after desired reaction time using an ice bath.

4.2.3.2 Large-Scale

A 4571 1000 mL Parr reactor with a magnetic stir bar was used for larger scale experiments. For the reaction, 10 to 40 g of 2-acetyl-5-methylfuran (Sigma-Aldrich, \geq 98%) or 30 g of 2-acetyl-5-ethylfuran were mixed with tetrahydrofuran at 0.7 g ml⁻¹ concentration and 0.5 to 2 g copper chromite catalyst was added to the mixture. The copper chromite was used as received, without prior reduction. The experimental procedure and reaction conditions are the same as described above for the smaller scale (50 mL reactor), except that the reaction time was 2 hours and after this time the reactor was allowed to cool in air to room temperature, instead of being quenched in an ice bath.

To produce 2-ethyl-5-methylfuran for the Diels-Alder step, the scaled procedure for the 10x scale was slightly modified by extending the reaction time to 3 hours. The product of two scaled up reactions was combined, filtered from the catalyst and dried with 4A molecular sieves. The resulting mixture contained 0.09 g mL⁻¹ 2ethyl-5-methylfuran, 0.001 g ml⁻¹ 2-ethyl-5-methyltetrahydrofuran and 0.008 g ml⁻¹ 2acetyl-5-methylfuran. This mixture was used for the data reported in Table 4.4-Table 4.7. 2-ethyl-5-methylfuran was also isolated with a microdistillation unit and obtained in at least 90% purity on a carbon basis as determined using gas chromatography (Agilent 7980A GC-FID equipped with a Polyarc methanizer) and used in the experiments reported in Table 4.7 (line 2). Its NMR spectrum is reported in Appendix B.2.

For Diels-Alder reactions with 2,5-diethylfuran as the reactant, the 2-ethyl-5acetylfuran hydrodeoxygenation product was filtered from the copper chromite catalyst and used directly (without drying with molecular sieves) in the following Diels-Alder experiment. The NMR spectrum of 2,5-diethylfuran is reported in Appendix B.3.

4.2.4 Diels-Alder Cycloaddition and Dehydration Reactions

In Diels-Alder cycloaddition and dehydration experiments with 2-ethyl-5methylfuran, 20 mL of product from scaled up hydrodeoxygenation reactions at a concentration of 0.09 g mL⁻¹ 2-ethyl-5-methylfuran was combined with 0.065 g zeolite (H-Beta, H-Y, H-ZSM-5) or 0.32 g Zr-Beta in a 4790 50 mL Parr reactor with a magnetic stir bar. For 2,5-diethylfuran, the reaction product of 2-acetyl-5-ethylfuran (approximately 15 mL and 0.075 ± 0.05 g mL⁻¹ 2,5-diethylfuran) was filtered and combined with 0.04 g H-Beta catalyst. The reactor was sealed and purged with nitrogen gas, and then it was filled with ethylene gas to 400 psi. The reactor was heated to 503 K with a ceramic band heater using a 30 minute ramp time (not included as part of the reaction time). After 18 hours, the reaction was quenched by placing the reactor in an ice bath. The H-Beta catalyst for this reaction was obtained by heating the ammonium form of zeolite Beta (Zeolyst, CP814E) at 1 K min⁻¹ to 823 K and holding for 12 hours in a furnace oven. This procedure is slightly different from that in the acylation experiments as the calcination procedure for the Diels-Alder experiments was copied from literature relating to similar Diels-Alder experiments.^[53]

4.2.5 Product Analysis

In each experiment a small sample $(200 \ \mu L)$ was taken from the reaction mixture for analysis prior to reaction. Conversion was defined as follows:

$$Conversion = \frac{C_{initial} - C_{final}}{C_{initial}}$$

where concentration is in mol L^{-1} .

Yield was defined with the same units as:

$$Yield = \frac{C_{product}}{C_{reactant, initial}}$$

Selectivity was defined as:

$$Selectivity = \frac{C_{product}}{C_{reactant, initial} - C_{reactant, final}}$$

Liquid samples were analyzed by gas chromatography (Agilent 7890A) equipped with a flame ionization detector. An HP-Innowax column (Agilent) was used with the following temperature program: hold at 313 K for 4.5 min, 10 K min⁻¹ ramp to 523 K and a final hold for 3 minutes. Reaction side products were identified with a GC-MS (Shimadzu QP2010 Plus) equipped with an HP-Innowax column following the same temperature program.

Retention times and calibrations of reactants and products that could be purchased were determined from calibration solutions. For 2-acetyl-5-ethylfuran, the GC response factor was estimated as equivalent to that of 3-acetyl-2,5-dimethylfuran (Aldrich, 98%). For alkylfurans that are not commercially available (2-ethyl-5methylfuran and 2,5-diethylfuran) the GC response factors were estimated from the additive increase in response factor with additional carbons based on furan, methylfuran and dimethylfuran. In acylation experiments, response factors for diacylated side products were estimated as same as those for the mono-acylated species. In hydrodeoxygenation experiments, the response factor of the tetrahydrofuran overhydrogenated side product was estimated to be equal to that of the desired alkylfuran product, and the response factor of the alcohol intermediate was estimated to be equal to that of the acetylfuran reactant. Finally, in Diels-Alder experiments, the response factor of the alkylated side product was estimated from the additive increase in response factor with additional carbons based on ethyltoluene and diethylbenzene. The response factor of 2,5-heptanedione and 2,3-dimethyl-2-cyclopenten-1-one were estimated to be the same as that estimated for 2-ethyl-5-methylfuran. The response factor for the two adduct side products were estimated to be the same as that of the ethyltoluene side product.

When error is reported, it is the standard error of the mean of two or three experiments.

4.3 Results

4.3.1 Para-Ethyltoluene

4.3.1.1 Acylation

Friedel-Crafts acylation of methylfuran (1) with acetic anhydride was investigated using Brønsted acid zeolites. Table 4.1 lists the microporous volume, Si/Al ratio and estimated particle size of each material. A Lewis acidic Zr-Beta material was tested for the last Diels-Alder step. XRD patterns and SEM images are reported in Figures 4.3 and 4.4. The micropore volumes and XRD patterns are consistent with the sample's pore architecture, and both the XRD patterns and SEM

images are consistent with pure phases without any crystalline or amorphous impurities.

Catalyst	Si:M*	Si:M (XRF)	Micropore Volume [cm ³ /g]	Estimated Crystal Size from SEM [nm]
H-Beta	12.5	12.3	0.18	100
H-Y	15	18.2	0.28	500
H-ZSM-5	11.5	12.9	0.13	300
Si-Beta	n/a	n/a	0.20	10,000
Zr-Beta	n/a	166 [†]	0.20	5000

Table 4.1: Catalyst physical properties and chemical composition. *As reported by Zeolyst International. †Determined by ICP-AES. n/a= not applicable



Figure 4.3: XRD Patterns of (a) Zeolyst H-Beta CP814E, (b) Zeolyst H-Y CBV720, (c) Zeolyst H-ZSM-5 CBV 2314, (d) Si-Beta, (e) Zr-Beta



Figure 4.4: SEM of SEM of zeolite catalysts (a) Zeolyst H-Beta CP814E, (b) Zeolyst H-Y CBV720, (c) Zeolyst H-ZSM-5 CBV 2314, (d) Si-Beta, (e) Zr-Beta

Three different frameworks of Brønsted acid zeolites were tested with similar Si/Al ratios, as well as a siliceous Beta zeolite without any aluminum sites. The reaction was selective to the desired product 2-acetyl-5-methylfuran (**2**) over all the aluminum zeolite catalysts, but the reaction proceeded much more quickly over H-Beta (Table 4.2, lines 1-3). Superior aromatic acylation reactivity on H-Beta compared

to H-Y and H-ZSM-5 has been reported for the acylation of toluene with isobutyryl chloride,^[122] as well as acylation of anisole with acetic anhydride.^[123] Two side products were detected in small amounts (and are included in the carbon balance reported in Table 4.2). First, an isomer where methylfuran was acylated at the 3 or 4 position was detected at less than 0.9% yield. Second, a product with a molecular weight of 166 g mol⁻¹, consistent with **2** undergoing a second acylation was present at less than 0.4% yield. Siliceous zeolite Beta and the uncatalyzed reaction resulted in very little product, even over an extended reaction period (Table 4.2, line 4 and 5). Higher conversions on H-Beta were achieved with longer reaction times, as shown in Figure 4.5. Even while the reaction slows down significantly at longer reaction times, the selectivity remains high, above 90%. Spent catalyst (after one 15 minute run) that was regenerated via calcination and tested again (Table 4.2, line 7) had a loss of approximately 5% in conversion and yield, but maintained selectivity above 98%.

Catalyst	Time [min]	1 Conversion [%]	2 Yield [%]	Carbon Balance [%]
H-Beta	5	64.3	62.9	98.9
H-Y	15	38.6	35.9	98.2
H-ZSM-5	15	25.5	23.7	98.7
Si-Beta	360	1.8	0.5	
No Catalyst	360	4.5	0.1	
H-Beta	15	82.1±2.2	81.3±2.4	100.5±0.2
H-Beta (regenerated)	15	76.8	75.4	99.5

Table 4.2: Acylation of methylfuran with acetic anhydride. Conditions: 5 mL methylfuran in 15 mL acetic anhydride, 453K, 200 psi, 0.1 g catalyst



Figure 4.5: Acylation of methylfuran with acetic anhydride. Conditions: 5 mL methylfuran in 15 mL acetic anhydride, 453 K, 200 psi, 0.1 g H-Beta catalyst

4.3.1.2 Hydrodeoxygenation

The addition of an electron withdrawing acetyl group to **1** decreases the rate of the subsequent Diels-Alder step. In normal demand Diels-Alder reactions, with ethylene used as the dienophile, electron donating groups are needed on the diene (i.e., the furan compound). In the case of **2**, the oxygen in the ring is electron-donating, but the acetyl group is too electron withdrawing for the reaction to proceed easily. While reactions between ethylene and furans with electron withdrawing groups take place in low yields on Lewis acid zeolites,^[54] we chose instead to hydrodeoxygenate the intermediate and reduce the acetyl group to an ethyl group. The ethyl group is electron donating on the diene and the Diels-Alder reaction may proceed with less difficulty, resulting in higher yields. It is possible to employ the direct alkylation of methylfuran with ethylene to add an ethyl group, instead of this two-step process, but the alkylation

of furan with ethylene produces poor yield of the desired ethylfuran product.^[124] The hydrodeoxygenation (HDO) step utilizes cooper chromite which is not compatible with acetic anhydride. It is therefore necessary to isolate **2** before proceeding with HDO. Since **2** is available from commercial sources, it is used for the HDO step.

Copper chromite was used to reduce the acetyl group of 2-acetyl-5methylfuran (2). The evolution of this reaction over time is shown in Figure 4.6. There was a small amount of over-hydrogenated 2-ethyl-5-methyltetrahydrofuran (2E5MTHF) side product, as well as 2,5-heptanedione, the hydrolysis product of **3**. The alcohol intermediate (1-(5-methylfuran-2-yl)ethan-1-ol), similar to the furfuryl alcohol intermediate in HDO reactions of furfural over copper chromite,^[125] was found in the product after one hour of reaction, but its formation was suppressed with longer reaction time. As shown in Figure 4.6, conversion and selectivity were very high (>89%) after 5 hours of reaction for the reduction of 2 to 3. The subsequent Diels-Alder step can be carried out in the same solvent (tetrahydrofuran) and should not be affected by side products of the hydrodeoxygenation. Therefore, the copper chromite can simply be filtered from the product before being used in the Diels-Alder reaction. Since **3** is not available commercially, the reaction was scaled up (as detailed below) to have sufficient material to test multiple catalysts. The product of two scaled up reactions (300 mL total) was filtered to remove copper chromite and desiccated with 4A molecular sieves to remove water. It was then used as reactant for the last Diels-Alder step.



Figure 4.6: Hydrodeoxygenation of 2-acetyl-5-methylfuran. Conditions: 0.12 g mL⁻¹ 2acetyl,5-methylfuran in tetrahydrofuran, 503K, 400 psi H₂, 0.1 g copper chromite

4.3.1.2.1 Scale-Up of Hydrodeoxygenation Step

The HDO reaction of 2-acetyl-5-methylfuran (2) was scaled up gradually from 5 to 20 times the initial reactant amount (Table 4.3), keeping the catalyst amount to the minimum needed to achieve the results obtained in the smaller scale experiments (Table 4.3, line 1). By scaling up the reactant concentration, a conversion of **2** of up to 99.8% was achieved (for a scale up factor of 15 times). At higher reactant amount (40 g of **2**, corresponding to a scale up factor of 20) the conversion was limited to 80.0%, possibly due to the effect of mass transport between the three phases involved in the reaction (hydrogen gas, reactant liquid mixture and the solid catalyst), or insufficient catalytic sites. The highest yield of **3** was also achieved for the 15x scale up factor

(81.5%). The ring-hydrogenated side product (2-ethyl-5-methyltetrahydrofuran) was not detected in the experiments carried out in the 1000mL reactor. The only observed side product was the partly hydrogenated alcohol intermediate 1-(5-methylfuran-2yl)ethan-1-ol (estimated <6.0% yield). This side product is easier to separate via microdistillation, as it has a higher boiling point than **3**; whereas the tetrahydrofuran side product has the same boiling point. The isolated yield of pure **3** from a 10x scale up run (20 g of **2**) with the microdistillation unit was approximately 40%.

