SOLID ACID CATALYSTS FOR BIOMASS AND SUGAR UPGRADING TO FURANS

by

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ABSTRACT

Platform chemicals derived from biomass provide a viable alternative to petroleum-based fuels, chemicals, and materials. The efficient production of chemical building blocks, such as 5-hydroxymethylfurufral (HMF) and furfural, requires an optimized catalyst and reaction system, as well as an efficient system in which catalysts and products can be easily recovered. While homogeneous acid catalysts have historically been a popular choice for furan production, additional safety, material, and corrosion considerations motivates the exploration of heterogeneous solid acid catalysts. Furthermore, biphasic reaction systems, which use an organic solvent to continuously extract products, have shown increased furan yields over aqueous and monophasic systems and can allow for easy product recovery if the boiling point is selected carefully. One class of heterogeneous catalysts known as zeolites, has unique potential for furfural and HMF production with its controlled acidic and structural properties. A novel SAPO-34/5A zeolite bead is presented in this thesis, showing promise in catalyst design for activity, product selectivity, and stability. The combination of optimized solvent systems with carefully designed solid acid catalysts lays a framework for the progression of platform chemical production from biomass. Additionally, a comprehensive review of heterogeneous catalysts for furan production in biphasic systems is presented here, which informs decisions on optimized solvent selection.

CHAPTER ONE

INTRODUCTION

Global chemical production is largely dependent on fossil fuels. Petroleum derived products dominate power generation and transportation fuels, and additionally make up a large portion of chemicals and manufactured materials. With rising concerns about the environmental and economic impacts of petroleum dependency, there is motivation to seek alternative sources for fuels, chemicals, and materials.

Biomass from plants is recognized as a viable alternative source for fuels and chemicals. Since the mid-1980s significant research has focused on biomass as an energy source.[1] One potential feedstock is lignocellulosic biomass, such as perennial grasses, and other food crop wastes, such as corn stover.[2-3] Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin (Figure 1). Hemicellulose and cellulose are polymers that consist mainly of xylose (C5) and glucose (C6), [2, 4-5] which can be upgraded into an array of different chemicals.

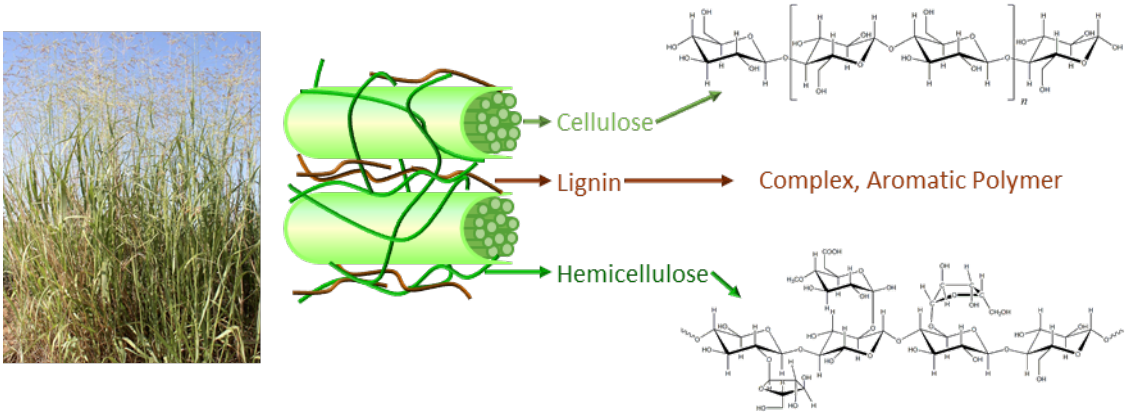

Figure 1. The composition of biomass, such as switchgrass, is broken down into cellulose, lignin, and hemicellulose which are valuable feedstocks.

From C5 and C6 sugars found in biomass, you can synthesize platform chemicals that serve as valuable intermediates for upgrading to a wide range of products (Figure 2). Of particular interest are furfural and 5-hydroxymethylfurfural (HMF), both recognized in the top 30 value-added chemicals from biomass by the Department of Energy,[6] which are important building blocks for energy dense fuels and chemicals.[7] Furfural has been used in bioplastics, pharmaceutical synthesis, and agricultural solvents,[8] as well as a platform for C_{10}-C_{15} biofuels. Hydrogenation, rearrangements, and furan coupling upgrading for furfural are viable routes to drop-in fuels and diesel hydrocarbons.[2] HMF has also found applications in bioplastic materials, pharmaceuticals and chemical synthesis, solvents, fuels, and even metal organic frameworks.[9-10] Polymers such as 2,5-furandicarboxylic acid are easily derived from HMF and can substitute petroleum derived polyethylene terephthalate (PET),[11] which has an annual global production

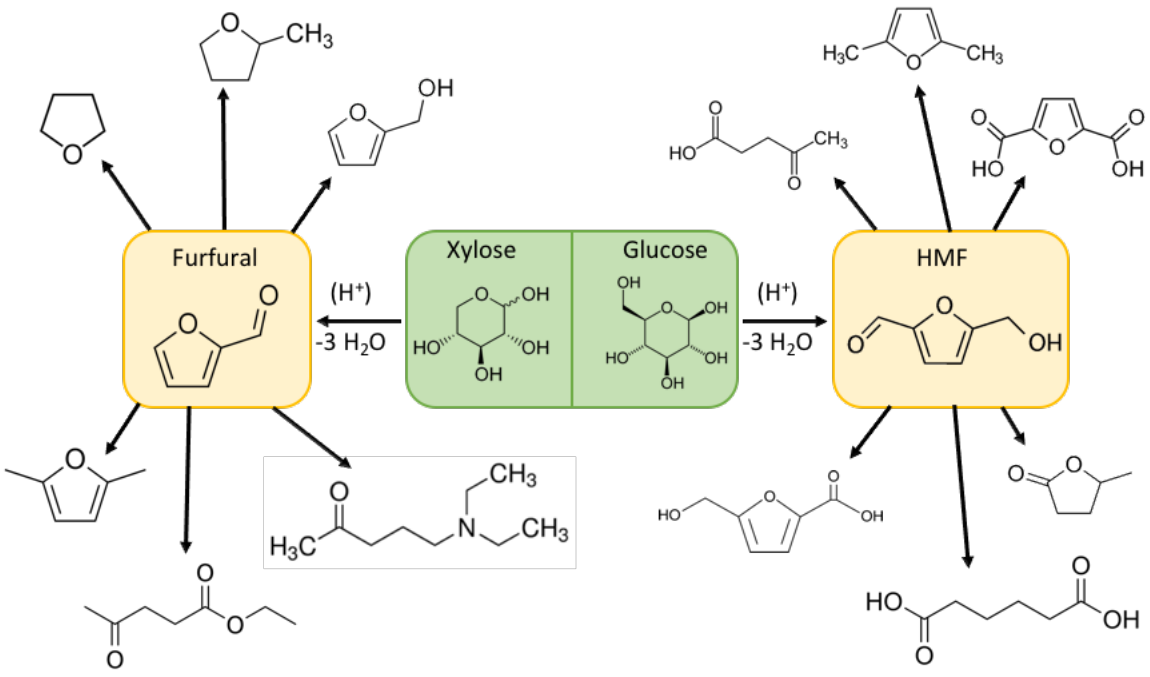

Figure 2. The reaction pathways of xylose and glucose to platform chemicals furfural and 5-hydroxymethylfurfural and subsequent upgrading to potential commodity chemicals.

greater than 50 million tons.[12] Upgrading HMF by oxidation, reduction, hydrolysis, and esterification provide routes to many value-added products, including fuel additives like 2,5-dimethylfuran.[13]

The efficient production of furfural and HMF from biomass and model sugars has been a major focus of research and has significantly increased in the last decade.[14] Homogeneous acid catalyzed dehydration of xylose to furfural and glucose to HMF have shown high yields in multiple solvent systems[2, 9-10, 15-16] and considerable research has also focused on heterogeneous acid catalysts, which are less corrosive and do not require special handling. Several classes of heterogeneous catalysts, including metal oxides, ion-exchange resins, carbon-based, and zeolites, have been explored for furan production (Figure 3).[7, 9, 15, 17-20] Heterogeneous catalysts have unique structural and chemical properties, such as porosity and acidity, which can be tuned to increase product selecitivity.[17, 21] With the potential for increased furan yields, developing efficient heterogeneous catalysts has been recognized as core areas initiatives by the Department