Table 4.3: Conditions and results of scaling up the hydrodeoxygenation reaction to 2ethyl-5-methylfuran

Scale-up factor [v _{reactants}]	P [Psi]	m _{catalyst} [g]	g 2A5MF: g catalyst	Time [h]	Conversion [%]	Yield [%]
x1	400	0.1	20	5	99.2±0.05	89.4±1.1
x5	200	0.5	20	2	90.3	76.9
x10	200	0.5	40	2	83.8	86.5
x15	400	1.5	20	4	99.8	81.5
x20	400	2.0	20	4	80.0	78.6

The conditions for the 15x scale up were also applied to the HDO of 2-acetyl-5-ethylfuran (**9**) resulting in a conversion of 99.6% and a 2,5-diethylfuran (**10**) yield of 80%. In this case, there was a 4% yield of the alcohol intermediate 1-(5-ethylfuran-2yl)ethan-1-ol as side product.

4.3.1.3 Diels-Alder Cycloaddition and Dehydration

In the final step to prepare *p*-ethyltoluene (**4**), ethylene was combined with **3** over zeolite catalysts. Cycloaddition between ethylene and **3** followed by dehydration of the oxanorbornene Diels-Alder adduct resulted in the formation of the *p*-aromatic species. The same Brønsted acid zeolites screened for the acylation reaction were screened for this Diels-Alder step (see the characterization reported in Table 4.1). In addition, a Zr-Beta Lewis acid zeolite was screened as these catalysts have been reported to show high selectivity for Diels-Alder cycloaddition and dehydration of dimethylfuran to *p*-xylene.^[105] As shown in Table 4.4, the yield of the desired product was highest on H-Beta catalyst (67%). The *para* isomer selectivity (selectivity to *para* out of all ethyltoluene isomers) was also highest on this catalyst at 99.5%.

Table 4.4: Diels-Alder cycloaddition and dehydration of 2-ethyl-5-methylfuran on various catalysts. Conditions: 0.09 g mL⁻¹ 2-ethyl-5-methylfuran in tetrahydrofuran, 523 K, 400 psi C₂H₄, 18 hours, 0.065 g catalyst. *0.32 g catalyst used.

Catalyst	3 Conversion [%]	4 Yield [%]	para Selectivity [%]
H-Beta	95.5±1.4	67.3±1.4	99.48±0.03
H-Y	33.0	15.9	97.8
H-ZSM-5	26.2	13.0	97.0
Zr-Beta*	73.6	42.1	99.1
H-Beta (regenerated)	85.4	58.9	99.3

Several side products were identified for this reaction: 2,5-heptanedione (from the hydration of **3**), 2,3-dimethyl-2-cyclopenten-1one (the intramolecular aldol condensation product of 2,5-heptanedione), butyltoluene (produced from alkylation of **4**) and two intermediates with a molecular weight of 138, consistent with the weight of the Diels-Alder cycloadduct before it is dehydrated. These two intermediates could be the oxanorbornene cycloadduct and its ring-opened isomer, analogous to those intermediates identified for the same reaction with dimethylfuran.^[102] GC-MS patterns of these side products are included in Appendix B.4. The selectivity of side products on each catalyst is detailed in Table 4.5.

Table 4.5: Diels-Alder cycloaddition and dehydration of 2-ethyl-5-methylfuran on various catalysts. Conditions: 0.09 g mL⁻¹ 2-ethyl-5-methylfuran in tetrahydrofuran, 523 K, 400 psi C₂H₄, 18 hours, 0.065 g catalyst. *0.32 g used in reaction.

	H-Beta	H-Y	H-ZSM-5	Zr-Beta*
3 Conversion [%]	95.5±1.4	33.0	26.2	73.6
4 Yield [%]	67.3±1.4	15.9	13.0	42.1
Selectivities [%]				
Butyltoluene	4.7±0.6	4.4	20.4	6.1
2,5 Heptanedione	1.1±0.4	5.6	5.0	0.0
2,3-dimethyl-2-cyclopenten-1- one	4.6±0.8	4.8	4.6	19.0
Adduct 1	2.1±0.1	1.7	2.2	1.1
Adduct 2	2.1±0.1	1.5	0.9	0.0
meta-Ethyltoluene	0.19±0.01	0.42	0.61	0.31
ortho-Ethyltoluene	0.18±0.01	0.69	0.93	0.23
Carbon Balance	86.5±1.1	89.2	95.9	88.2

Previous investigations of the Diels-Alder cycloaddition and dehydration of dimethylfuran and ethylene identified H-Y as a superior catalyst to H-Beta under solvent-free conditions.^[101] Later it was reported that, in heptane, H-Beta was more efficient for this reaction.^[53] In this work THF is used as a solvent, and it is clear that, as in heptane solvent, H-Beta is more active than H-Y for this chemistry. The conversion is much lower on H-Y than H-Beta, as is the selectivity to *p*-ethyltoluene.

H-ZSM-5 exhibits similar low conversion and low selectivity compared to H-Beta. Much of the selectivity on H-ZSM-5 is lost to over-alkylated butyltoluene, which is not surprising considering H-ZSM-5 is used for the alkylation of benzene with ethylene in the Mobil-Badger process.^[126]

Due to the low incorporation of Zr in the Zr-Beta sample, significantly more catalyst is needed to match the acid site concentration provided by the Brønsted-acidic materials. More than 800 mg of catalyst would be needed to provide the same acid site concentration. This is a significant demand of catalyst since the synthesis of these types of Lewis acids typically yield about 2 grams of product per batch. Thus, only 320 mg of Zr-Beta was used to screen its activity for the Diels-Alder step. As shown in Table 4.4, the overall selectivity to *p*-ethyltoluene as well as *para* isomer selectivity were lower for Zr-Beta compared to H-Beta. Comparing these catalysts on a per site basis, turnover on Zr-Beta was higher: 12 mol p-ethyltoluene/mol Zr/h compared to 7.5 mol p-ethyltoluene/mol Al/h on H-Beta. In previous studies on Zr-Beta for dimethylfuran cycloaddition, its high selectivity was credited to low selectivity to the hydrolysis pathway.^[105] In this work, however, 19% selectivity to 2,3-dimethyl-2cyclopenten-1-one (the intramolecular aldol condensation product of 2,5heptanedione) clearly shows that this hydrolysis pathway is prominent on Zr-Beta. While the formation of the dione is reversible and may go back to regenerate the furan, the lack of dione detected in the product indicates that instead of this route, the dione is irreversibly trapped as the cyclopentenone. Given the lower overall and *para* selectivity of Zr-Beta, it is clear that H-Beta is the superior catalyst of those tested for the Diels-Alder step.

Selectivities of side products over the course of reaction time on H-Beta is shown in Table 4.6. Slightly higher *para* selectivity of 99.7% was able to be achieved in 3 hours of reaction, but at very low yield. Much higher yields achieved at longer reaction times still exhibited excellent *para* selectivity of 99.5%. Increasing reaction time increased selectivity to butyltoluene, which would be expected due to the longer residence time of ethyltoluene product. Previous work on *p*-xylene production from dimethylfuran has shown that the hydrolysis path way is reversible and selectivity to the dione decreases with increasing reaction time, as dimethylfuran is consumed and equilibrium shifts in favor the furan over the dione.^[53, 105] The same was observed here as the selectivity to heptanedione decreased with increasing reaction time.

Table 4.6: Diels-Alder cycloaddition and dehydration of 2-ethyl-5-methylfuran on H
Beta over time. Conditions: 0.09 g mL ⁻¹ 2-ethyl-5-methylfuran in
tetrahydrofuran, 523 K, 400 psi C ₂ H ₄ , 0.065 g H-Beta

	3 h	6 h	12 h	18 h
3 Conversion [%]	27.7	80.6	89.0	95.5±1.4
4 Yield [%]	10.5	55.5	52.4	67.3±1.4
para Selectivity [%]	99.7	99.5	99.5	99.5±0.05
Selectivities [%]				
Butyltoluene	2.2	3.6	4.8	4.7±0.6
2,5 Heptanedione	9.5	5.1	2.8	1.1±0.4
2,3-dimethyl-2-	12.4	4.1	67	16+08
cyclopenten-1-one	12.4	4.1	0.7	4.0±0.8
Adduct 1	1.5	2.2	2.4	2.1±0.1
Adduct 2	2.4	2.1	2.2	2.1±0.1
meta-Ethyltoluene	0.10	0.17	0.14	0.19±0.01
ortho-Ethyltoluene	0.0	0.16	0.18	0.18±0.01
Carbon Balance	90.6	88.9	80.5	86.4±1.1

The regenerability of H-Beta for this reaction was investigated by calcining spent H-Beta catalyst and testing it under the same conditions (Table 4.4, line 5). There is an approximately 10% loss in conversion after reactivation and a very small loss in *para* isomer selectivity, but no loss in overall selectivity to **4**.

The side products from the hydrodeoxygenation are expected to be spectators in the Diels-Alder reaction. Unconverted 2-acetyl-5-methylfuran reactant will not undergo cycloaddition due to the electron withdrawing acetyl group. The other main side-product is over-hydrogenated 2-ethyl-5-methyltetrahydrofuran, which cannot undergo cycloaddition because it is not aromatic. To confirm that there is no detrimental effect of the HDO side products, **3** was also isolated with a microdistillation unit and tested neat in tetrahydrofuran. No significant difference was found between using the filtered product and the isolated product (Table 4.7).

Table 4.7: Diels-Alder cycloaddition and dehydration of 2-ethyl-5-methylfuran. Conditions: 0.09 g mL⁻¹ 2-ethyl-5-methylfuran in tetrahydrofuran (20 mL total), 523K, 400 psi C₂H₄, 18 hours, 0.065 g H-Beta

Reactant Source	3 Conversion [%]	4 Yield [%]	para Selectivity [%]
3 from filtered hydrodeoxygenation product	95.5±1.4	67.3±1.4	99.5±0.03
3 isolated and diluted in THF	95.2±0.1	68.4±1.9	99.4±0.06

Taking into account the acylation yield after 1 hour of reaction (88.9%), the hydrodeoxygenation yield with copper chromite (89.4%) and the yield of **4** in the last Diels-Alder step (67.3%), the overall yield of **4** from methylfuran is 53.5% and the overall selectivity is 59.5%. The dehydrogenation of generate the desired p-methylstyrene product (**5**).

4.3.1.4 One-pot Acylation and Diels-Alder Cycloaddition

Although it was explained earlier that the electron-withdrawing acetyl group significantly slows down the Diels-Alder step, attempts were made to combine the acylation and cycloaddition steps in a one-pot reaction. Since the superior catalyst in both steps was H-Beta, it was tested as a catalyst to do the reactions in sequence where methylfuran is acylated to 2-acetyl-5-methylfuran, which then reacts with ethylene to produce *p*-methylacetophenone. In a 5 hour experiment at 503 K with 0.1 M methylfuran and 0.1 M acetic anhydride in 15 mL acetic acid, 0.1 g H-Beta and 500 psi C₂H₄, 95% of methylfuran was converted with yields of only 29% 2-acetyl-5methylfuran and 3.7% methylacetophenone. Additionally, some of the methylfuran reacted with ethylene before acylation resulting in 3% yield of toluene. As Lewis acid zeolites have been shown to be more reactive for Diels-Alder cycloaddition and dehydration of furans with electron-withdrawing groups,^[54, 55] Lewis acidic Sn-Beta was also tested for this reaction at the same conditions. This resulted in 80% conversion of methylfuran, 16% yield to 2-acetyl-5-methylfuran, 29% yield to toluene and no methylacetophenone. The high yield to toluene on this catalyst demonstrates that it is not suitable for this one-pot reaction where it is required that methylfuran acylation be faster than methylfuran cycloaddition to produce the desired methylacetophenone. Thus, due to the inability to find suitable conditions for combining the acylation and Diels-Alder reactions, the three-step process described was pursued to reach appreciable yields of *p*-ethyltoluene.

4.3.2 Para-Diethylbenzene

p-Diethylbenzene is used as a desorbent in the UOP Parex process to selectively make *p*-xylene,^[127] and divinylbenzene is used extensively as a cross-

linking agent with styrene. Analogous to the traditional production of *para*ethyltoluene, *para*-diethylbenzene may be synthesized from the alkylation of ethylbenzene. Using a modified H-ZSM-5 catalyst 99.6% *p*-diethylbenzene has been reported for the alkylation of ethylbenzene with ethylene, but with excess ethylbenzene and at less than 30% conversion of ethylene and ethylbenzene.^[11] Divinylbenzene can then be obtained from diethylbenzene via catalytic dehydrogenation, as in the production of styrene. Here, we describe how to prepare divinylbenzene from furan, another feedstock that can be produced renewably from hemicellulosic biomass.

4.3.2.1 Acylation of furan

As illustrated in Figure 4.2, two acetyl groups need to be added to furan (**6**) to prepare diethylbenzene (**11**). Figure 4.7, shows the results for acylation of **6** and **8** (as well as **1** for reference). The acylation of **6** proceeds selectively to form 2-acetylfuran (**7**). Only a trace amount (0.03% yield) of 3-acetylfuran was detected in the product. Another side product, consistent with **7** undergoing a second acylation (MW=152), was found at approximately 0.2% yield. Because the acetyl group is electron withdrawing, this second acylation will not occur rapidly on the other side of the furan ring.^[128, 129] In fact, any second acylation would most likely add to the acetyl group itself, as occurs in the acylation of 2-acetylthiophene and acetophenone.^[130, 131] Due to this constraint, the first acetyl group was reduced before the addition of the second acetyl group.



Figure 4.7: Acylation of furans with acetic anhydride. Conditions: 5 mL furan, 2methylfuran or 2-ethylfuran in 15 mL acetic anhydride, 453 K, 200 psi, 15 minutes, 0.1 g H-Beta catalyst

4.3.2.2 Hydrodeoxygenation of 2-Acetylfuran

Following the same protocol used for the hydrodeoxygenation of **2** resulted in no conversion of 2-acetylfuran (**7**). Even at an extended reaction time of 10 hours, there was still no 2-ethylfuran (**8**) observed. Attempts were made to improve the catalyst activity by pre-reducing it, as has been described in the reduction of furfural with copper chromite,^[125] however this did not improve conversion. At a much higher ratio of catalyst to reactant, however, the hydrodeoxygenation to **8** was successfully completed at high conversion (99%) and 84% selectivity, which is slightly lower selectivity than observed in the hydrodeoxygenation of **2** (Figure 4.8). The only side product detected was the over-hydrogenated 2-ethyltetrahydrofuran at 6% average yield.



Figure 4.8: Hydrodeoxygenation of acetylfurans. Conditions: 0.065 g mL-1 2acetylfuran in tetrahydrofuran with 0.5 g copper chromite or 0.11-0.12 g mL⁻¹ 2-acetyl-5-ethylfuran or 2-acetyl-5-methylfuran in tetrahydrofuran with 0.1 g copper chromite, 503 K, 400 psi H₂, 5 hours

4.3.2.3 Acylation of 2-Ethylfuran

2-ethylfuran (8) was acylated at the same conditions as 1 and 6 using acetic anhydride and zeolite H-Beta. As shown in Figure 4.7, this catalyst system exhibits excellent selectivity to 2-acetyl-5-ethylfuran (9). The conversion of alkylfurans was higher than furan because the alkyl group is electron donating and accelerates electrophilic aromatic substitution reactions such as this one. As with the other reactants, two small side products were detected. The product acylated at a different position was found in 0.4% yield, and the di-acetylated product was found at 0.6% yield. 9 was purified prior to the second dehydrogenation step by distilling off acetic anhydride and acetic acid at ~413 K using a microdistillation unit. The isolation of 9 was necessary due to the incompatibility of acetic anhydride and acetic acid with copper chromite, as described earlier. The isolation yield of **9** from the product mixture of a 15 minute reaction was 82%.

4.3.2.4 Hydrodeoxygenation of 2-Acetyl-5-ethylfuran

9 was reduced following the same protocol for the reduction of **2**, and produced the desired product 2,5-diethylfuran (**10**) in 72% yield (Figure 4.8). A compound with a molecular weight of 246 g mol⁻¹ was the only side product found. This molecular weight is consistent with the dimerization of two 2-vinyl-5-ethylfuran intermediates. As with the previous process for *p*-ethyltoluene, the product of this reaction was filtered from the catalyst and used for the last Diels-Alder step.

4.3.2.5 Diels-Alder Cycloaddition and Dehydration

The cycloaddition and dehydration of 2,5-diethylfuran (**10**) with ethylene to *p*diethylbenzene (**11**) exhibits a similar yield of 71.3 \pm 4.3% (at 92.0 \pm 4.2% conversion) compared to **3** under the same reaction conditions. The isomer selectivity of the desired *p*-diethylbenzene was 99.0%, and a small amount of *m*-diethylbenzene and *o*diethylbenzene was also observed, accounting for ~0.6 and 0.4% of total diethylbenzene, respectively. In this reaction, only three major side products were found. The hydration product of **10** is 3,6-octanedione. While this dione was not detected, the intramolecular aldol condensation product of 3,6-octanedione (2-methyl-3-ethyl-2-cyclopenten-1-one) was found at ~3.9% selectivity. The most abundant side product was the alkylated product at 7.4% selectivity. There was also one side product with a molecular weight of 152, consistent with weight of the Diels-Alder intermediate cycloadduct before dehydration, found at ~5.2% selectivity. *p*-Divinylbenzene (**12**) may then be obtained from the dehydrogenation of **11**.

4.4 Discussion

In the first step of the process described here, furan acylation proceeded quickly and selectively. The acylation of furans is more selective compared to the acylation of aromatic hydrocarbons, as acylation at the alpha carbons of furans is highly favored.^[124, 132, 133] Although zeolites were found to greatly increase *para* selectivity for acylation of toluene compared to traditional Lewis acids like aluminum chloride,^[115] they still do not allow for a very selective substitution at a single position, as we have observed for the acylation of furans. As mentioned earlier, removal of the polar product from the active site can lead to deactivation during the acylation of aromatic hydrocarbons like toluene and anisole over zeolites. In the batch reactions in this study, catalyst deactivation was not quantified, but other studies have found the product yield to decrease with time-on-stream. This deactivation may also be caused by product retention in the zeolite pores.^[134, 135] A more detailed understanding of the reaction and deactivation mechanisms of furan acylation is the subject of the next chapter.

Up to 80% aromatic yield has been reported previously for Diels-Alder cycloaddition with dimethylfuran at high conversion, slightly higher than the yields obtained for 2-ethyl-5-methylfuran and 2,5-diethylfuran reported here. The side products of the cycloaddition of furans with ethyl groups are analogous to those reported previously in studies of dimethylfuran. A study of side products for dimethylfuran cycloaddition and dehydration with ethylene on H-Y zeolite found 2,5hexanedione (a byproduct from dimethylfuran hydrolysis), an alkylated *p*-xylene (*p*methyl-propylbenzene), and a cycloadduct intermediate.^[102] For the reaction over various solid acids, Wang et al. reported that the major side products were 2,5hexanedione and dimethylcyclohexenone, the latter of which is an isomer of the

cycloadduct intermediate identified in the previous study. They also reported finding the intramolecular aldol condensation product of 2,5-hexanedione at high conversions.^[103] A lower rate of hydrolysis and dione formation from dimethylfuran has been proposed for higher selectivity to *p*-xylene observed on Zr-Beta compared to H-Beta,^[105] but with 2-ethyl-5-methylfuran as reactant this is clearly not the case, as the intramolecular aldol condensation product of the dione is found at 19% selectivity on Zr-Beta (Table 4.5).

While many studies use nonpolar solvent for this reaction, tetrahydrofuran is used in this study so that the same solvent can be used in the last two steps, thus requiring only a filtration of the copper chromite catalyst before the Diels-Alder step. In the Diels-Alder cycloaddition and dehydration of dimethylfuran (DMF), the use of heptane solvent was found to reduce selectivity to oligomers and 2,5-hexanedione (from hydrolysis of DMF), resulting in increased p-xylene selectivity compared to reactions without solvent.^[101] It was suggested that reduction of these hydrolysis pathways was related to the hydrophobicity of the solvent. Later, however, Wijaya et al. reported enhanced *p*-xylene production rate over zeolite Beta catalyst when dioxane or tetrahydrofuran were used as solvent compared to heptane. It should be noted that on Brønsted and Lewis acidic Beta zeolite catalysts, two regimes were identified for the production of p-xylene from DMF. At low (<2 mM) acid site concentration, the initial rate (<20% conversion) increases linearly with acid site concentration in what is believed to be a dehydration-limited regime and at higher acid site concentrations the initial rate plateaus in what is believed to be a cycloadditionlimited regime. Based on the plateau of the rate in this regime and modeling studies, the cycloaddition is believed to be uncatalyzed.^[105, 136, 137] Wijava found solvent only

affected p-xylene rate in the dehydration-limited regime and attributed the greater yield of *p*-xylene in polar solvents to enhancement in the dehydration rate.^[104] As shown in Table 4.8, the polar THF solvent also results in higher yield and *para* selectivity in the case of 2,5-diethylfuran Diels-Alder cycloaddition and dehydration (at slightly different reaction conditions than previously discussed). While the use of heptane solvent reduced selectivity for the hydrolysis pathway compared to solvent-free conditions, it is clear that the enhancement in selectivity cannot be attributed to solvent hydrophobicity, since further increases are achieved with polar solvents. Wijaya provided evidence that the solvent is affecting dehydration, but considering that the cycloaddition is likely occurring uncatalyzed in solution, it may be this step that the solvent is accelerating, and solvent effects have been described for both dehydration^[138] and Diels-Alder reactions.^[139, 140] While understanding these solvent effects was not the intent of this work, it is a worthwhile subject that is lacking in the growing literature for Diels-Alder cycloaddition and dehydration of furans on these materials.

Table 4.8: Diels-Alder cycloaddition and dehydration of 2,5-diethylfuran. Conditions: 523 K, 400 psi C₂H₄, 24 h, 0.1 g H-Beta, 0.1 g ml⁻¹ 2,5-diethylfuran in solvent

Solvent	10 Conversion [%]	11 Yield [%]	para selectivity [%]
Heptane	97.3	50.7	96.0
THF	90.0	59.4	99.0

4.5 Conclusions

A sequence of catalytic reactions has been demonstrated to prepare *p*ethyltoluene and *p*-diethylbenzene from renewable carbon sources. For *p*-ethyltoluene,
first biomass-derived methylfuran (1) was acylated over H-Beta catalyst with acetic anhydride. This anhydride could be produced from acetic acid obtained from biomass via pyrolysis.^[141, 142] Second, 2-acetyl-5-methylfuran (2) was reduced to 2-ethyl-5methylfuran (3) with hydrogen over copper chromite catalyst in high yield and selectivity. Finally, **3** underwent Diels-Alder cycloaddition and dehydration with ethylene over H-Beta catalyst to produce the desired *para* isomer of ethyltoluene in high selectivity. In addition to using a renewable feedstock (methylfuran) and the possibility to use other bio-derived reactants, this process lead to a 99.5% selectivity to the para isomer, a result that is not reported at high conversion by traditional routes of alkylation or acylation of toluene. This methodology was also demonstrated with the preparation of diethylbenzene (11), which also resulted in high para aromatic isomer selectivity of 99.0%. Overall, this process allows larger, more valuable molecules to be produced from bio-derived feedstocks. Acylation of furans, in particular, is proven to be an extremely efficient means of creating carbon-carbon bonds and incorporating additional functionality to bio-derived furans. The selectivity of furan acylation makes it an especially valuable reaction that can be used advantageously to target specific isomers, as demonstrated in this chapter. Numerous molecules and valuable products could be prepared using the methodology demonstrated here and other acylating agents besides acetic anhydride. For example, an extension of the chemistry described here was recently applied to the production of renewable surfactants from furans.^[143]

Chapter 5

ACYLATION OF METHYLFURAN USING BRONSTED AND LEWIS ACID ZEOLITE CATALYSTS

5.1 Introduction

The earliest examples of Friedel-Crafts acylation were carried out using homogenous Lewis acid catalysts such as aluminum chloride.^[144] Brønsted acid zeolites were subsequently found to catalyze this reaction with advantages over the classical Lewis acid catalysts in terms of separation, isomer selectivity and lower than stoichiometric catalyst amounts.^[115, 145, 146] The acylation of furans with Brønsted acid zeolites is a particularly efficient and selective means of forming C-C bonds and adding functionality to these bio-derived compounds.^[133, 134, 147, 148] In contrast to Brønsted acid zeolites that have framework trivalent metals like aluminum, solid Lewis acid zeolites are isomorphously substituted with tetravalent metals that have the properties of isolated Lewis acid sites in the framework. These materials have shown remarkable activity and selectivity for transformations of biomass like glucose isomerization and reduction and etherification of hydroxymethylfurfural,^[1, 21, 57] but they have yet to be investigated for acylation. It is of interest to determine how Brønsted and Lewis acid zeolites compare in Friedel-Crafts acylation of bio-derived furans and in this chapter, the rate and mechanism of methylfuran acylation with acetic anhydride to form 2-acetyl-5-methylfuran (2A5MF) and acetic acid (Figure 5.1) are compared for a number of Brønsted and Lewis acid zeolites.



Figure 5.1: Acylation of methylfuran with acetic anhydride to form 2-acetyl-5methylfuran and acetic acid from Wheland intermediate

The value of this reaction in the production of biomass-derived commodity chemicals has been demonstrated as a key step in the production of *para* aromatic species,^[148] and with fatty anhydrides this reaction can be used for the production of surfactants.^[143] Methylfuran may be produced from the hydrodeoxygenation of furfural, which is produced industrially from hemicellulosic feedstocks.^[4] Acetic anhydride is a suitable acylating agent as it requires much lower temperatures for reaction than acetic acid. A large fraction of the previous reports on zeolite-catalyzed acylation with acetic anhydride in the liquid phase focuses on toluene or anisole on aluminum zeolite Beta. These studies found that competitive adsorption between reactants and products contributes to deactivation and lower reaction rates, ^[91, 92, 111] and that an acylium ion, rather than ketene, is the acylating intermediate.^[120] Similarly, the mechanism of electrophilic aromatic substitution for homogeneous Lewis acids is known to proceed via the formation of an acylium ion from the interaction of the acylating agent and the Lewis acid catalyst. Solid Lewis acid catalysts have not yet been investigated for this chemistry and thus the reaction mechanism remains to be determined.