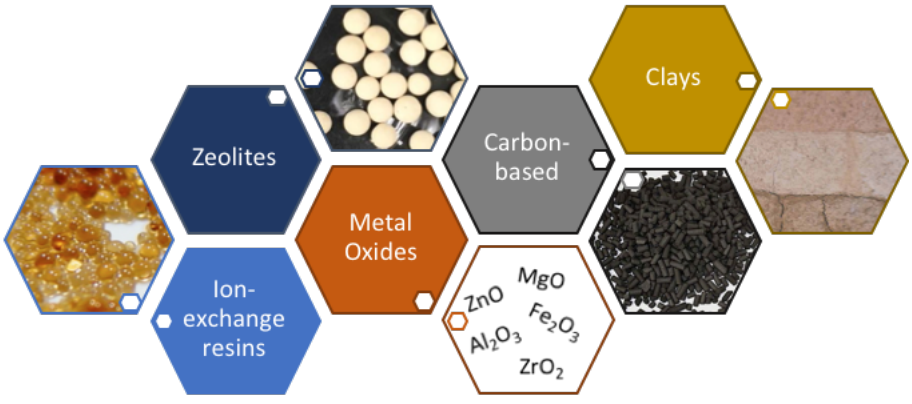

Figure 3. Different classes of heterogeneous catalysts commonly used in biomass conversion reactions.

of Energy,[22] and current research continues to make progress in furfural and HMF production to realize the potential of platform chemical production from biomass.

In addition to efficient catalysts, solvent systems can also be optimized to increase product yields. The simplest solvent for dehydration of biomass and model sugars to furans is water, which is favorable for sugar solubility and low cost. However, reactions in water often employ homogeneous acid catalysts and have lower furan selectivity, resulting in higher biproduct yields.[2, 23] The introduction of other solvents to heterogeneous reaction systems has the potential to increase furan yields, however, additional considerations arise, such as solvent adsorption to the catalyst surface, solvent participation in the reaction, and mass transport effects.[24] Biphasic systems, which employ an organic solvent to continuously extract and protect products from degradation, have shown increased furfural and HMF selectivity from biomass and model sugars.[10, 14-15, 18] In the second chapter of this work, a review on heterogeneous catalysts in biphasic solvent systems is presented, demonstrating the potential of biphasic systems for increased yields.

Increasingly popular for furan production are zeolites, a class of heterogeneous microporous aluminosilicate catalysts (Figure 4), with unique porous structures and tunable acidity that have been explored in a variety of solvent systems.[17, 25] The pore structure can be optimized with the selection of different frameworks, impacting shape selectivity. Additionally, acidity can be tuned by changing the Si/Al ratio, where increasing the Si/Al ratio decreases total acidity.[17] With their microporous structures, one consideration is that mass transport limitations, related to solvent properties, can affect

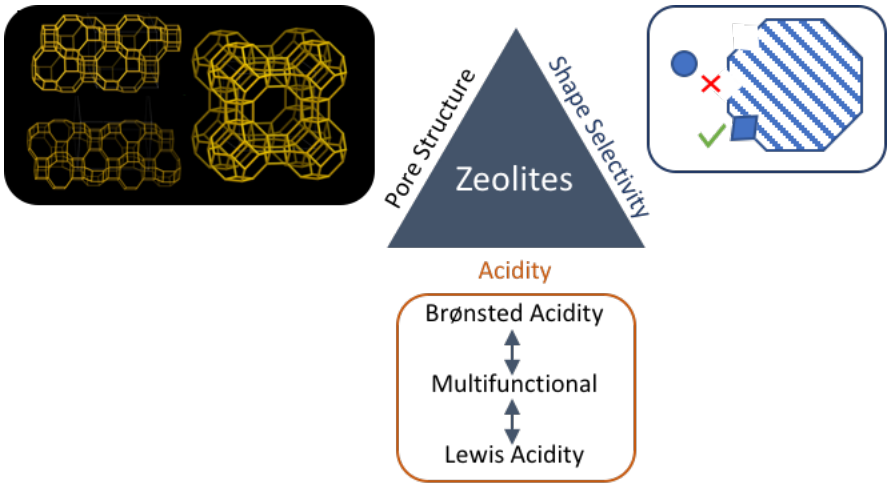

Figure 4. Heterogeneous zeolites have unique tunable properties, including pore structure, shape selectivity, and acidity.

the activity of zeolites since larger molecules, such as sugars, may have difficulty diffusing in the small pore channels.[24] Zeolites have shown moderate to high furan yields in both aqueous and biphasic systems, with a need for focus on catalyst stability in liquid phase reactions.[2, 10, 17, 25] In the third chapter, a novel SAPO-34/5A zeolite bead catalyst for furfural production from xylose, with good stability in aqueous systems, is presented. With potential for increased furan selectivity in biphasic systems, heterogeneous zeolites provide a promising avenue for platform chemical production from biomass.

In this thesis, a comprehensive review of biphasic solvent systems for use with heterogeneous catalysts for furfural and HMF production from model sugars and biomass is presented. With the promise shown by zeolites, the SAPO-34/5A zeolite beads present a unique solution to challenges in mass transport and catalyst stability. Careful consideration of both solvent system and catalyst activity will lead to the development of high furan yield reaction systems from lignocellulosic biomass.

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CHAPTER TWO

CONVERSION OF SUGARS AND BIOMASS TO FURANS USING HETEROGENEOUS CATALYSTS IN BIPHSAIC SOLVENT SYSTEMS

Contribution of Authors and Co-Authors

Manuscript in Chapter

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Contributions: Lead writing of the original draft. Lead writing for review and editing.

Co-Author: Nathan V. Bollar

Contributions: Supporting writing of original draft. Supporting writing of review and editing.

Co-Author: Coy J. Zimmermann

Contributions: Supporting data curation. Supporting writing of original draft.

Co-Author: Stephanie G. Wettstein

Contributions: Lead on conceptualization, project administration, and resources. Supporting writing of review and editing.

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Conversion of Sugars and Biomass to Furans Using Heterogeneous Catalysts in Biphasic Solvent Systems

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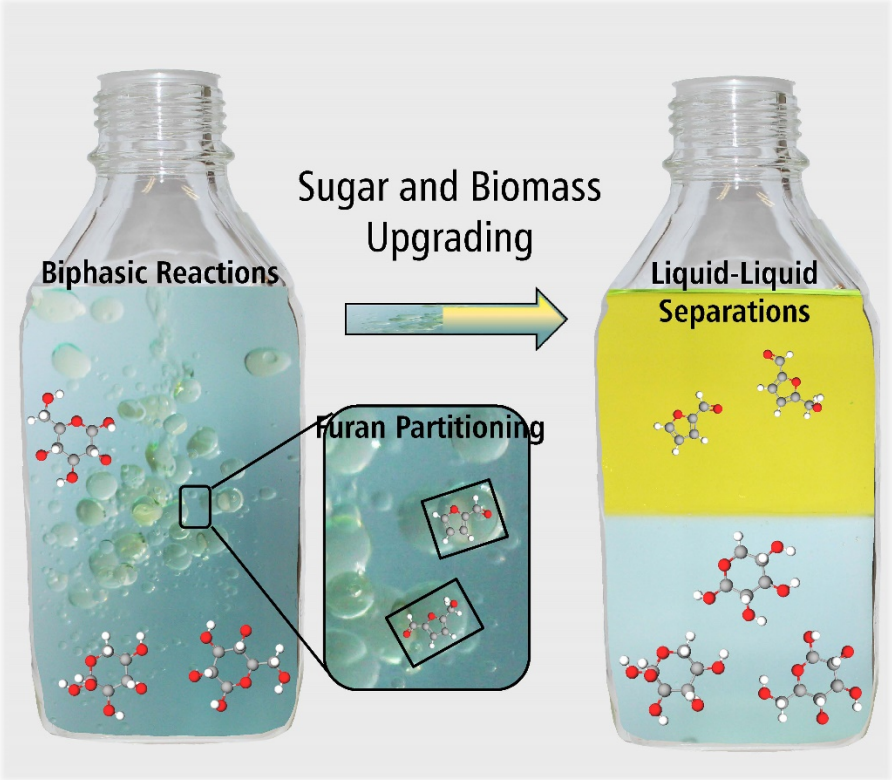

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Within the last decade, interest in using biphasic systems for producing furans from biomass has grown significantly. Biphasic systems continuously extract furans into the organic phase, which prevents degradation reactions and potentially allows for easier separations of the products. Several heterogeneous catalyst types, including zeolites, ion exchange resins, niobium-based, and others, have been used with various organic solvents to increase furan yields from sugar dehydration reactions. In this minireview, we summarized the use of heterogeneous catalysts in biphasic systems for furfural and 5-hydroxymethylfurfural production from the past five years, highlighting trends in chemical and physical properties that effect catalytic activity. Additionally, the selection of an organic solvent for a biphasic system is extremely important and we review and discuss properties of the most commonly used organic solvents.