While the mechanism is known to include the acylium ion in Friedel-Crafts acylation with acetic anhydride, the rate-determining step depends on the specific electrophile and nucleophile involved and can be probed with kinetic isotope effects. A concerted single-step substitution of the acetyl group would result in a primary kinetic isotope effect for deuterated aromatics. When no primary kinetic isotope effect was observed in some Friedel-Crafts reactions, a two-step mechanism was suggested, involving the formation of a Wheland intermediate followed by deprotonation (see Figure 5.1).^[149] This Wheland complex is the origin of the positional selectivity observed for electrophilic aromatic substitution (EAS) reactions, where a late Wheland-like transition state leads to high positional selectivity. This complex is also stabilized by electron donating groups, which accounts for the acceleration of EAS reactions by electron donating substituents on the aromatic. Whether the formation of this intermediate is the rate determining step was found to be dependent on the strength of the electrophile and nucleophile at hand. In the case of strong electrophiles or strong nucleophiles, the highest energy transition state resembles the starting aromatic and the formation of the Wheland intermediate is rate determining. In the case of weak electrophiles or weakly basic aromatics, the highest energy transition state resembles the Wheland intermediate and the deprotonation of this intermediate is rate determining.^[144, 149, 150] If formation of the Wheland complex is rate determining, only a small secondary inverse kinetic isotope effect would be expected due to change from sp² to sp³ hybridization of the hydrogen on the aromatic.^[151] If deprotonation of the Wheland complex is rate determining, or if the mechanism is concerted, a primary kinetic isotope effect would be expected due to breaking of the hydrogen bond.^[151] Strong primary kinetic isotope effects 3.25 and 2.25 were observed for toluene and

benzene acylation, respectively, with acetyl fluoride catalyzed by antimony pentafluoride.^[152] For the acylation of *p*-xylene with isobutyl chloride catalyzed by aluminum chloride, the lack of primary kinetic isotope effect ruled out deprotonation as the rate determining step.^[153] Here the rate determining step was probed experimentally with a kinetic isotope effect study of furan acylation on Brønsted and Lewis acid zeolites.

A complication with the investigation of Lewis acid zeolites is characterization of the true active site. While the tetravalent metal may exist with four bonds coordinated to the framework as a "closed" site, it has also been found that one of these bonds may hydrolyze to create an "open" site with one hydroxyl group bound to the metal and a corresponding silanol group, as depicted in Figure 5.2. Baeyer-Villiger oxidation, Meerwein-Ponndorf-Verley reduction and glucose isomerization have all be shown to be catalyzed by an open [Sn]-Beta site,^[38, 85] which involves a Lewis-acidic tin but also a Brønsted-acidic silanol. Here, experiments and modeling both support an open active site for methylfuran acylation on [Sn]-Beta.



Fully Coordinated Closed Site

Hydrolyzed Open Site

Figure 5.2: Schematic representation of [Sn]-Beta open and closed sites

In this chapter, initial screening of Brønsted and Lewis acid zeolites using batch reactors revealed that |H,Zn|-[Al]-Beta, with both Lewis and Brønsted acid sites, had the highest turnover to desired 2A5MF product on a per gram basis. However, H-[Al]-Beta with a high Si/Al ratio of 138 had the highest turnover on a per site basis where the turnover was normalized by heteroatom content of the catalyst. The Lewis acid catalyst with the highest turnover on a per site basis was [Sn]-Beta. Then H-[Al]-Beta and [Sn]-Beta were studied in a flow system under differential conditions. Flow reactor studies revealed deactivation with time on stream on all catalysts attributed to the formation of large byproducts as well as product inhibition. It was found that running the reaction in gamma-valerolactone rather than neat acetic anhydride greatly increased the reaction rate. A primary kinetic isotope effect for furan acylation was observed on both catalysts, which suggests the same rate-determining step of deprotonation. Density functional theory calculations performed by collaborators provide further support that this is the rate-determining step for both catalysts. This modeling also revealed that the [Sn]-Beta active site is a Brønsted-acidic silanol and not the Lewis-acidic tin atom.

5.2 Experimental

5.2.1 Materials

The aluminum Brønsted acid forms of zeolite Beta were purchased from Zeolyst. Specifically, the hydrogen form of zeolite Beta (Zeolyst, CP811C, Si/Al=150), H-[Al]-Beta-150, was used as received and the ammonium form of zeolite Beta (Zeolyst, CP814E, Si/Al=12.5), H-[Al]-Beat-12.5, was calcined as follows: ramp 1 K min⁻¹ to 823 K, hold 12 hours. |H,Zn|-[Al]-Beta was synthesized based off of a method described by Biscardi, et al.^[154] H-[Al]-Beta-12.5 was ion exchanged with 5 mM ZnNO₃· $6H_2O$ (Sigma-Aldrich, 98%) (100 mL/ g zeolite) at 353 K for 9 hours. Then the catalyst was filtered and washed with DI water and dried at 353 K overnight. Finally, it was calcined at 773 K for 12 hours (1 K/min ramp rate). [Si]-Beta, [Sn]-Beta-HT, [Zr]-Beta and [Hf]-Beta were synthesized as reported previously.^[121] [Ti]-Beta was synthesized as described previously.^[211] [Sn]-Beta prepared via solid-state-ion-exchange (SSIE), [Sn]-Beta-SSIE was synthesized as described in literature,^[155] the only difference being that the calcination was carried out in air. The dealumination of the commercial sample in this technique was confirmed by X-Ray fluorescence which indicated Si/Al = 750.

Si/M ratios of each material were determined as indicated by either X-Ray fluorescence (XRF) with a Rigaku Supermini200 or by inductively coupled plasma atomic emission spectroscopy (ICP-AES) performed by Galbraith Laboratories (Knoxville, TN). For H-[Al]-Beta-150, n-propylamine adsorption was performed in order to ensure the Al content was as advertised. In this experiment, which was performed by the Xu group at the University of Delaware, Brønsted acid site density was measured via n-propylamine decomposition into propylene and ammonia using a flow reactor with an on-line Agilent 7890A gas chromatograph (GC) equipped with an HP-PLOT Q column. This was accomplished using a microreactor system where all gas lines between the location of n-propylamine introduction and the GC were heat traced with temperature maintained at or above 348 K. Approximately 50 mg of H-[Al]-Beta-150 was loaded into a quartz tube in the reactor and was heated to 773 K at a rate of 10 K/min in flowing He (100 mL/min) and held at 773 K for 45 min. Then, the sample was cooled to 373 K and exposed to flowing He saturated with n-

propylamine for 15 min via a bubbler. The sample was subsequently heated to 473 K and held for 90 min to desorb excess n-propylamine and ensure a 1:1 ratio of adsorbed n-propylamine to Brønsted acid sites. Finally, the temperature was increased to 773 K at a rate of 30 K/min. The GC sampling loop was immersed in liquid nitrogen to collect the desorbed reaction products, which were subsequently quantified via a thermal conductivity detector (TCD).

Micropore volume for all samples was determined with nitrogen physisorption in a Micromeritics 3Flex system using the t-plot method. Samples were degassed overnight at 523 K and backfilled with nitrogen prior to analysis. X-ray diffraction (XRD) patterns were collected using a Bruker D8 diffractometer with Cu K α radiation. The pattern was collected for 0.5 seconds at each increment of 0.02 degrees between 5 and 50 degrees. Scanning electron microscopy (SEM) images were recorded on a JEOL JSM 7400F at 10 μ A.

Na-exchanged [Sn]-Beta was prepared following a procedure adapted from literature.^[85] Specifically, 300 mg of [Sn]-Beta was mixed with 45 mL of 1 M NaNO₃ (Sigma-Aldrich, \geq 99%) in distilled water for 24 hours at room temperature. The catalyst was recovered by filtration over a ceramic filter (Chemglass, CG-1402-16) and washed 3 times with 1 M NaNO₃ (50 mL solution for each wash). Then the material was calcined at 853 K for 5 hours (5 K/min ramp). The Na/Sn determined by ICP-AES was 8.2.

Thermogravimetric analysis (TGA) on spent catalysts was collected on a Mettler Toledo TGA/DSC Thermal Gravimetric Analyzer with STARe software. Samples were heated at a rate of 5K/min under 80 mL/min of air flow. The first derivative (dTGA) of the TGA curves was calculated numerically using Origin. The

differential curves were smoothed with an FFT filter with the number of points specified as 100.

Extraction of retained organics on spent catalysts was performed as previously described^[86]: 30 mg of spent catalyst was dissolved in 1 g HF (Acros, 48%) and 2.6 g DI water and allowed to react for 1 hour at room temperature. The organic species in the mixture were extracted with methylene chloride and analyzed with a GC-MS (Shimadzu QP2010 Plus, HP-Innowax column).

5.2.2 Batch Reaction Experiments

For batch reaction experiments, 5 mL of 2-methylfuran (Sigma Aldrich, 99%, BHT-stabilized) and 15 mL of acetic anhydride (Sigma-Aldrich, ≥99%) were loaded into a 45 mL 4714 Parr reactor with 50 mg of catalyst and a magnetic stir bar for mixing. The reactor was pressurized with nitrogen to 200 psi, placed in an oil bath at a temperature of 383 K, and quenched with an ice bath after the desired reaction time. The reaction product was filtered from the catalyst with a 0.2 micron syringe filter (Corning). Product samples were analyzed by gas chromatography (Agilent 7890A) equipped with a flame ionization detector. An HP-Innowax column (Agilent) was used with the following temperature program: hold at 313 K for 4.5 min, 10 K min⁻¹ ramp to 523 K and a final hold for 3 minutes. Reaction side products were identified with a GC-MS (Shimadzu QP2010 Plus) equipped with an HP-Innowax column following the same temperature program.

For kinetic isotope effect experiments, 1 g furan (Aldrich, 99%) or 1.06 g furan-d₄ (Aldrich, 98 atom% D) and 3.2 g acetic anhydride (Sigma-Aldrich, \geq 99%) was loaded into a 10 mL vial with 50 mg catalyst and a magnetic stir bar and sealed with crimp seal septum (Chemglass, CG-4920-10). The vial was then placed in a

reactor block with oil at 393 K. After 20 minutes, the vial was quenched in an ice bath. The catalyst was filtered from the reaction product and analyzed as described above.

In another set of kinetic isotope effect experiments, 1.91 g acetic acid (Acros, 99.5%) or 1.94 g acetic acid-d (Sigma-Aldrich, 99 atom% D) was added to 1.875 g acetic anhydride (Sigma-Aldrich, \geq 99%) and 0.5 g 2-methylfuran (Sigma Aldrich, 99%, BHT-stabilized) and loaded into a 10 mL vial with 10 mg catalyst and a magnetic stir bar and sealed with crimp seal septum (Chemglass, CG-4920-10). The vial was then placed in a reactor block with oil at 378 K. After 10 minutes, the vial was quenched in an ice bath. The catalyst was filtered from the reaction product and analyzed as described above.

For batch experiments probing apparent activation energy with and without GVL, 0.5 g of methylfuran (Sigma Aldrich, 99%, BHT-stabilized), 1.865 g of acetic anhydride (Sigma-Aldrich, \geq 99%) and 2.42 g GVL (Sigma-Aldrich, \geq 99%) were loaded into a 10 mL vial with 10 mg catalyst and a magnetic stir bar and sealed with crimp seal septum (Chemglass, CG-4920-10). For reactions without GVL, 1 g methylfuran (Sigma Aldrich, 99%, BHT-stabilized) and 3.73 g acetic anhydride (Sigma-Aldrich, \geq 99%) were loaded in a 10 mL vial with 25 mg catalyst and a magnetic stir bar and sealed with crimp seal septum (Chemglass, CG-4920-10). Either H-[Al]-Beta-150 or [Sn]-Beta-HT was used as catalyst. The vial was then placed in a reactor block with oil at 383, 398 or 413 K. At 383 and 398 K, the reaction time was 10 minutes, and at 413 K the reaction time was 5 minutes. After the desired reaction time, the vial was quenched in an ice bath. The catalyst was filtered from the reaction product and analyzed as described above.

5.2.3 Flow Reaction Experiments

A flow reactor previously described in Chapter 3 was used to study the reaction under continuous flow conditions. Gamma-valerolactone (GVL) (Sigma-Aldrich, $\geq 99\%$) was used as solvent to reduce the concentration of acetic anhydride. This was necessary because the back pressure regulator (Equilibar, EB1ULF1) diaphragm (Polyimide-5) and o-ring (Viton) is sensitive to acetic anhydride concentrations in excess of 50% v/v. A few experiments carried out without the addition of GVL were performed with a stainless steel diaphragm and Kalrez o-ring. Typically, 45.5g methylfuran, 150 mL acetic anhydride and 200 mL GVL were supplied at 4 mL/min with an HPLC pump (Alltech) at 200 psi. The reactor consists of ¹/₄ inch (6.4 mm) stainless steel tube between two VCR fittings. 50 mg of uniformly sized catalyst pellets (80-120 U.S. mesh, 125-180 µm) was held by a VCR gasket (Swagelok, SS-4-VCR-2-10M) on the bottom and glass wool was used to hold the catalyst in place, filling the space up to the top VCR gasket. Unless otherwise stated, the reactor was submerged in the oil bath and heated under GVL flow until the desired temperature was reached; at that point, flow of the desired reaction mixture was started. For reactions at a flow rate of 4 mL/min, the first sample was taken after 15 min of time-on-stream and then periodically for the next 75 minutes. Experiments with H-[Al]-Beta-150 were run at 2 mL/min and the initial sample was taken after 30 minutes and then periodically for the next 150 minutes. A lower space velocity was used for this sample in order to get appreciable conversion and yield with 50 mg of catalyst. At each time point, 2 mL of sample was collected at the outlet and analyzed offline via gas chromatography (Agilent 7890A) equipped with a flame ionization detector. An HP-1 column (Agilent) was used with the following temperature

program: hold at 313 K for 4 min, 15 K min⁻¹ ramp to 473 K and a final hold for 1 minute.

5.3 Results and Discussion

H-[Al]-Beta zeolites result in a higher conversion of methylfuran to 2-acetyl-5methylfuran (2A5MF) compared to zeolite H-[Al]-Y or H-[Al]-ZSM-5.^[148] Beta has been shown to be superior for the acylation of other reactants with acetic anhydride,^[92, 123, 156] as well as with other acylation agents.^[122] Zeolite Beta has also been the subject of many other acylation studies, where other zeolite structures were not explicitly compared to Beta.^[111, 112, 117, 120, 133, 134, 157, 158] In addition, there is an array of Lewis acid zeolites formed by the isomorphous substitution of group IV metals (Ti, Zr, Sn, Hf) into the framework of zeolite Beta which can be compared to the Brønsted acid form of [Al]-Beta.

Here two Brønsted acid Beta zeolites were investigated: H-[Al]-Beta-12.5, with high aluminum content (Si/Al=12.5) and H-[Al]-Beta-150, with low aluminum content (Si/Al=150). Lewis acid Beta zeolites (Sn, Zr, Hf, Ti) were synthesized hydrothermally, and a siliceous zeolite Beta (Si-Beta) was synthesized hydrothermally as a control. Because this hydrothermal synthesis is slow (>14 days) and requires the use of HF, two other Lewis acid forms of Beta that are easier to synthesize were also investigated. First, a post-synthetic [Sn]-Beta was synthesized via solid-state ion exchange. This material, [Sn]-Beta-SSIE, was formed by grinding tin acetate with dealuminated H-[Al]-Beta-12.5 followed by calcination. This technique allows a much higher incorporation of tin compared to what is possible via a hydrothermal technique. Finally, a |H,Zn|-[Al]-Beta was synthesized via ion exchange between ZnNO₃ and H-[Al]-Beta-12.5. This material is known to have both Lewis and Brønsted acidity.^[26] The Si/M (M=heteroatom) and micropore volumes are reported in Table 5.1 for each material. XRF was found to not be reliable for determining Si/M ratios for materials with low heteroatom incorporation. Thus, XRF is used only for samples with low Si/M ratios, as noted in Table 5.1. For the other samples, ICP-AES was used for an accurate measure of heteroatom concentration. In the case of H-[Al]-Beta-150, which was purchased from Zeolyst, Si/Al=75 was determined from XRF which is about twice as high as advertised. Instead of ICP-AES, this sample was characterized with n-propylamine decomposition to determine Brønsted acid site concentration. 120 µmol Brønsted acid sites per gram was measured, which corresponds to Si/Al=138, similar to the expected Si/Al=150. Normalized rates for H-[Al]-Beta-150 were based on this 120 µmol/g concentration.

XRD patterns and SEM images are shown in Figure 5.3 and 5.4. Micropore volumes and XRD patterns were all consistent with the structure of zeolite Beta for all the materials investigated. [Sn]-Beta-SSIE shows signals in the XRD pattern consistent with the formation of SnO₂ from incomplete incorporation into the dealuminated sites. These signals are highlighted in Figure 5.3g. The micropore volume of [Sn]-Beta-SSIE was low (0.13 vs. 0.2 cc/g) possibly due to the presence of this amorphous SnO₂ in the zeolite pores. It is not an effect of the dealumination procedure, as the micropore volume of the dealuminated parent material was 0.17 cc/g.

Table 5.1: Framework metal composition and micropore volume for zeolite catalyst investigated. *Determined from n-propylamine decomposition

Catalyst	Si/M	Micropore	Estimated Crystal
		Volume [cc/g]	Size [nm]

H-[Al]-Beta-12.5	12.3 (XRF)	0.18	100
H-[A1]-Beta-150	138 (120 µmol Al/g*)	0.20	300
[Sn]-Beta	110	0.22	3000
[Zr]-Beta	173	0.20	5000
[Hf]-Beta	147	0.21	8000
[Ti]-Beta	58 (XRF)	0.21	20,000
[Sn]-Beta-SSIE	11.7 (XRF)	0.13	100
H,Zn -[Al]-Beta	Si/Al=13.6; Zn/Al=0.2 (XRF)	0.17	100
Si-Beta		0.20	10,000





Figure 5.3: XRD Patterns of (a) H-[Al]-Beta-12.5, (b) H-[Al]-Beta-150, (c) [Sn]-Beta-HT, (d) [Zr]-Beta, (e) [Hf]-Beta, (f) Si-Beta, (g) [Sn]-Beta-SSIE, (h) [Ti]-Beta, (i) |H,Zn|-[Al]-Beta





Figure 5.4: SEM of zeolite catalysts (a) H-[Al]-Beta-12.5, (b) H-[Al]-Beta-150, (c) [Sn]-Beta-HT, (d) [Zr]-Beta, (e) [Hf]-Beta, (f) Si-Beta, (g) [Sn]-Beta-SSIE, (h) [Ti]-Beta, (i) |H,Zn|-[Al]-Beta

5.3.1 Batch Reactions

The results of acylation of methylfuran with acetic anhydride to form 2A5MF (Figure 5.1) over various zeolite Beta catalysts at 383 K using a batch reactor are shown in Table 5.2. Average turnover frequency (TOF) was normalized by metal content of the catalyst as determined by XRF or ICP-AES. TOF is not reported for |H,Zn|-[A1]-Beta because Zn can be exchanged to Al, but the low Zn/Al ratio (Zn/Al=0.2) means there is remaining Brønsted acidity from Al sites that are not

exchanged with Zn. Additionally, it is not known whether the Zn(II) is exchanging two Al sites or just one (as $[ZnOH]^{+1}$), and thus the total number of acid sites is not known quantitatively. On a per gram basis, this Zn catalyst (line 8) exhibited the highest product yield, but it was only marginally better than H-[Al]-Beta-12.5 (line 1). Similar TOFs were found on H-[Al]-Beta-12.5 (line 1) and hydrothermally synthesized [Sn]-Beta (line 3). H-[Al]-Beta-150 (line 2) exhibited the highest turnover of all the catalysts tested. Note that the TOF is different for the same material with only a different concentration of active sites. Similar findings have been reported for the acylation of toluene with isobutyric chloride on H-[Al]-Beta,^[122] and for the acylation of anisole with phenylacetyl chloride on H-Y.^[145] In both cases, this was suggested to be the result of increased hydrophobicity with lower aluminum incorporation. This is consistent with higher turnover of hydrothermally prepared [Sn]-Beta ([Sn]-Beta-HT) compared to [Sn]-Beta prepared by solid-state ion exchange (line 7), as hydrothermally prepared [Sn]-Beta-HT is more hydrophobic than [Sn]-Beta prepared post-synthetically.^[45] However, the increased TOF could also be a result of more active T-sites that populate first at high Si/Al, or due to higher activity of isolated Al sites found in the H-[Al]-Beta-150 sample. The difference in TOF in the case of the Sn materials is also certainly affected by the presence of SnO₂ (observed via XRD) in [Sn]-Beta-SSIE since the rate is normalized by the total Sn content and the SnO₂ phase is inactive for this reaction (line 9). Despite the "spectator" character of some of the Sn in this sample, the reaction rate on a per gram basis is significantly better than [Sn]-Beta-HT. The other hydrothermally synthesized Lewis acid zeolites had comparatively low activity for this reaction, less than half the TOF measured for [Sn]-Beta at similar conversion (lines 4-6). The TOFs of [Zr]-Beta and [Hf]-Beta after

1 hour (the same reaction time as Sn-and Ti-Beta) were only slightly higher: 2.7 and 2.6, respectively. [Ti]-Beta showed the least activity for this reaction, similar to previous comparisons of Lewis acid Beta zeolites for Meerwein-Ponndorf-Verley reduction where Sn, Zr and Hf-Beta are significantly better catalysts than Ti.^[22, 23] Control experiments using siliceous Beta or with no catalyst (lines 10-11) did not result in the formation of acylated product. While [Sn]-Beta-HT had a TOF slightly higher than H-[Al]-Beta-12.5, its TOF was much lower than that of H-[Al]-Beta-150 which has a similar heteroatom concentration. While it is clear the Brønsted acid material is superior for this acylation chemistry, the Al- and Sn-Beta materials were next investigated in a flow reactor under differential conditions to better understand their differences.

Table 5.2: Conversion, yield and TOF from batch reactions of 5 mL methylfuran and 15 mL acetic anhydride with 50 mg catalyst at 383 K, 14 bar. Numbers reported are average and the standard deviation of two experiments.

No Catalyst		Time	Conversion	Yield	TOF [mol 2A5MF/min/
TNO. Catalyst	[h]	[%]	[%]	mol metal]	
1	H-[A1]-Beta-12.5	0.5	18.7±0.2	15.9±0.7	5.0±0.2
2	H-[Al]-Beta-150	1	6.8±0.5	5.3±0.2	8.4±0.3
3	[Sn]-Beta-HT	1	5.2±0.7	4.6±0.4	5.7±0.4
4	[Zr]-Beta	3.5	4.6±1.1	3.0±0.1	$1.7{\pm}0.1$
5	[Hf]-Beta	3.5	5.7±0.9	3.6±0.3	1.8±0.2
6	[Ti]-Beta	1	1.6	0.1	0.08
7	[Sn]-Beta-SSIE	0.5	8.3±0.1	5.3±0.5	2.0±0.2
8	H,Zn -[Al]-Beta	0.5	19.4±0.1	17.9±0.1	
9	SnO ₂	1	3.9	0	0
10	Si-Beta	1	2.2	0	0
11	No catalyst	1	0.4	0	0

5.3.2 Flow Reactions

All catalysts tested under continuous flow conditions deactivated with time on stream (Figure 5.5). H-[Al]-Beta-150 was tested for longer times on stream because it was studied at a lower flowrate. To determine the initial rate, the product was sampled over time, and the rate was extrapolated to t=0 with an exponential fit. This fit was not excellent (r^2 =0.93-0.99), but the fit on each catalyst is similar enough that the activation energy determined from the exponential fit is close to the activation energy calculated from using the rate at the same time point. This demonstrated for each catalyst in Appendix C.1. Catalyst lifetimes were compared by determining the half-life of the catalyst (the time at which half of the rate at t=0 is observed, see Table 5.3).



Figure 5.5: Rate with time on stream for methylfuran acylation with acetic anhydride. Conditions: 393K, 200 psi, 45.5 g MF, 150 mL acetic anhydride, 200 mL GVL, 0.05 g catalyst, 4 ml/min (2ml/min for H-[Al]-Beta-150)

5.3.2.1 Activation Energy

An Arrhenius analysis of the experimental rates was conducted on each material to determine the apparent activation energy of the reaction (Figure 5.6 and Table 5.3). Given the low activation energy on Sn compared to Al and the large crystal size of [Sn]-Beta-HT (Figure 5.4c), the possibility of mass transfer limitations was considered. However, [Sn]-Beta-SSIE prepared via solid state ion exchange had a crystal size that was much smaller (Figure 5.4g) and comparable to the crystal size of the H-[Al]-Beta-12.5 (Figure 5.4a) that it was synthesized from. Since a very similar activation energy was found on these two Sn catalysts with very different crystal sizes, it is unlikely that mass transfer effects are affecting the apparent activation energy. Additionally, the Weisz-Prater criterion was estimated and falls below the limit where pore diffusion is limiting (Appendix C.2).

Table 5.3: Apparent activation energies and half-life of catalysts tested under differential conditions with a flow reactor. Estimated error is for a 90% confidence interval.

Catalyst	E _{a,app} [kcal/mol]	Half-life [min]
H-[Al]-Beta-12.5	16.6±2.9	23-25
H-[Al]-Beta-150	20.9±4.0	26-32
[Sn]-Beta-HT	9.0±3.9	18-22
[Sn]-Beta-SSIE	8.8±3.6	19-23



• H-[A1]-Beta-150 • H-[A1]-Beta-12.5 • [Sn]-Beta-HT • [Sn]-Beta-SSIE

Figure 5.6: Arrhenius plot for methylfuran acylation with acetic anhydride. Conditions: 200 psi, 45.5g MF, 150 mL acetic anhydride, 200 mL GVL, 4 ml/min (2ml/min for H-[Al]-Beta-150), 0.05 g catalyst

5.3.2.2 **TGA of spent catalysts**

All catalysts deactivated with time on stream. Among the catalysts investigated, the half-life was in the range of 18-32 minutes (total length of experiments was 180 minutes for H-[Al]-Beta-150 and 90 minutes for all others). The spent catalyst obtained from the lowest-temperature measurement of each catalyst was analyzed using TGA (Figure 5.7). H-[Al]-Beta-12.5 exhibited the most weight loss (43%), followed by [Sn]-Beta (37%). H-[Al]-Beta-150 and [Sn]-Beta-SSIE had less weight loss of 21% and 19%, respectively. Since the catalysts were only dried under nitrogen flow at room temperature, and the boiling points of the reactants and products are quite high, a portion of this weight loss is probably from the removal of reactants

or products left both internally and externally of the catalyst pores. The boiling points of the reactants and products in this system are: 336 K (methylfuran), 414 K (acetic anhydride), 373 K (2A5MF), 391 K (acetic acid), and 480 K (GVL). The differential of the TGA is shown in Figure 5.8, but even from Figure 5.7 it is clear that there is significant weight loss on H-[A1]-Beta-12.5 and [Sn]-Beta-HT between 380-400 K that is not observed on the other two catalysts. Based on boiling points, the weight loss in this region seems consistent with loss of either acetic acid or anhydride.



Figure 5.7: TGA of spent catalyst from flow experiments at temperature indicated in parentheses and same conditions as Figure 5.5.



Figure 5.8: Differential TGA of spent catalyst from flow experiments at temperature indicated in parentheses and same conditions as Figure 5.5.