1. Introduction

Biphasic reaction systems present a viable route to platform chemicals, such as furfural and 5-hydroxymethylfurfural (HMF), from lignocellulosic biomass. These systems take advantage of the differences in hydrophobicity of reactants and products and typically lead to higher product yields than with monophasic, aqueous systems. In the case of biomass reactions, products that might degrade in the aqueous layer, such as furans, partition to the organic layer while the sugar and acids remain in the aqueous layer. Therefore, better downstream separations occur and less energy is needed for recycling solvents since the products are concentrated in the organic phase. Additionally, the solvent properties, such as boiling point, can be selected to improve separations. For example, a higher boiling solvent could be used to obtain desired products from the top of a distillation column or a lower boiling solvent could be used if the product is heat sensitive.

Lignocellulosic biomass is abundant in the form of corn stover, pulp and paper mill waste, food waste, switchgrass, and many other sources.[1] Biomass is composed of three main fractions: cellulose, a glucose polymer, hemicellulose, a polymer mainly composed of xylose, and lignin, which is made up of aromatic compounds. Additionally, biomass contains inorganic salts, ash, and proteins, among other components that may affect heterogenous catalysis.[2] Although much progress has been made in upgrading the sugar fractions to fuels and chemicals,[3] obtaining high yields of platform chemicals economically remains a challenge. Using biphasic systems for biomass hydrolysis is a potential solution that has many advantages since solvents can prevent furan polymerization,[4] concentrate products by using a lower volume of solvent,[5] and enhance biomass solubility, which leads to less solids remaining after reaction and potentially faster reactions.[6]

An ideal solvent for a biphasic system would be one that has minimal solubility in the carrier (in biomass processing, the carrier is likely water), a high relative volatility when compared with the solutes for easy recovery, and a high partition coefficient for the solute, which is the amount of solute in the organic phase relative to the amount of solute in the aqueous phase.[7] The simplest biphasic system is one that naturally separates and does not require the use of modifiers. Modifiers, such as NaCl, are sometimes used to create biphasic systems when they would not normally exist and/or increase the partition coefficient of the solute. (The increase in the partition coefficient is commonly referred to as the salting-out effect.) However, modifiers may interact with heterogeneous catalysts; for example, ion exchanging with active sites, which adds a layer of complexity to the system. Since modifiers may require an additional separation step to recover and add cost to the process, a biphasic system without modifiers is preferred.

The addition of a solvent will likely require an additional separation step, which adds cost to the process. Due to the elevated price of many organic solvents, the organic layer must be recovered and reused in order for the process to be economically viable.[8] If the solvent is soluble in the carrier (and vice versa), additional processing volume and a separation step to recover the carrier may be needed. Other properties, such as viscosity and toxicity, also need to be considered, but perhaps the most important property for catalysis is if the solvent participates in the reaction since that could significantly affect resulting products. For the vast majority of biphasic reactions, an inert solvent is preferred.

One common use of biphasic systems is to produce furans, such as HMF from glucose or fructose and furfural from xylose. The organic solvent extracts the furans and reduces degradation and further reactions. HMF is a building block for many chemical applications including liquid fuels, platform chemicals, polyester building blocks, and others.[9] Furfural can also be used as a solvent or upgraded to many chemicals such as furfuryl alcohol, which can then be used to produce furan resin prepolymers, and with further hydrogenation, tetrahydrofurfuryl alcohol, which is used as a solvent in agricultural applications.[10]

Publications on furfural, HMF, and biphasic reactions have grown considerably in the last decade (Figure 1). Previous works have reviewed furfural and HMF as value-added products derived from biomass, including discussion of suitable feedstocks, synthesis methods, and pathways for upgrading to fuels.[5,9a,11] Reviews by Saha et al.[9a] and van Putten et al.[11b] provide a thorough review of biphasic systems used for synthesizing HMF with homogeneous and heterogeneous

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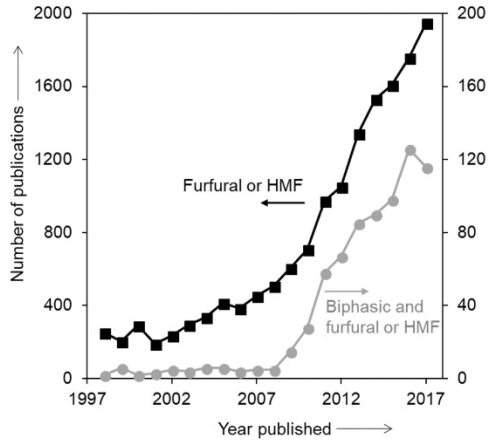

Figure 1. Number of review or research articles published per year containing "Furfural or HMF" (■) or "Biphasic and furfural" and "Biphasic and HMF" (●) that appeared on a sciencedirect.com search 5/4/18.

catalysts through 2013, while Dutta et al.,[11a] Lange et al.,[5] and Delbecq et al.[12] reviewed multiple upgrading reactions and methods for furfural production. To the best of our knowledge, no reviews thoroughly cover biphasic furan production in publications since 2013.

In this paper, we review publications from the last five years regarding biphasic production of furfural and HMF using heterogenous catalysts ranging from zeolites to polymers. We discuss the physical and chemical properties of heterogeneous catalysts that contribute to their activity, the use of phase modifiers to increase partitioning in biphasic systems, considerations of solvent selection, and overall trends in conversion and yields using biphasic reactions.

2. Heterogenous Catalysts

Heterogeneous catalysts have been increasingly popular for furan production.[13] Unlike homogeneous acid catalysts that can be corrosive and require special handling, heterogeneous catalysts can easily be integrated into reaction systems and are easier to recover. Different classes of heterogeneous catalysts have unique acidities, hydrophobicities, and surface structures that contribute to their activity.[14] Included among these are zeolites, polymer-based, niobium-based, clays, and carbon-based catalysts.

2.1. Zeolites

Microporous zeolites have been widely used as catalysts for the production of furfural and HMF in biphasic systems due to their chemical resistance, acidic properties, and stability in high temperature environments. A review by Ennaert et al. on using zeolites for biomass conversion contains an excellent background on fundamental zeolite catalysis including the challenges of using zeolites in high temperature, liquid reactions.[15]

The zeolite framework can be chosen to select pore size, and the acidity can be tuned by atom composition, including changing the Si/Al ratio. The amount of Al is related to the Brønsted acidity, which, for example, directly contributes to the dehydration of xylose to furfural.[16] Table 1 lists some of the

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Nathan Bollar received his BSc in chemistry at Carroll College in Helena, Montana in 2015 and received his master's in chemical engineering at Montana State University in 2018 working under the guidance of Dr. Stephanie G. Wettstein. Nathan researched biomass fractionation using organic solvent systems.

Coy Zimmermann graduated with a BSc in Chemical Engineering summa cum laude from Montana State University in 2018. He performed research under the guidance of Dr. Stephanie G. Wettstein on biomass fractionation using organic solvents. In the Fall of 2018, Coy began his doctoral program at Colorado School of Mines in Chemical Engineering. His general research interests involve reaction kinetics and transport phenomena.