5.3.2.3 Analysis of retained products

While much of the weight loss in TGA could be from reactants and products left in the intracrystalline voids of the samples, TGA analysis also revealed some weight loss at higher temperatures that might be due to the occlusion of large byproducts in the pores. Spent catalyst from the flow reactions were dissolved with HF, and the organics were extracted and analyzed with GC-MS (Table 5.4) to identify the retained molecules. GVL was found retained on all the catalysts, which is likely due to its high boiling point since the catalyst is "dried" under nitrogen flow at room temperature. While a small amount of acetic acid was detected in the extracted organic phase for H-[Al]-Beta-12.5, it is also possible that acetic acid and acetic anhydride were retained on the other catalysts, but stayed in the aqueous HF phase due to their polarity. Products with a higher molecular weight than the desired 2A5MF product (MW=124) were found retained on the catalyst which suggests some deactivation from pore blockage by these large molecules. The MW=206 product detected on H-[Al]-Beta-12.5 could be from the condensation of hydrated methylfuran (1,4-pentanedione) with 2-acetyl-5-methylfuran. The MW=290 product detected on [Sn]-Beta could be from acylation at both ends of the double bond in the 206 molecule.

Table 5.4: Organics extracted from spent catalyst run at temperature specified and reaction conditions as described in Figure 5.5.

Catalyst	Reaction Temperature [K]	Molecules Observed
H-[A1]-Beta-12.5	383	GVL, acetic acid, higher MW product (206)
H-[Al]-Beta-150	383	GVL
[Sn]-Beta-HT	393	GVL, higher MW product (290)
[Sn]-Beta-SSIE	393	GVL, 2A5MF

5.3.2.4 Co-feeding of products

The retention of acylation products can contribute to the reduction in rate over time as detailed in previous literature.^[110, 111, 117, 118] Acetic acid and 2A5MF products were co-fed to determine their effect on the reaction rate on the catalyst with the highest turnover, H-[AI]-Beta-150. As shown in Figure 5.9, co-feeding just a small amount (5 mol% based on methylfuran) of acetic acid resulted in decreased rate. Similarly, co-feeding 5 mol% of 2A5MF decreased the initial rate, though not as severely as 5 mol% of acetic acid. A further increase of 10 mol% 2A5MF product in the feed reduced the initial rate more. Initial rates (from extrapolating to t=0) and catalyst half-lives are reported for these runs in Table 5.5. The co-feeding of 2A5MF also slowed the rate of deactivation and the catalyst half-life was increased from 32 to

44 minutes. The reduced reaction rate upon co-feeding of products indicates product inhibition is contributing to the decrease in rate with time on stream, similar to what is reported in other acylation studies.



Figure 5.9: Methylfuran acylation with acetic anhydride and co-fed products. Conditions: 200 psi, 393 K, 2 ml/min, 0.05 g H-[Al]-Beta-150, 45.5g MF, 150 mL acetic anhydride, 200 mL GVL and specified mol % (with respect to methylfuran) of product

	-	
Feed	ro [mol 2A5MF/min/mol metal]	Half-life [min]
No products	18.0	32
5 mol% 2A5MF	11.6	44

10.6

11.7

43

29

10 mol% 2A5MF

5 mol% acetic acid

Table 5.5: Initial rate and catalyst half-life for co-feeding experiments with H-[Al]-Beta-150. See Figure 5.9 for conditions.

5.3.2.5 Effect of solvent

Since gamma-valerolactone (GVL) is clearly retained on the catalyst, acetonitrile was tested as a solvent in order to see if the GVL retention had a negative effect on the reaction rate. Compared to runs diluted in GVL, dilution with acetonitrile resulted in the same rate on H-[Al]-Beta-12.5 (Figure 5.10) and lower rates on [Sn]-Beta-HT (Figure 5.11). Extraction and analysis of the organics on spent catalyst from these experiments showed the presence of both 2A5MF and GVL retained in the catalyst. It is possible that methylfuran is hydrated by water forming an unstable 1,4pentanedione that then isomerizes to GVL. There are no products corresponding to the molecular weight of 5,5-bismethylfuran-2-pentanone, a trimer of two methylfuran molecules with 1,4-pentanedione described by Corma et al.^[159] The observation of 2A5MF in the spent catalyst in acetonitrile but not GVL indicates that GVL may have a promoting effect in removing the 2A5MF product from the active site resulting in the higher rates observed for [Sn]-Beta with GVL as solvent.



Figure 5.10: Reaction rate with time on stream for H-[Al]-Beta-12.5 catalyst. Conditions: 383K, 200 psi, 45.5 g MF, 150 mL acetic anhydride, 200 mL GVL or acetonitrile (ACN), 0.05 g H-[Al]-Beta-12.5, 4 ml/min



Figure 5.11: Reaction rate with time on stream for [Sn]-Beta-HT. Conditions: 393K, 200 psi, 45.5 g MF, 150 mL acetic anhydride, 200 mL GVL or acetonitrile (ACN), 0.1 g [Sn]-Beta-HT, 4 ml/min

GVL was used as solvent to reduce the acetic anhydride and acetic acid concentration in the effluent and minimize potential damages to the back-pressure regulator. In some experiments, a backpressure regulator configuration compatible with acetic anhydride was used to investigate the reaction without solvent on H-[Al]-Beta-150. Figure 5.12 shows that removal of GVL resulted in a dramatic decrease in the rate (no GVL) compared to when GVL (with GVL) was used, which further reveals the positive effect of GVL solvent on this reaction. When the bed was heated under GVL flow and then fed methylfuran and acetic anhydride once temperature was reached (heat with GVL), the initial rate was improved over heating under acetic anhydride flow, but still reached a regime of no product evolution after about two hours of time on stream.



Figure 5.12: Methylfuran acylation with acetic anhydride. Conditions: 200 psi, 403 K, 2 ml/min, 0.05 g H-[Al]-Beta-150. With GVL: 45.5g MF, 150 mL acetic anhydride, 200 mL GVL and heated under GVL flow. Heat with GVL: 45.5 g MF, 350 mL acetic anhydride and heated under GVL flow. No GVL: 45.5 g MF, 350 mL acetic anhydride and heated under acetic anhydride flow.

The effect of GVL on the apparent activation energy was studied on H-[Al]-Beta-150 and [Sn]-Beta in order to see if the effect of GVL was related to the formation of the transition state. The apparent activation energies determined from batch experiments of methylfuran acylation with and without GVL are reported in Table 5.6. It is not clear why the apparent activation energy for H-[Al]-Beta-150 with GVL is lower than what was found in flow experiments. The similar apparent activation energy with and without GVL indicates that GVL is not greatly affecting the transition state and the positive effect on reaction rate must have another origin.

Catalyst	Apparent Activation Energy [kcal/mol]		
Cataryst	Without GVL	With GVL	
H-[Al]-Beta-150	16	14	
[Sn]-Beta-HT	10	11	

Table 5.6: Apparent activation energies of methylfuran acylation with and without GVL on H-[Al]-Beta-150 and [Sn]-Beta-HT

5.3.3 Reaction Mechanism

5.3.3.1 Kinetic isotope effect

5.3.3.1.1 Labeled furan

The acylation mechanism over Al- and Sn-Beta was probed with labeled furand₄. Furan was selected because deuterated furan is more readily available than deuterated methylfuran. In the case of furan, the electron-donating oxygen in the ring makes it more nucelophilic than benzene and toluene, the reactants used in many early Friedel-Crafts studies. As described before, if the formation of the Wheland complex is the rate determining step for acylation, a secondary inverse kinetic isotope effect would be expected due to change from sp² to sp³ hybridization of the carbon on the aromatic.^[151] If deprotonation of the Wheland complex is the rate-determining step, or if the mechanism is concerted, a significant primary kinetic isotope effect would be expected due to breaking of the carbon-hydrogen bond.^[151] In fact, a significant primary isotope effect was found for both H-[Al]-Beta-150 and [Sn]-Beta-HT, indicating deprotonation (either in a concerted or stepwise manner) is the rate-determining step (Table 5.7). As explained by Effenberger, the different magnitudes of the kinetic isotope effect is a function of the Wheland complex formation and deprotonation rates.^[160] Since methylfuran is a stronger nucleophile than furan due to the electron-donating methyl group, and strong nucleophiles are associated with no primary kinetic isotope and an earlier rate-determining step, it might be argued that the rate-determining step would be different for methylfuran compared to furan. However, a primary kinetic isotope effect for both toluene and benzene with the same acylating agent (as discussed earlier) indicates that this additional methyl group is not enough to change the rate-determining step. With the same acylating agent, it is likely that furan and methylfuran acylation share the same rate-determining step of deprotonation. This conclusion is supported by the computational modeling discussed in the section 5.4.

Table 5.7: Acylation of labeled and unlabeled furan with acetic anhydride. 1 g furan or 1.06 g furan-d4, 3.2 g acetic anhydride, 393 K, 0.05 g catalyst, 20 minutes

	Yield [%]		
Catalyst	Unlabeled	Labolad furan	$k_{\rm H}/k_{\rm D}$
	furan		
H-[Al]-Beta-150	13.3	5.3	2.5
[Sn]-Beta-HT	3.4	1.9	1.8

5.3.3.1.2 Labeled acetic acid

A subtlety of the acylation mechanism using labeled furan is that deprotonation to produce the acetylfuran product involves removal of deuterium from the furan and thus when the acid site is regenerated it is formed with a deuterium instead of a proton. Hence, after the first turnover at each site, it is possible that the kinetic isotope effect observed is from the hydrogen bond breaking at the acid site to form acetic acid and the corresponding the acylium ion at the active site. In order to probe this potential mechanism, methylfuran and acetic anhydride were reacted with excess labeled and unlabeled acetic acid. The labeled acetic acid is expected to readily exchange with the acid site, and if a kinetic isotope effect was observed in this system, then it would be clear that formation of the acylium ion is the rate determining step instead of deprotonation of the Wheland intermediate. Reactions with 3:2:1 acetic acid:acetic anhydride:methylfuran on H-[Al]-Beta-150 did not result in a kinetic isotope effect. k_H/k_D was 1.02, indicating that formation of the acylium ion is not rate-determining.

5.3.3.2 Na-exchanged [Sn]-Beta

To determine whether the active site for acylation on [Sn]-Beta is open or closed, a [Sn]-Beta-HT sample was exchanged with sodium to replace the hydroxyl groups at the open sites, in the same manner as Bermejo-Deval, et al.^[85] The Na/Sn ratio determined by ICP-AES for this sample was 8.2, indicating there was likely exchange at the Sn sites as well as silanols from framework defects. One would expect a ratio of 2:1 if exchanging only at the Sn hydroxyl and corresponding silanol in the open sites. When the exchanged sample was tested under the same conditions as line 3 in Table 5.2, no 2A5MF was formed, suggesting that sodium had exchanged in the open site and suppressed the reaction: consequently, the open site is the active one. Quantification of open and closed sites, particularly under reaction conditions, is not possible at this time, and the active site concentration has been estimated to be the

same as the metal content, however, if only a fraction of tin is an open configuration this would result in an underestimate of the true turnover frequency.

An additional consideration arising from the identification of the tin open site as the active site is the possibility of Brønsted acid catalysis at this site. Recent computational modeling of [Sn]-Beta open sites revealed that the silanol associated with the tin open site is more Brønsted acidic than the internal silanol at framework defects and comparable in binding strength to the Sn site for strong bases like ammonia and pyridine.^[50] Given that this chemistry can be catalyzed by either Brønsted or Lewis acids, it is possible that the reaction is occurring at the open Sn site and thus is actually catalyzed by the Brønsted acidic silanol and not the Lewis acidic Sn atom. The reaction was investigated computationally in order to address this question and to compare the mechanism on Al- and Sn-Beta.

5.4 Computational Studies

Collaborators at the Catalysis Center for Energy Innovation at the University of Delaware investigated methylfuran acylation with H-[Al]-Beta and [Sn]-Beta computationally to help elucidate the reaction mechanism. Density functional theory simulations indicate that deprotonation is the rate determining step on both materials, in agreement with the experimentally observed kinetic isotope effect. In contrast to experiments, the simulations predicted a similar energy span on Al- and Sn-Beta of 27.5 kcal/mol, which is not consistent with the different activation energies described earlier (approximately 18 and 9 kcal/mol for Al and Sn, respectively). The simulations indicate that the open site is the active site, as the closed site has a much larger energy span of 37.9 kcal/mol. This modeling also suggests that the open Sn site catalyzes the acylation through Brønsted acid catalysis at the silanol of the open site, rather than Lewis acid catalysis at the Sn atom.

While it is encouraging that the model agrees with experimental evidence for the rate determining step, the model is not consistent with some other experimental findings. Al- and Sn-Beta were both modeled with substitution in the framework at the T2 site. Perhaps Al and Sn substitution occur at a different T site or at multiple T sites, leading to the differences between computational and experimental results. In addition, the models used for the simulations are not sufficiently large to account, in example, for differences between Beta with high and low Al content, where different reaction rates were clearly observed. It is suggested that in future work, the effect of the siting of substituted atoms in the crystal structure is computed to ascertain if this is the reason behind differences between the models and the experiments.

5.5 Conclusions

A comparison of Brønsted and Lewis acid zeolite Beta catalysts for methylfuran acylation reveals that |H,Zn|-[Al]-Beta and H-[Al]-Beta-12.5 exhibit the highest activity on a per gram basis. When turnover is normalized on a per site basis, H-[Al]-Beta-150 exhibits higher turnover compared to all Lewis acid zeolite Beta materials tested as well as H-[Al]-Beta with more framework aluminum. With the respect to the two aluminum materials, the difference in turnover could be due to a positive effect of the hydrophobicity of the low aluminum catalyst, as has been hypothesized previously.^[122] It is also possible that at high aluminum content, aluminum populates different T-sites, since studies have suggested that this siting is non-random,^[161] and that these T-sites may be less active for acylation. High aluminum content is associated with higher concentrations of extra-framework Lewis
acidic aluminum and although Friedel-Crafts chemistry is also Lewis acid-catalyzed these sites are potentially less active than the framework Brønsted acid sites.

The contrast of reaction rate and activation energy on Al- and Sn-Beta is interesting since the apparent activation energy is lower on [Sn]-Beta despite having a lower rate compared to H-[Al]-Beta. The apparent activation energy measured is the difference between the true activation energy and the heat of adsorption of the adsorbate so it is possible that the intrinsic activation energy is higher for [Sn]-Beta and a more exothermic adsorption makes it appear lower. Kinetic compensation effects have been known to occur in which an increased pre-exponential offsets a higher apparent activation energy on different catalysts for the same reaction.^[162] It is also possible that the rate on [Sn]-Beta is underestimated since the open site was established as the active site and the fraction of these sites is unknown. In this case it would be possible that [Sn]-Beta has a higher turnover frequency than H-[Al]-Beta that more typically aligns with the observed lower apparent activation energy. Regardless of accurate accounting of sites for these Lewis acid materials, this work demonstrates that Brønsted acid zeolites which are commercially available exhibit excellent activity and selectivity for this reaction. Although all the materials deactivate with time on stream, GVL has a promotional effect on the rate which may be helpful in applying this chemistry industrially. Similar apparent activation energies on H-[Al]-Beta with and without GVL suggests this effect is not due to participation of GVL in the reaction transition state.

Chapter 6

SUMMARY AND OUTLOOK

6.1 Lewis Acid Zeolites for Transformations of Biomass-Derived Molecules

6.1.1 Summary

In Chapter 2, Lewis acid zeolite Beta with framework Sn, Zr or Ti was screened for several reactions related to the conversion of renewable derivatives of biomass. These investigations clearly show that Ti-Beta is the least effective catalyst among these materials; it does not catalyze either the MPV reduction or etherification. In contrast, Ti-Beta is well known for catalyzing epoxidation reactions that neither Zr-or Sn-Beta catalyze.^[22] Sn-Beta was found to catalyze sugar isomerization at the fastest rates. This isomerization is an important reaction for the industrial production of fructose from more abundant glucose. This reaction is also an important step for the production of hydroxymethylfurfural (HMF) from cellulose. This chemistry is carried out industrially with enzymes (glucose isomerase) and the use of Sn-Beta would allow for easier separation and more flexibility in terms of operating conditions.

Safety concerns relating to the use of HF in the synthesis of Sn-Beta as well as concerns relating to the reproducibility of the zeolite synthesis need to be addressed before Sn-Beta can be considered a practical catalyst, but nonetheless its development is a major breakthrough. Sn-Beta was also the catalyst displaying highest rates for etherification, but was not as effective as Zr-Beta for MPV reduction. These results show the importance of the specific reaction and Lewis base on the performance of these catalysts.

6.1.2 Future Research Directions

To better understand the unique behavior of Ti-Beta in relation to analogous Lewis acid Beta materials, the ability of this material to hydrolyze and form an open site should be investigated. The lower susceptibility of this material for hydrolysis of Ti-O-Si bonds to form an open site has been reported,^[43] and this may be a key part of the explanation for its unique activity. However, this explanation is not supported by isotopic labelling studies that show that glucose isomerization follows the same mechanism on Ti-Beta as it does on Sn-Beta, since the open site has been established as the active site for Sn-Beta.^[36, 72] A simple test to probe the open site on Ti-Beta would be to study a sodium-exchanged Ti-Beta for glucose isomerization. Particularly, if open sites are not prevalent, this should be readily apparent if fructose productivity is not affected by the sodium. Another approach that might be applied to the same question is EXAFS, which can probe the local environment of the Ti. Especially if open sites are not really present or are rare, the spectra interpretation will be simpler than with similar materials due to the homogeneity of the Ti sites.

Although the MPV reduction was studied in more detail in chapter 3, it could be further probed by studying this reaction for various molecules with the same functional group. As discussed above, Zr-Beta has been found to be superior to Sn-Beta for benzaldehyde and furfural, and it would be interesting to test aliphatic aldehydes to see if this trend holds for other aldehydes as well. Similarly, it would be interesting to see if one catalyst is superior for reducing ketone groups. Since this

reaction is bimolecular, the donor alcohol should also have an effect on the reaction rate, so it would also be interesting to test other alcohol donors. MPV reduction of methyl levulinate was found to proceed at faster rates with secondary alcohols (isobutanol, isopropanol and cyclopentanol) compared to primary alcohols (n-butanol, n-propanol and ethanol).^[23] Methyl levulinate reduction rate was also found to increase with higher alcohols.^[23] A similar study with furfural or HMF would be valuable to determine if the same trends are observed.

Understanding the coordination of different functional groups (alcohol, aldehyde and ketone) with these materials may be aided by EXAFS investigations. This might be complicated by the existence of a mixture of open and closed sites, which both interact with Lewis bases, but the spectra might be fitted to a two-site model to address this problem. Coordination with adsorbates may not be distinguishable from the water coordinated at the site in hydrated samples, so a starting point for these experiments would be to observe coordination with adsorbates on a dehydrated sample. A more direct technique to distinguish the interaction of these Lewis acid materials with reactants is temperature programmed desorptionthermogravimetric analysis. Here interactions between Lewis acids and bases can be investigated based on Lewis base uptake and desorption temperature. These techniques could measure the strength of interaction of each of these materials to these different groups, and this may help in choosing the best material for a desired chemistry.

Understanding of the etherification reaction would also benefit from testing various alcohol reactants. In one-pot reductive etherification of HMF on Sn-Beta, the highest yield of desired product was found with isopropanol (compared to isobutanol,

n-butanol, n-propanol and ethanol). It would be instructional to investigate the effect of added alcohol on etherification of furfuryl alcohol to isolate the etherification activity from that of the MPV reduction, especially since this thesis has shown that the activity for these reactions varies substantially between Zr- and Sn-Beta. While Hf-Beta was studied for MPV reduction in the chapter 3, it would be worthwhile to also look at the etherification activity of this material.

There are also other chemistries where these solid Lewis acids are active that should be investigated. For example, the production of methyl lactate from fructose involves a retro-aldol reaction, isomerization, dehydration and esterification.^[51] Sn-, Zr- and Ti-Beta have all been studied for this set of reactions in one-pot reaction but each of these reactions could be probed individually to better understand the best application of these Lewis acidic materials. Isolating these chemistries is useful, as it has been shown that these materials can have drastically different activities for different chemistries in these cascade reactions. For example, in the reduction and etherification of HMF, Zr- and Sn-Beta have very different activities for each step. Applying each one separately in a setup with two beds in sequence may be more productive than using a single catalyst.

A final chemical reaction that these materials could be screened for that is useful in biomass transformations is aldol condensations.^[94] Aldehyde and ketone groups are available in HMF, furfural and their ring-opened derivatives, and these groups could be taken advantage of in aldol condensations to create C-C bonds to make larger products as well as reduce oxygen content. Establishing the activity of each of these Lewis acid materials for these various chemistries will allow for the efficient development of processes to produce valuable compounds from renewable feedstocks.

6.2 MPV Reduction of furfural

6.2.1 Summary

In Chapter 3, the MPV reduction of furfural was investigated under continuous flow conditions on Zr-, Sn- and Hf-Beta. Ti-Beta was not studied as its inactivity for this reaction was established in Chapter 2. Hf-Beta was found to be significantly more reactive than the other catalysts. This was a surprising result considering that Zr and Hf are so similar that they are among the hardest elements to separate. The apparent activation energy on the materials was very similar, differing by only 10 kJ/mol. The rate was found to decrease with time on stream on all the materials, but the rate with time on stream could stabilized by operating at higher temperatures.

6.2.2 Future Research Directions

The similar magnitudes of the apparent activation energies in Hf-, Zr- and Sn-Beta in the MPV reaction leads to the question of whether the true activation energy is the same or if the similar apparent activation energy is the result of compensation between different true apparent activation energies and different heats of adsorption of the reactants. At this point it is impossible given the characterization techniques currently available to deconvolute the apparent activation energies found on each material into the heat of adsorption and the true activation energy. Heats of adsorption have been estimated for adsorbates on zeolites through adsorption loading experiments,^[163] where the concentration of a solution, before and after a zeolite is introduced, is used to estimate the uptake by the zeolite. However, this technique is difficult to apply to these Lewis acid zeolites because of their low metal content. To achieve a practical concentration of active sites to do these experiments, grams of catalyst would have to be used at a time, which is the same scale as the product yield from the synthesis of these materials. Microcalorimetry is an alternative to access heat of adsorption information, but could be complicated by the likely different adsorption on open and closed sites. Despite their difficulty, these types of measurements would be a start at understanding how much adsorption plays a role in differentiating these materials. Particularly since these reactions are done at low temperature and in liquid phase, adsorption could be a significant differentiator. The positive effect of increased temperature on the catalyst half-life in this chapter suggests that adsorption is important, even if it is not significantly different between the different Lewis acidic materials.

6.3 Production of *para*-methylstyrene and *para*-divinylbenzene from furanic compounds

6.3.1 Summary

In Chapter 4, *para*-ethyltoluene was produced in 99.5% *para* isomer selectivity from renewable methylfuran in a three step process of reactions. First, methylfuran was acylated with acetic anhydride on H-[Al]-Beta zeolite to produce 2-acetyl-5methylfuran (2A5MF) at 90% yield. After this step, the 2A5MF needs to be fully separated from acetic anhydride due to incompatibility between acetic anhydride and the copper chromite catalyst in the next step. In the second step, 2A5MF in tetrahydrofuran (THF) solvent is reduced with hydrogen over copper chromite to make 2-ethyl-5-methylfuran (2E5MF) in 90% yield. The reaction product is used directly in the final step after being filtered from the copper chromite. In the final step, 2E5MF is combined with ethylene over H-[Al]-Beta zeolite for a Diels-Alder cycloaddition and dehydration to form *p*-ethyltoluene. This chemistry was then extended to make *p*-diethylbenzene from furan at 99.0% *para* selectivity.

6.3.2 Future Research Directions

Given the multiple chemical reactions investigated in Chapter 4, there are a number of aspects that ought to be the subject of further study. . Attempts to accomplish the acylation and cycloaddition reactions in one-pot were discussed in section 4.3.1.4. Yield of the desired methylacetophenone was poor due to the electron withdrawing acetyl group on the furan. Since then, Zn-based Lewis acid zeolites have been demonstrated to be promising materials to accomplish Diels-Alder cycloaddition and dehydration on furans with electron withdrawing groups. Specifically, CIT-6, a zeolite Beta with framework Zn, and Zn exchanged H-[Al]-Beta were shown to catalyze the Diels-Alder cycloaddition and dehydration of furans with electron withdrawing methyl ester groups.^[164] Because the Zn exchanged H-[Al]-Beta was also active for acylation (Chapter 5), this would be an exciting material to investigate for the one-pot reaction of methylfuran to methylacetophenone. A Zn-based catalyst might be able to catalyze the acylation of methylfuran and then the cycloaddition of the acetyl-methylfuran in one-pot. Further, using acetic anhydride as both reactant and solvent in this one-pot reaction could be advantageous to the Diels-Alder step. Recent patent literature for similar reactions describes the use of acetic anhydride as solvent as a trap for the water formed from the dehydration step, which prevents undesirable hydrolysis reactions with the furan.^[165] The ability to accomplish these cycloadditions with Zn catalysts without having to remove the oxygenate groups will be a significant advancement in making aromatics from furans, as it will allow these functionalities to

stay intact, rather than having to remove them and then re-add them as is done now for making *p*-xylene for terephthalic acid from dimethylfuran. *p*-methylacetophenone itself is molecule used for fragrances and thus, the ability to make this selectively via acylation of methylfuran and subsequent cycloaddition and dehydration with a Zn catalyst would be useful.

Although it was discussed that alkylation of furans is difficult, investigation of this reaction would be useful as another approach to optimize the synthesis of *p*-aromatics from furans. Successful alkylation of furan with butyl groups has been described,^[166] so even if it is found to be too slow to add ethyl groups to furan via alkylation, it may be feasible to add other desired alkyl groups. If it is possible to add ethyl groups directly to furan, this would greatly increase the efficiency of the process described in this work by replacing the acylation and hydrodeoxygenation steps with just one alkylation step. In the case of p-divinylbenzene, the process would be even more optimized as the alkylation of furan does not prevent, but rather accelerates, further alkylation.^[166] Further, butylation of furan was selective to the 2 and 5 positions of furan, which is the substitution required to result in a para-aromatic after cycloaddition and dehydration.^[166] Thus, for divinylbenzene, successful addition of ethyl groups via alkylation of furan would allow for 2,5-diethylfuran to be made in one alkylation step rather than through the four steps described in this work. This would be a great improvement in efficiency for the manufacture of this molecule.

If alkylation of furan is successful, the hydrodeoxgenation step would be eliminated, but if this is not the case, a better catalyst for this step should be investigated. Copper chromite was chosen as the catalyst for hydrodeoxygenation of the acetyl group because it is known to be effective at selectively reducing carbonyl

groups. However, the environmental hazards of chromite are well-known.^[167] The intent of this work was a proof of concept for the production of *p*-ethyltoluene from methylfuran, but in practice this step should be accomplished with a more environmentally-friendly catalyst for the process to satisfy its intention of being sustainable, utilizing a renewable feedstock. Nickel and copper based catalysts free of chromium are a good starting place for achieving this.^[167]

For the Diels-Alder step, recent work has shown that a phosphorous containing zeolite Beta results in exceptional yields (97%) for the production of p-xylene from dimethylfuran.^[168] This is significantly higher than yields previously obtained for Zror Al-Beta catalysts. If yields this high can also be obtained with 2-ethyl-5methylfuran and 2,5-diethylfuran, it would significantly improve the overall process yields, since the yields in the preceding acylation and hydrodeoxygenation steps are high. For example, if 97% yield of p-ethyltoluene was achieved in the Diels-Alder step, the overall yield from methylfuran would be 77% (compared to 54% in the current process). As discussed above, acetic anhydride has been applied as a solvent in these reactions as a desiccant for the water made in the dehydration step. Since solvent was shown to have an effect on the product yield (Table 4.8), screening of various solvents, including acetic anhydride, could be useful to maximize the yield of this last step.