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Table 1. Properties of zeolites used for furfural production from xylose at 170 °C, unless otherwise noted, in biphasic systems.

Zeolite	Framework	Pore size[a] [nm]	Si/Al ratio	Surface area	Total acidity [μmol/g]	Reaction time [h]	Yield	Ref.
H-Y	FAU	0.74	4	617	1384	1	19[b]	[17]
MOR-10	MOR	0.7	10	400	480	6	61	[18]
H-USY	FAU	0.61	15	873	550	6	56	[19]
CHA-20	CHA	0.38	20	548	1030	6	60	[18]
ITQ-2	–	0.7	24	623	198	16	66	[20]
H-MCM-22	MWW	0.55	24	333	204	16	70	[20]
H-MCM-22	MWW	0.55	38	497	168	24	60	[20]
H-MCM-22	MWW	0.55	38	497	168	32	68	[20]

[a] From http://www.iza-structure.org/databases/ ; [b] At 160 °C.

recently used zeolites in biphasic systems and shows the wide range of pore sizes and acidities that have been used for furfural production from xylose in recent years. Antunes et al. used H-MCM-22 zeolite and achieved higher furfural yields (70%) from xylose in a toluene/H_2O biphasic system (7:3 volume ratio) compared to the pure water system (54%). Decreasing the Si/Al ratio from 38 to 24 increased the acidity of the catalyst from 168 to 204 μmol/g, which increased furfural yields at shorter reaction times (Table 1).[20] The catalyst with the lower Si/Al ratio required less reaction time (16 versus 24 h), which represents a higher turn-over frequency, and was recyclable four times with no loss of furfural yield.[20] Other researchers used zeolites with Si/Al ratios ranging from 4–20 and higher acid site concentrations, but did not achieve the yields Antunes et al. did with H-MCM-22 (Table 1).

Researchers also used bamboo and bagasse as the xylose source, multiple solvents, and different zeolites with the highest furfural yields around 55% (Table 2). For bagasse, compared to the monophasic, aqueous system, where only 18% furfural was obtained, the biphasic systems led to significantly higher yields and showed that zeolites can be successfully used in biphasic dehydration reactions with biomass.[19]

Zeolites have also been explored for converting fructose to HMF in biphasic systems. Similar to work for furfural production from H-USY,[19] Pande et al. optimized HMF production in a biphasic MIBK/H_2O system with modified H-USY zeolites since MIBK resulted in higher HMF yields than toluene, IPA, and ethanol. The polar IPA and ethanol solvents had lower partition coefficients than the nonpolar MIBK and toluene solvents, which are also less miscible in water. HMF yields of 32% and 65% and furfural yields of 31% and 11% (resulting from HMF degradation to formaldehyde) were achieved using commercial H-USY and 10 wt% H_3PO_4 treated H-USY, respectively.[21] The acid treatment decreased the Al content (from 2.8 wt% to 1.2 wt%) of the H-USY and therefore, increased the Si/Al ratio. The total acidity decreased from 860 μmol/g to 270 μmol/g with the H_3PO_4 acid treatment, which the authors hypothesized enhanced hydrothermal stability, hydrophobicity, and increased the mesoporosity of the catalyst. H-USY treated with H_2SO_4 also had lower acidity and Al content, but did not have increased mesoporosity like the H_3PO_4 treated zeolite. For the H_2SO_4 treated H-USY, the HMF and furfural yields were equivalent or less than the non-treated H-USY indicating that the increased mesoporosity of the H_3PO_4 treated H-USY was an important factor to the increased yields.[21]

Despite results showing increased activity with lower acidity for furfural production,[21] higher catalyst acidity was an important factor to achieve high HMF product yields. Ordomsky et al. tested zeolites, including ZSM-5, BEA, and MOR for HMF production in a MIBK/H_2O system. MOR had the highest acidity (11.7 Si/Al, 1100 μmol/g) and had the highest HMF selectivity achieving approximately 65% selectivity at 80% conversion (165 °C). Although ZSM-5 had a relatively high acidity (13 Si/Al, 966 μmol/g), its pore size of 0.55 nm[22] may have restricted the diffusion of fructose (0.9 nm[23]), leading to many of the acid sites not being accessible. Both MOR and BEA have larger pores (0.7 and 0.75 nm,[22] respectively), which would reduce mass transfer limitations of fructose[24] since it is known that zeolites can adsorb molecules up to 0.1[25] to 0.2[5] nm larger than the pore diameter. When using microporous catalysts, internal diffusion limitations are an important consideration; however, the lower HMF yields with BEA, despite its larger pore diameter, were attributed to the lower acidity (15.6 Si/Al, 860 μmol/g) compared to MOR.[24]

The addition of modifiers to biphasic systems when using zeolite catalysts is uncommon, perhaps due to catalyst deactivation from mineral salts. Biomass impurities, including Na and K, are known to decrease zeolite activity[12] and salts can cause the Si and Al sites to leach, which, even though the crystalline structure remains intact, significantly impacts the

Table 2. Furfural yields using zeolite catalysts and different biomass sources at 170 °C.

Xylose source	Weight percent	Org:H_2O ratio	Solvent	Catalyst	Reaction time [h]	Furfural yield [%]	Ref.
Bamboo	3.5	4:1	toluene	CHA-20	10	55	[18]
Bamboo	3.5	4:1	toluene	MOR-10	10	49	[18]
Bagasse	1	1:1	toluene	H-USY	6	54	[19]
Bagasse	1	1:1	MIBK	H-USY	6	55	[19]
Bagasse	1	1:1	p-xylene	H-USY	6	56	[19]
Bagasse	1	–	water	H-USY	6	18	[19]

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catalyst acidity.[26] However, introducing NaCl in a sec-butylphenol (SBP)/H_2O biphasic system using ZSM-5 as the catalyst showed increased HMF selectivity from glucose. Unmodified systems without NaCl had low HMF selectivity compared to the modified system, which had 81% HMF selectivity at 100% conversion (170 °C, 30 min). Gardner et al. hypothesized a synergistic effect with the NaCl present in the aqueous phase. The hydrolysis was enhanced by releasing the Al^{3+} species from the zeolite, which isomerized the glucose to fructose, in addition to increasing product into the organic phase.[26] Although high HMF yields could be obtained from the leached acid sites in the solution,[26] recyclability is likely poor and regeneration would be extensive.

The high furan yields resulting from the zeolite catalysts demonstrate the utility of multiple organic solvents as extracting solvents in biphasic systems in addition to the wide variety of zeolites that can be used for platform chemical production. Furan yields benefited from some acidity and the increased mesoporosity created with acid treatments. Additionally, some zeolites may have had internal diffusion limitations, which shows that pore size is an important consideration for catalytic reactions.

2.2. Polymers/Ion Exchange Resins

Acidic, ion exchange resins are attractive catalysts with high activity, mechanical stability, and low cost. These resins have tunable properties related to the monomer type, degree of polymerization, and functional groups added to the polymer framework. Additionally, their macroporous structures have high surface area with large pores that can be formed during polymerization.[27] The large pores in ion exchange resins allow sugar molecules to easily diffuse into their macropores to access acid sites.[16] These polymeric catalysts, typically supplied as spherical pellets, have been shown to have excellent recovery and reusability, but can have performance issues due to leaching of acid sites.[27]