6.4 Acylation of methylfuran with Brønsted and Lewis acid zeolites

6.4.1 Summary

In Chapter 5, it was found that Brønsted acid zeolites are more effective catalysts for Friedel-Crafts acylation of methylfuran than Lewis acid zeolites. Higher

turnover frequencies were observed for aluminum Beta zeolites than Sn-Beta despite a lower activation energy on Sn-Beta and evidence of the same rate determining step from kinetic isotope effect experiments.

In flow experiments, co-feeding of products was found to be detrimental to reaction rate, indicating product inhibition. This type of inhibition has previously been described for other acylation reactions. Gamma-valerolactone (GVL) used as solvent was found to have a very positive effect on reaction rate compared to running without any solvent. Since GVL was not found to have an effect on the activation energy, GVL does not affect the transition state and could instead be affecting the rate through competitive adsorption.

6.4.2 Future Research Directions

In Chapter 5, the best catalyst for methylfuran acylation was a Brønsted and Lewis acidic zinc-exchanged Al-Beta. This material deserves follow up in several aspects. First, it would be interesting to try to isolate the Brønsted and Lewis acidity in this material by making a sample exchanged with Zn and then trying to remove its Brønsted acidity by then exchanging with sodium. Exchanging Zn on low Si/Al materials is typical to try to exchange Zn^{2+} at two adjacent Al sites, but since a sample with less Al resulted in higher turnover on a per site basis, it would be interesting to see the effect of decreasing Al concentration for Zn exchanged materials as well. Finally, this material should be studied in a flow system, and compared to the time on stream behavior of the other materials studied.

Although the Brønsted acid materials were found to be best for the acylation of methylfuran, the performance of the solid-state ion exchanged (SSIE) Sn-Beta is an interesting aspect that deserves more study and could be applied to other chemistries

like MPV, where Brønsted acid catalysts are not effective. While this work demonstrates that Sn-Beta-SSIE does not result in the same turnover on a per metal basis, it does have higher productivity than conventional Sn-Beta on a per gram basis. This is a more relevant parameter for industrial applications, particularly with a nonprecious metal like Sn. In addition to increasing the per gram activity of the material, these materials are more attractive from a synthesis perspective, since the synthesis does not require hazardous HF, is faster, and is more reproducible than the hydrothermal synthesis of Sn-Beta. The material studied in this work was made from tin acetate, but synthesis from dealuminated beta and tin chloride has also been reported to result in less extra-framework SnO2.^[169] It would be interesting to compare the activity of materials obtained from this post-synthetic route with different tin precursors. Additionally, the SSIE material in this work was intended to greatly increase the number of Sn sites in the Beta framework, but from an academic standpoint it would be interesting to look at intentionally putting less Sn into a dealuminated Beta originally of low Si/Al (12.5) which may reduce the amount of spectator SnO₂ formed. Furthermore, given the higher per site activity of high Si/Al H-[Al]-Beta, it would also be interesting to dealuminate this material and use it to synthesize a SSIE Sn-Beta to see the effect of Sn concentration with this synthesis technique on the acylation reaction rate.

These post-synthetic Sn-Beta materials have been compared to the hydrothermally synthesized material for several chemistries, such as Bayer-Villiger oxidation,^[45, 170] MPV reduction,^[45] and glucose isomerization,^[155, 171] often with better productivity on per gram basis in the post-synthetic sample. These postsynthetic materials should also be compared for chemistries like aldol condensation

and Diels-Alder cycloaddition and dehydration so that the highest productivity on a weight basis can be achieved. Sn has been the main focus of post-synthesis insertion, but procedures to insert Zr and Ti in the framework post-synthesis have been described in the literature.^[35] Zr and Ti samples prepared post-synthetically should be compared to their hydrothermal counterparts for these chemistries as well. By avoiding the use of HF and reducing synthesis time, Lewis acid zeolites made by post-synthesis techniques are more likely to find success in industrial applications.

Finally, recent work has described acylation of furan using acetic acid as the acylating agent.^[172] While acetic acid is harder to activate than acetic anhydride, requiring reaction temperatures over 473 K, the acid is much cheaper. Finding operating conditions to utilize acetic acid rather than anhydride is worth exploring. Cerium exchanged zeolites were previously applied to the acylation of aromatics with carboxylic acids,^[115] and returning to this type of material is a good starting point. These cerium-exchanged materials were found to be more active for acylation with longer carboxylic acids (3 carbons or greater). The acylation of furan to make surfactants involves the addition of a 12 carbon acetyl group.^[143] Thus, these catalysts might be particularly useful if applied to this surfactant chemistry.

6.5 Outlook

This thesis has shown that both Lewis and Brønsted acid zeolites can be applied to the selective transformations of biomass that have the potential to make a significant impact on the sustainable production of fuels and chemicals. There are several drawbacks to the hydrothermal synthesis of Lewis acid zeolite materials, including: use of HF, long crystallization time, product inconsistency, and low metal incorporation. Thus, Lewis acidic materials made post-synthetically and Zn-

exchanged Al-Beta that are easier to make might have more potential industrially. These materials should be screened against their hydrothermally synthesized Lewis acid counterparts to see if they result in comparable catalysis, without the drawbacks of the synthesis. Further development of post-synthetic techniques to make Lewis acid zeolites, including avoiding the existence of inactive oxide phases, will also allow for better turnover of these reactions on a weight basis.

Characterization of the Lewis acid materials is another priority. The development of characterization techniques as well as computational modeling can help to achieve deeper understanding of active site concentration as well as the dynamics of the active site under reaction conditions. The methods used recently to quantify open and closed sites on Sn-Beta could be extended to the other Lewis acid materials. This would allow one to begin to address the questions related to true active site concentrations in these materials, at least before and after reaction. Recently, the open site population was measured for several samples of Sn-Beta and less than half were determined to be the open configuration.^[39] This highlights how grossly underestimated TOF can be when assuming all the Sn content is active. To be able to accurately compare these materials and understand their varying activity, it is necessary to develop the ability to quantify the active sites.

By way of either the catalyst or the reactants, the chemistries discussed in this work have the major advantage of being particularly selective. For example, the MPV reduction is highly selective on Lewis acid zeolites compared to Brønsted acid zeolites. The acylation of methylfuran is very selective to the 5 position of the furan ring, regardless of the acidity of the catalyst used. In this way, there is great potential for these zeolite materials to be applied to specifically designed processes to convert

renewable sugar and furanic feedstocks to desired products selectively. Thus, despite the current limitations in synthesis and characterization of Lewis acid zeolites, they should continue to be developed as catalysts for these processes to utilize biomass.

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Appendix A

LEWIS ACIDIC ZEOLITE BETA FOR THE MEERWEIN-PONNDORF-VERLEY REDUCTION OF FURFURAL



A.1 Furfuryl alcohol rates with time on stream

Figure A.1: Rate of furfuryl alcohol production with time on stream at 328 K. Reaction conditions: 14 bar, [Furfural]₀=52 mmol/L in isopropyl alcohol. WHSV [mol Furfural/mol metal/min]=Hf: 34.4, Zr: 11.3, Sn: 5.5



Figure A.2: Rate of furfuryl alcohol production with time on stream at 338 K. Reaction conditions: 14 bar, [Furfural]₀=52 mmol/L in isopropyl alcohol. WHSV [mol Furfural/mol metal/min]=Hf: 34.4, Zr: 11.3, Sn: 5.5



Figure A.3: Rate of furfuryl alcohol production with time on stream at 358 K. Reaction conditions: 14 bar, [Furfural]₀=52 mmol/L in isopropyl alcohol. WHSV [mol Furfural/mol metal/min]=Hf: 34.4, Zr: 11.3, Sn: 5.5

A.2 Rate and half-life of MPV reduction on Lewis acid zeolite

Table A.1: Initial rates of furfuryl alcohol and furfural diisopropyl acetal formation and catalyst half-life at various temperatures. See Figure 3.6 for conditions. *Units:[hours]

	Sn-Beta		Zr-Beta		Hf-Beta	
	Rate [*]	Half-life*	Rate [*]	Half-life [*]	Rate [*]	Half- life [*]
328 K						
Furfuryl alcohol	0.1	19.1	0.5	5.0	1.2	6.2
Furfural acetal	0.2	9	0.2	5.4	0.3	5.8
338 K						
Furfuryl alcohol	0.3	3.1	1.1	5.2	2.8	3.9
Furfural acetal	0.3	3.0	0.2	6.7	0.3	5.7
358 K						
Furfuryl alcohol	0.5	7.8	2.8	7.9	6.9	7.5
Furfural acetal	0.9	4.9	0.2	4.4	0.4	8.7

A.3 Spent catalyst before and after calcination



Figure A.4: Hf-Beta after reaction at 338 K (left) and after calcination at 853 K (right)



Figure A.5: Zr-Beta after reaction at 348K



Figure A.6: Sn-Beta after reaction at 348 K

Appendix B

PRODUCTION OF PARA-METHYLSTYRENE AND PARA-DIVINYLBENZENE FROM FURANIC COMPOUNDS

B.1 NMR Spectra of 2-acetyl-5-ethylfuran

¹H NMR (400 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 3.5 Hz, 1H), 6.18 (dt, *J* = 3.5, 0.9 Hz, 1H), 2.81 – 2.69 (m, 2H), 2.45 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 186.24, 163.40, 151.36, 119.38, 107.36, 77.36, 77.04, 76.72, 25.73, 21.75, 11.78.



Figure B.1: ¹H NMR spectrum of 2-acetyl-5-methylfuran

B.2 NMR Spectra of 2-ethyl-5-methylfuran

¹H NMR (400 MHz, Chloroform-*d*) δ 5.87 (s, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.28 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.04, 150.07, 105.72, 104.33, 21.36, 13.50, 12.29



Figure B.2: ¹H NMR spectrum of 2-ethyl-5-methylfuran

B.3 NMR Spectra of 2,5-diethylfuran

¹H NMR (400 MHz, Chloroform-*d*) δ 5.89 (s, 2H), 2.64 (q, *J* = 7.5 Hz, 4H), 1.25 (t, *J* = 7.6 Hz, 6H) ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.92, 104.08, 21.36, 12.24.



Figure B.3: ¹H NMR spectrum of 2,5-diethylfuran



B.4 GC-MS fragmentation patterns of Diels-Alder cycloaddition and dehydration products


Figure B.4: GC-MS fragmentation patterns of 2-ethyl-5-methylfuran Diels-Alder cycloaddition and dehydration side products

Appendix C

ACYLATION OF METHYLFURAN USING BRONSTED AND LEWIS ACID ZEOLITE CATALYSTS

C.1 Arrhenius analysis of flow experiment data

Extrapolation of time on stream data can result in over estimations of the initial rate, however, the exponential fits on each catalyst were very similar, so that the activation energy was similar whether the initial rate from extrapolation, the first time point collected, or the last time point collected was used to calculate the activation energy, as shown in Table C.1. For all the samples but H-[Al]-Beta-150, the first time point was after 15 minutes time on stream and the last was 90 minutes time on stream. For H-[Al]-Beta-150, the first time point was 30 minutes time on stream and the last

	E _{a,app} from	$E_{a,app}$ from rate at	E _{a,app} from last
Catalyst	extrapolated rate	first time point	time point
	[kcal/mol]	[kcal/mol]	[kcal/mol]
H-[Al]-Beta-12.5	16.6	16.0	15.0
H-[Al]-Beta-150	20.5	19.9	14.7
[Sn]-Beta-HT	9.0	9.3	11.5
[Sn]-Beta-SSIE	8.8	10.1	7.7

Table C.1: Activation energy calculated from various rates for methylfuran acylation

C.2 Weisz-Prater Analysis of [Sn]-Beta-HT

Based on the SEM of [Sn]-Beta-HT and H-[Al]-Beta-150, the crystal size of [Sn]-Beta-HT is approximately 2.5 µm, significantly larger than the 500 nm crystal size observed for the commercial H-[Al]-Beta sample. The large crystal size and low activation energy may imply that the reaction on [Sn]-Beta-HT could be mass transfer limited. Since the activation energy on the [Sn]-Beta-SSIE made from solid state ion exchange, which has a small crystal size, is very similar to that of [Sn]-Beta-HT made hydrothermally, this suggests the [Sn]-Beta-HT is not mass transfer limited or the activation energy for the small crystal sample would be approximately twice as high as the large crystal sample. However, the Weisz-Prater criterion was also computed as further evidence that the [Sn]-Beta-HT rates are not limited by mass transfer. The W-P criterion at both the highest and lowest temperatures that [Sn]-Beta-HT rates were collected at in the flow reactor are reported below. The effective diffusivity is estimated from values reported for the diffusion of toluene, which has a greater kinetic diameter (5.85 Å) compared to methylfuran (5.3 Å) [1], in zeolite H-[Al]-Beta at 400K and 450K [2]. Typically a W-P number less than 0.3 indicates no mass transfer limitations.

	393 K	423 K
r' [mol/g/sec]	2.35E-5	5.42E-5
$\rho_{\rm c} [g/{\rm cm}^3]$	0.46	0.46
R [cm]	0.00025	0.00025
$D_e [cm^2/sec]$	10E-9	10E-918E-9
C _{As}	1.31E-3	1.31E-3
C _{WP}	0.051	0.12 0.07

Table C.2: Weisz-Prater criterion for [Sn]-Beta-HT

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