Commercially available ion exchange resins, including Amberlyst, Purolite, and Nafion have been used for furan dehydration reactions with varying results. These solid, sulfonated polymers have strong Brønsted acidity, high activity, and hydrophobic structural characteristics.[14] Mittal et al. used Purolite CT275 and Nafion NR50 in MIBK biphasic systems to convert pentose-rich corn stover hydrolysate into furfural. Unlike common ion exchange resins, which are only stable to around 150 °C, Purolite and Nafion showed increased thermal stability up to 180 °C and 200 °C, respectively. The highest yields were achieved at an organic to aqueous volume ratio of 2:1 using hydrolysate equivalent to 8 wt% monomeric pentose sugars (170 °C; 20 min). The MIBK/H_2O biphasic system resulted in high furfural yields for both Purolite (80%) and Nafion (78%) catalysts, but the Nafion system required eight times the catalyst loading (400 mg/g pentose sugar) than the Purolite system. The significantly lower catalyst loading for the Purolite system was attributed to the higher H^+ concentration compared to the Nafion catalyst,[28] which despite its high acidic properties, had a lower surface area (0.02 m^2/g) that limited its performance.[16] The furfural yields from the heterogeneous systems were similar to using 0.05 M H_2SO_4 indicating that solid-acid catalysts in biphasic systems could be used to replace homogeneous catalysts. However, upon catalyst recycling (no washing or regeneration), the furfural yields decreased significantly with the Purolite catalyst from 71.5% for 1st run to 38.0% for the 4th run, resulting from what the researchers attributed to the blocking of active sites.[28]

Despite challenges that arise from Nafion's low surface area, Le Guenic et al. used Nafion NR50 in a cyclopentyl methyl ether (CPME)/H_2O NaCl modified biphasic system, obtaining maximum furfural yields of 80% (170 °C, 40 min) from xylose under microwave irradiation. Decreasing the NaCl content from 2.5 wt% to 0.25 wt% decreased furfural yields by approximately 12% indicating that the salting-out effect was stronger at higher NaCl concentrations.[29] In a similar study, Wang et al. presented an alternative biopolymer, sulfonated sporopollenin, for furfural production due to its high thermal stability and unique hydrophobic cavity within its structure. In a CPME/H_2O biphasic system modified with NaCl, furfural yields of 69% were achieved (190 °C, 40 min) under microwave irradiation. The catalyst was able to be recycled 10 times with only a 5% decrease in furfural yield with NaCl present and a 10% decrease in furfural yield with no NaCl present.[30] As also seen by Le Guenic et al.,[29] Wang et al. found that increasing the NaCl content produced higher furfural yields in CPME/H_2O biphasic systems (3:1 volume ratio; Figure 2). In the modified biphasic system, NaCl interacts with carbocation intermediates in the dehydration reaction in addition to increasing the partitioning of furfural into the organic phase; thus, furfural production is increased compared to aqueous systems.[30]

In addition to these benefits, the NaCl modifier was also found to have synergetic effects with the Nafion NR50 catalyst

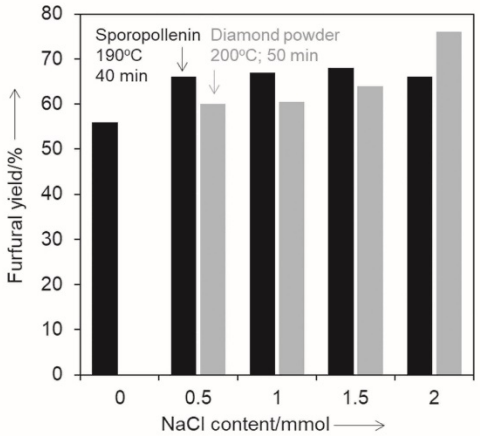

Figure 2. The effect of NaCl content on furfural yields with heterogeneous catalysts in CPME/H_2O biphasic systems from Wang et al. for dehydration of xylose over sulfonated sporopollenin[30] (black bars) and Delbecq et al. for sulfonated diamond powder[31] (gray bars).

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by Le et al. A cation exchange between the sulfonated polymer catalyst and modifier released HCl which contributed to the dehydration of xylose as a homogeneous catalyst. Further studies on the pH of the Nafion NaCl system compared to homogeneous HCl reactions confirmed that the Nafion NR50 activity contributed to higher furfural yields, but was not a completely heterogenous reaction.[29]

Along with the zeolite catalysts mentioned in the previous section, Ordomsky et al. also used Amberlyst-15 in a biphasic MIBK/H_2O system to increase selectivity to HMF compared to a monophasic aqueous system. The addition of MIBK as an extracting organic solvent increased HMF selectivity to a maximum of 77% (135 °C, 5:1 ratio MIBK/H_2O) compared to 66% selectivity with a 1:1 ratio MIBK/H_2O and 55% selectivity in water all at 35% conversion.[32] As seen by Mittal et al. with furfural and Purolite,[28] increasing the organic to aqueous ratio increased the HMF selectivity and running the reaction in a biphasic system was found to suppress further HMF conversion.[32] MIBK has a high partition coefficient for both furfural (6.4 in 2:1 volume ratio[28]) and HMF (2.7 in 3:1 volume ratio[32]), which makes it an effective extracting solvent in biphasic systems.

High furfural yields can be achieved using ion exchange resins but leaching of the active sites could result in homogeneous reactions and the inability to recycle the catalyst. Nevertheless, synergistic effects between modifiers and ion exchange resins could increase furan selectivity and yield. Ion exchange resins benefited from increasing the organic to aqueous ratio, increased acidity, and adding a modifier to the system.

2.3. Niobium-based

Niobium-based catalysts can be used for dehydration reactions due to their acidic properties, high stability in aqueous reactions, chemical safety, and relatively low cost.[33] Niobium-based catalysts have been used as promoters, with supports, and as solid acid catalysts in catalytic reaction systems.

Compared to monophasic systems, using niobium catalysts in biphasic systems increased furfural yields with CPME, toluene, THF, and xylene as organic solvents. Research by Molina et al. showed that biphasic CPME/H_2O systems increased furfural yields of up to 14% from xylose over aqueous and monophasic GVL/H_2O systems (130 °C, 6 h) using niobium oxide (Table 3).[34] Garcia-Sancho et al. investigated acidic mesoporous niobium pentoxide (Nb_2O_5; 198.6 μmol/g) catalysts to convert xylose into furfural in toluene/H_2O biphasic systems achieving yields of 54% (170 °C; 90 min).[35] Further work found that using 12 wt% Nb on a mesoporous silica support (SBA-15) with moderate acidity (318 μmol/g) significantly increased the furfural selectivity. The furfural selectivity was found to be 93% at 85% conversion (160 °C) compared to the monophasic system, which had around 54% furfural selectivity at approximately 84% conversion.[36] Similar work using amorphous niobium oxide by Gupta et al. evaluated THF, toluene, and xylene as organic solvents. The biphasic toluene/H_2O system was found to have the highest selectivity for furfural (72% at greater than 99% conversion) compared to the pure water system (48% furfural selectivity at 93% conversion).[37]

Pholjaroen et al. used acidic niobium phosphate (NbP, 402 μmol/g) as the catalyst to convert xylose to furfural in biphasic systems, but achieved lower yields than the other niobium-based catalysts (Table 3).[17] As seen with other niobium catalysts,[37] in biphasic systems toluene provided the highest furfural yield compared to MIBK, n-butanol, and 2-butanol. The researchers hypothesized that toluene provided higher yields due to its low polarity and higher furfural affinity. Additionally, increasing the organic to aqueous volume ratio increased furfural yield up to a 1.5 toluene/H_2O ratio.[17]

Niobium-based catalysts have also been used for glucose and fructose dehydration to HMF. Yang et al. used hydrated Nb_2O_5 in a 2-butanol/H_2O biphasic system resulting in HMF yields of 89% from fructose (50 min) and 54% from glucose (140 min) at 160 °C. Catalysts recycled seven times did not lose activity or stability and reactions with real biomass, hydrolyzed Jerusalem artichoke, yielded 65% HMF (160 °C, 120 min).[33]

Peng et al. explored Nb/SBA-15 in biphasic THF/H_2O systems modified with NaCl for HMF production. In reactions with glucose (165 °C, 3 h) and cellulose (170 °C, 8 h), HMF yields were 62% and 51%, respectively. The Nb/SBA-15 catalyst had minimal loss in activity after 10 cycles with regeneration between each cycle.[38]

These results demonstrate the capabilities of niobium type catalysts for furan production with moderate to high yields in biphasic systems using different organic solvents. No researchers reported leaching and, when reported, recyclability was good. Niobium-based catalysts benefited from low polarity solvents and increased organic to aqueous ratios.

Table 3. Furfural yields for the biphasic dehydration of xylose over niobium-based catalysts in biphasic systems.

Solvent	Org:Aq ratio [v/v]	Catalyst	Temp [°C]	Time [h]	Xylose [wt%]	Furfural yield [%]	Ref.
CPME	8:3	NbO	130	6	4.5	58	[34]
Toluene	7:3	Nb_2O_5	170	1.5	3.2	53.5	[35]
Toluene	3:2	NbO	120	3	1.4	72	[37]
Toluene	5:3	NbP	160	1	4.2	22.5	[17]
Toluene	5:3	NbP	210	1	4.2	42	[17]

2.4. Clays

Inexpensive clay minerals as solid acid catalysts have received increased attention due to their tunable acidity and reusability.[14]

Nanao et al. used montmorillonite-type clays (JCSS-3101, JCSS-3102, and K10) to convert xylose and bamboo powder into furfural in toluene/H_2O biphasic systems (4:1 volume ratio). Furfural yields ranged from 31–47% for the three clay types at 140 °C and 0.22 wt% xylose in the biphasic system. With bamboo powder catalyzed by JCSS-3102 and K10 (170 °C; 10 h), furfural yields were 46% and 55%, respectively;[39] however, the

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xylose loadings were low and higher xylose loadings would likely result in lower yields.

Significant research has been performed on montmorillonite-type (MMT) clays with modifiers in biphasic systems with improved yields. Li et al. investigated a montmorillonite with tin (Sn-MMT) catalyst for the conversion of xylose to furfural in a SBP/H_2O biphasic system with both DMSO and NaCl as modifiers in the aqueous phase. Addition of the modifiers improved furfural yields (Table 4) and running the reaction as a SBP/H_2O biphasic system increased furfural yields to a maximum of 77% (180 °C, 0.5 h). Reactions with extracted biomass from corncob instead of xylose resulted in a maximum furfural yield of 54% (180 °C, 2 h), demonstrating the practical applications of Sn-MMT in the modified biphasic system.[40] In other research, Lin et al. also used sulfated Sn-MMT as a solid acid catalyst for the conversion of xylose and xylan to furfural in a MTHF/H_2O biphasic system. Saturating the system with NaCl increased furfural yields from xylose by almost 13% over the aqueous system and had the highest furfural yields of near 80% from xylose (2 h) and 77.3% from xylan (1.5 h) at 160 °C.[41] Using the same modified biphasic system (SBP/NaCl-DMSO-H_2O) with pretreated corncob, a maximum furfural yield of 58% (190 °C; 10 min) was obtained from hemicellulose using Sn-MMT.[42] In subsequent work using structural characteristics of alkali-extracted corncob liquid analyzed with NMR, Li et al. hypothesized that polydispersion contributed to increased furfural production. The corncob fractions with the highest polydispersity, HO_{30} (6.3) and HF_{30} (5.7), had the highest furfural yields compared to fractions with lower polydispersity (<4).[43]

Pretreated corncobs were also used by Qing et al. along with Sn-MMT catalysts, NaCl as a modifier, and solvents including toluene, MIBK, CPME, and GVL. Toluene yielded the most furfural at 82% (190 °C; 15 min) from xylose compared to only 44% in the aqueous system. Using pretreated corncob in the optimized reaction system (1:1 volume ratio, 4 wt% NaCl) led to furfural yields of 66% compared to 44% with no modifier present. Further increasing the reaction time showed decreased furfural yields due to accelerated degradation reactions of furfural.[44]

Clay catalysts have been demonstrated effective for furan production with moderate yields from both sugars and biomass. The catalysts benefited from using aqueous phase modifiers as well as increased reaction temperatures.

Table 4. Furfural yields for the dehydration of 10 wt% xylose over clay-based catalysts at 150 °C and 3 h unless noted.[40]

Solvent	Modifier(s)	Catalyst	Furfural yield [%]
H_2O	none	–	3.2
H_2O	DMSO	–	8.7
H_2O	DMSO	Sn-MMT	27.2
H_2O	NaCl + DMSO	Sn-MMT	31.8
H_2O/SBP	DMSO	Sn-MMT	55
H_2O/SBP	NaCl + DMSO	Sn-MMT	67
H_2O/SBP[a]	NaCl + DMSO	Sn-MMT	76.8

[a] 180 °C and 0.5 h.

2.5. Carbon-based Catalysts

Carbon-based heterogeneous catalysts are attractive since they have high BET surface area, good stability, and controllable acidity with modified functional groups.[14]

Wang et al. demonstrated the use of a heterogeneous sulfonated carbon-based catalyst for the dehydration of xylose and xylan to furfural in a CPME/H_2O 3:1 volume ratio biphasic system. Optimization of the reaction system resulted in furfural yields of 60% and 42% from xylose and xylan, respectively (190 °C; 1 h), which were higher than the 37% furfural yield in water.[45] In a similar study using a carbon-based catalyst synthesized from waste biomass, Antonyraj et al. optimized furfural and HMF production from xylose and fructose, respectively, in a MIBK/H_2O (7:3 volume ratio) system. Sulfate-modified lignin derived catalysts had yields of up to 65% furfural (175 °C, 3 h) from xylose and 27% HMF (150 °C, 3 h) from fructose. With regeneration, the catalyst was recycled six times with minimal loss in activity.[46]

Mazzotta et al. showed the combined benefit of a carbon-based catalyst with both Brønsted and Lewis acidity by using a sulfonated carbonaceous TiO_2 catalyst (405 nm pore size) in a biphasic MTHF/H_2O system. HMF yields of 59% were achieved from fructose (180 °C, 1 h) and 46% from glucose (180 °C, 2 h). The Lewis acidity of the TiO_2 isomerized glucose to fructose, allowing for increased activity, such as with cellobiose where 39% HMF yield was achieved (180 °C, 1 h). This sulfonated carbon-based catalyst also had 51% furfural from xylose (180 °C, 30 min).[47]

Increased partitioning of furfural to the organic phase with NaCl has been applied with carbon-based catalysts as well. Deng et al. demonstrated the use of a dichloromethane/H_2O biphasic system to convert the xylose in concentrated pre-hydrolysis liquor (CPHL) of corncob to furfural. Using bio-char catalysts, CPHL containing 5 wt% xylose resulted in 81% furfural yield in the modified biphasic system compared to only 61% furfural without NaCl (170 °C; 1 h).[4] In another study with carbon-based catalysts, sulfonated nano-sized diamond powder was used by Delbecq et al. in a modified CPME/H_2O biphasic system.[31] Similar to work done with polymer catalysts,[30] increasing the NaCl concentration increased the furfural yield, with a maximum furfural yields of 76% with 2 mM NaCl (200 °C, 50 min; Figure 2).[31]

Carbon-based catalysts resulted in high furfural yields likely due to the high surface area and acid functionality of the catalyst. The catalysts also have high thermal stability, are recyclable, and benefit from the addition of a modifier (NaCl). As with other catalysts discussed in this review, carbon-based catalysts also benefited from higher organic to aqueous ratios.

2.6. Other Catalysts

Although zeolites, polymer-based, niobium, and carbon catalysts are the most commonly reported heterogeneous catalysts used in biphasic systems in the past five years, researchers have

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reported using other catalysts ranging from metal oxides to phosphate-based catalysts to produce furans.

Hydrothermally stable, supported metal oxide catalysts have been used for efficient one-pot furfural synthesis by Bhaumik and Dhepe in a toluene/H_2O biphasic system,[48] similar to the one-pot method previously mentioned using H-USY zeolite.[19] Improving upon 54% furfural obtained with H-USY (170 °C; 6 h),[19] the reaction system with sol-gel-synthesized, silica-supported tungsten oxide catalysts yielded 71% furfural (170 °C; 10 h) from isolated xylan. Pentosane from various crop wastes yielded 72–87% furfural (170 °C; 8 h), which demonstrated the utility of the tungsten oxide catalysts.[48]

Metal oxide catalysts have also been used with phase modifiers to increase furfural yields in biphasic systems. Solid acid SO_4^{2-}/TiO_2-ZrO_2/La^{3+} was used as the catalyst by Li et al. in a modified biphasic system to convert xylose to furfural. Different aprotic organic solvents (DMSO, DMF, and 1,3 dimethyl-2-imidazolidinone) were added to the aqueous phase while the MIBK organic phase was modified with 2-butanol.[49] As was seen in work with Sn-MMT,[40] the addition of DMSO to the aqueous phase increased furfural yields. Adding 2-butanol to the 1,3 dimethyl-2-imidazolidinone organic layer resulted in approximately 12 times the yield of furfural compared to the system without modifiers; however, yields (34%) were still lower than compared to other catalyst systems. The polar aprotic solvents modifying the biphasic system did decrease side-reactions, improving furfural selectivity even though the reaction time was long.[49]

Aluminum oxides, in acidic, neutral, and basic forms, have been used with NaCl and $CaCl_2$ modifiers for the conversion of glucose to HMF in biphasic MIBK/H_2O systems. As with the other heterogeneous catalysts reviewed, the NaCl modified system showed increased HMF yields, however, the highest yield, 52%, was observed with the acidic Al_2O_3 in a $CaCl_2$ modified system (175 °C, 15 min). Garcia-Sanco et al. found that the addition of calcium cations favored α-D-glucopyranose, confirmed by H-NMR, which potentially was more favorable for dehydration to HMF than β-D-glucopyranose.[50]

Another catalyst, inexpensive potassium aluminum sulfate (PA) with high porosity was used by Gupta et al. in biphasic systems for furan production. Increasing the reaction temperature from 140 °C to 190 °C (6 h) increased furfural yields from 5% to 55% from xylose, but further increasing the reaction time resulted in lower furfural yields due to furfural degradation. Using saturated NaCl as a modifier for HMF production increased HMF yields from 40% to 49% and 58% to 64% from glucose and fructose, respectively. As was seen with numerous other catalysts, the introduction of NaCl as a phase modifier increased HMF yields, which was attributed to the salting out effect.[51]

Another type of catalyst, chromium phosphate ($CrPO_4$) has been used in biphasic THF/H_2O systems modified with NaCl. The simultaneous optimization of both furfural and HMF (180 °C, 1.5 h) resulted in maximum yields of 67% and 32%, respectively. Although $CrPO_4$ is heterogeneous in nature, a filtered aqueous solution with solubilized $CrPO_4$ resulted in 57% furfural from xylose, suggesting a homogeneous reaction may be the primary reaction mechanism.[52] In a similar study by Xia et al. to synthesize both furfural and HMF, biphasic THF/H_2O systems modified with NaCl were used with $FePO_4$ and NaH_2PO_4 as co-catalysts. For reactions at 150 °C and 1 h, furfural and HMF yields of 92% and 34%, respectively, were achieved; HMF yields increased to 44% at 160 °C and 1 h at the cost of decreasing furfural yields by 4%.[53] Despite this decrease in furfural yield, the NaCl modified THF/H_2O biphasic system shows the potential for the simultaneous synthesis of furfural and HMF at reasonable yields. $FePO_4$ is soluble at the increased reaction temperatures and observed patterns of recrystallization suggested a possible contribution of a homogeneous reaction.[53]

In a true heterogeneous reaction, Alam et al. demonstrated titanium hydrogen phosphate with high acidity (1400 μmol/g) for HMF production. In biphasic THF/H_2O systems modified with NaCl, HMF yields of 55% from fructose and 35% from glucose were achieved. Reactions increasing the catalyst loading with fructose showed non-linear HMF trends, which indicates mass transport limitations associated with the heterogeneous catalyst.[54]

Unlike the previous phosphate-based catalysts, Dutta et al. used a mesoporous tin phosphate catalyst for HMF production in biphasic MIBK/H_2O. This large pore (10.4 nm diameter) material achieved 50%, 39%, and 32% HMF from glucose, cellobiose, and cellulose, respectively (150 °C, 20 min). The addition of NaCl increased HMF partitioning into the organic phase via the salting-out effect, resulting in a 12% increase in HMF yield from glucose.[55]

Metal-oxide, phosphate, and sulfate catalysts follow similar trends to the previously discussed catalysts. They benefited from the addition of a modifiers to the aqueous and organic phases as well as increased reaction temperatures, to a point.

2.7 Catalyst Summary

Numerous types of heterogeneous catalysts have been applied in biphasic systems producing high furan yields. When considering all of the data presented in this paper, several trends emerged based on catalyst type and across all catalysts.

For zeolites, correlations between the acidity and furfural yields were expected; however, the correlation did not trend as expected, which would have been that the yield increased with acidity. From the furfural yield data presented in Table 1 for zeolites, Figure 3a shows the positive correlation in furfural yield with increasing Si/Al ratio. (As previously mentioned, as the Si/Al ratio increases, the total acidity decreases.[16]) Below a Si/Al ratio of approximately 20, the furfural yield decreased with decreasing Si/Al ratio. Figure 3b shows that as the total acidity of the zeolite catalyst increased, the furfural yield decreased and that the highest yields were achieved at total acidities of less than 200 μmol/g. Although Antunes et al. showed increasing acidity from 168 μmol/g to 204 μmol/g increased furfural yields by 10%,[20] considering all zeolites in Table 1, the high acidities may have resulted in furfural degradation reactions and unwanted by-products. This trend was also seen with clay

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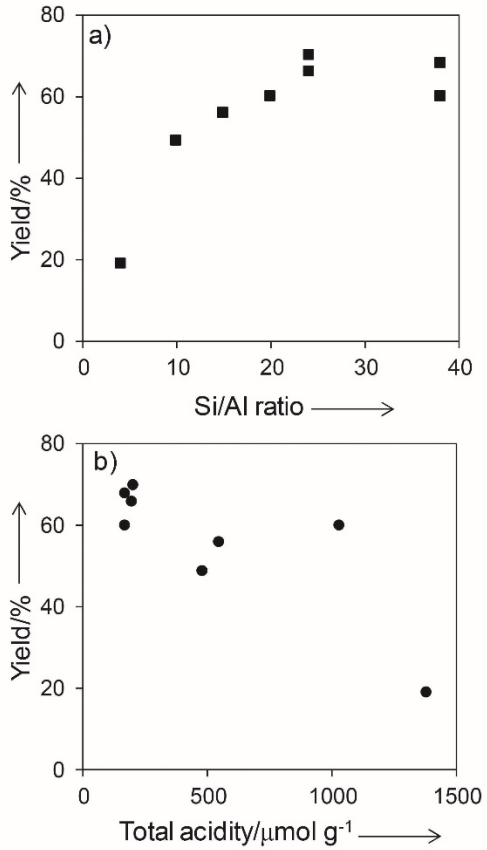

Figure 3. Correlations of furfural yields and a) Si/Al ratio and b) total acidity of the zeolites reported in Table 1.

and Nb-based catalysts. Li et al. reported that decreasing the acidity of MMT with the addition of tin (from 2050 μmol/g to 1300 μmol/g) increased furfural yields by approximately 12%.[40] Additionally, Pholjaroen et al. saw 8% increase in furfural yields with lower acidity NbP (402 μmol/g) compared to ZrP (633 μmol/g).[17] No obvious trends in catalyst acidity arose with HMF production from zeolites investigated by Pande et al.[21] or supported niobium catalysts by Garcia-Sancho et al.[36]

Diffusion limitations with heterogeneous catalysts can also significantly affect their activity. Although inconsequential with macroporous (>50 nm) catalysts, such as ion exchange resins, the kinetic diameters of sugars, including xylose (0.68 nm[2]) and glucose (0.86 nm[2,56]), as well as furans (0.55–0.62 nm[56]) are of similar size to microporous (<2 nm) catalysts such as zeolites. Although some zeolite pore diameters are smaller than sugars, such as with H-MCM-22 (0.55 nm) which exhibited high activity,[20] molecules up to 0.2 nm[5] larger can diffuse into the crystalline structure.[25] Additionally, zeolites are flexible, especially at high temperatures, allowing the pores to flex and molecules larger than the pore size to adsorb.[57] Even with high acidity, the limited diffusion of a reactant in a catalyst can decrease reactivity. For example, Pholjareon et al. saw similar yields using high Lewis acid microporous zeolites, H-BEA (890 μmol/g; pore diameter: 0.74 nm) and H-Y (850 μmol/g; pore diameter: 0.61 nm), as they did with low Lewis acid site, phosphate-based mesoporous catalysts (220–300 μmol/g; pore diameter: 0.71–0.107 nm).[17] This could be due to the xylose being able to diffuse to the acid sites of the mesoporous catalyst more easily.

Improved mass transport in zeolites has been shown by introducing mesoporosity,[58] which was seen with mesoporous H-USY.[21] With larger pores, mesoporous materials have increased accessibility to acid sites resulting in increased activity.[16] For example, synthesized mesoporous Nb_2O_5 showed approximately 20% increase in furfural yield from xylose (150 °C, 45 min) over commercial Nb_2O_5, attributed to the increased accessibility of xylose molecules to the acid sites in the pores.[35] This high activity is also seen with other mesoporous heterogeneous catalysts, such as Nb on silica support (SBA-15)[36] and tin phosphate.[55] In addition to mass transport benefits, mesoporous silicas, such as SBA-15, also have increased hydrothermal stability.[16,38] With higher furan yields resulting from mesoporous heterogeneous catalysts, biphasic systems have a unique potential to recover more product by preventing degradation and reducing the chance of pore blockage and product adsorption. The improved yields using mesoporous materials was shown using multiple catalyst types and multiple solvents, which is another important factor in biphasic reactions.

3. Solvent Selection

There are many properties to consider when choosing a solvent for biphasic systems. Toxicity, cost, viscosity, volatility, solubility of solute and carrier, the partition coefficient of the solute, and necessity of modifiers, amongst other properties, need to be balanced to find the most desirable solvent.[7] As seen in Table 5 (ordered by polarity), the solvents explored for synthesizing furans have a wide range of properties, but this table covers only a small fraction of considerations. More details and discussion about other properties have been discussed in other reviews and articles by Jessop et al.,[59] Sievers et al.,[58] and Knochel et al.[60] to name a few.

The most commonly used solvent for furfural extraction was toluene, which has low solubility in water and a low boiling point compared to both furfural (162 °C[61]) and HMF (291 °C[62]). The exceptionality of toluene as a solvent for furfural was demonstrated by Moreau et al.[63] and has further been supported by recent works, especially in the last five years. Due to their boiling points, toluene would be the top product in distillation, which leads to a lower purity furfural product. However, as the top product in distillation, high purity toluene would be preferred solvent reuse. For HMF, the most commonly researched solvent was MIBK, which gained popularity since Moreau et al. demonstrated its use as a solvent for HMF

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Table 5. Properties of solvents used in this review.

Solvent	Boiling point [°C]	Melting point [°C]	Density [g/mL]	Water solubility [g/100 g]	Flash point [°C]	Polarity
p-Xylene	138.4	13.3	0.861	0.2	27	0.43[59b]
1-Butanol	117.7	−88.6	0.8095	6.3	37	0.47[59b]
o-Xylene	144	−25.2	0.897	0.17	32	0.48[59b]
2-Propanol	82.4	−88.5	0.785	miscible	12	0.5[59a]
Ethanol	78.5	−114.1	0.789	miscible	13	0.51[59b]
2-Methyltetrahydrofuran (MTHF)	79	−20	0.86	14	-10	0.53[59b]
Toluene	110.6	−93	0.867	0.05	4	0.55[66]
Tetrahydrofuran (THF)	65	−108.4	0.8833	30	-14	0.6[59a]
Methylisobutylketone (MIBK)	117	−80	0.8	2	14	0.63[66]
gamma-Valerolactone (GVL)	207	−31	1.05	miscible	96	0.83[67]
Dimethyl Sulfoxide (DMSO)	189	18.4	1.092	25.3	95	1[68]
1,2-Dicholorethane	83.5	−35.7	1.245	0.861	13	n/a
2-Butanol	98	−115	0.808	miscible	27	n/a
Cyclopentyl methyl ether (CPME)	106	−140	n/a	0.3	-1	n/a
Cyclohexanol	161	21	0.948	3.6	68	n/a
1,3 Dimethyl-2-Imidazolidinone	225	7.5	1.056	miscible	95	n/a
2-sec-Butylphenol	227	12	0.982	0.15	112	n/a

production in 1994.[64] As with toluene and furfural, MIBK has a lower boiling point (117 °C[61]) than HMF, resulting in a lower purity HMF product. Additionally, MIBK has some solubility in water, which would need to be accounted for in the aqueous volume of the process. Another solvent used recently is SBP and even with low solubility in water, it is a less attractive solvent due to the difficulty of separating HMF and SPB as highlighted by Pagan-Torres et al.[65]

As an alternative processing method for when HMF and furfural are not the desired end products, the solvent can be selected to improve downstream processing. For example, Roman-Leshkov et al. used alcohols as the solvent and homogeneous catalysts to convert HMF to dimethylfuran over a CuRu based-catalyst. They found that toluene and MIBK were not inert in the hydrogenolysis reaction, but 1-butanol was. Additionally, 1-butanol can be produced from biomass.[69]

THF has been employed as an organic solvent in several biphasic systems[37–38,52–53] and in order to achieve sufficient phase separation, the use of NaCl (or other solvents or salts) as a modifier was necessary at the temperatures used. Modifiers added to monophasic systems can induce phase separation to biphasic systems and can be used to initiate the salting-out effect. NaCl is the most common modifier for heterogeneous catalytic systems and several papers demonstrated increased product yields with higher NaCl concentration.[29–31] For two different heterogeneous catalysts, one polymer-based the other carbon-based, an increase in furfural yield was observed when the concentration of NaCl was increased (Figure 2). This has also been observed with other polymer catalysts as well as clays.[30,40–41,44] Similar results have been observed for HMF with increasing NaCl concentration for modified biphasic systems.[26,50] The addition of modifiers increased partitioning of furans into the organic phase, and, in the case of a Nafion catalyst, created a synergetic catalytic effect that increased yields.[29] The addition of an aprotic organic solvent modifier to the organic phase has also shown the potential to increase furfural yields.[40,42] Researchers hypothesized that increasing solvent polarity with a modifier improved furfural yields,[70] but when comparing the polarity values available in the literature (Table 5), there may be a lower limit versus "higher is better."

Another consideration of solvent selection is the environmental friendliness of the solvent. For example, MTHF, a biorenewable solvent,[41] is a common choice for the organic solvent in biphasic systems. MTHF is an effective extractant, has good stability, and has a relatively low-cost.[47] Other solvents obtainable from biomass include GVL and 1-butanol.[69,71] The selection of an environmentally friendly solvent, and solvent in general, may be more attractive if the solvent is easy to recover and recycle or can be produced from the reaction products.

Unique to biphasic systems, increasing the organic to aqueous volume ratio increased furan yields.[17,28,32] This was likely due to the furans having a lower concentration in the aqueous phase, which reduces product degradation and decreased side reactions. Additionally, with heterogeneous catalysts, yields may be higher in biphasic systems since the extracting organic solvent may reduce pore-blockage on the catalyst surface from the products and humins.[32]

4. Conclusions and Outlook

There are many benefits to using biphasic systems for sugar and biomass reactions with the main benefit being increased furan yields. Biphasic media is favorable for the continuous extraction of furans during the reaction and using modifiers has been shown to improve yields in some cases.[11a] Additionally, biphasic systems could potentially reduce the energy demand associated with product recovery due to increased furan yields[5] and more concentrated products. Although aqueous systems are inexpensive and have historically shown moderate success for furan synthesis from lignocellulosic biomass, biphasic systems have shown significantly improved yields and selectivity towards furans using heterogeneous acid catalysts, including zeolites, oxides, and carbon-based catalysts among others. One setback of biphasic systems could arise in the

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recovery of expensive extracting solvents, potentially reducing the economic advantages of the in situ extraction of furans.[5]

Producing furans in biphasic systems eliminates some of the issues seen in monophasic systems (e.g., furan degradation), but similar reaction trends still remain. Lower furan yields occurred at too high of acid concentrations, longer reaction times,[28] and high temperatures[44] due to side and degradation reactions. Too short of reaction time leads to incomplete xylose conversion[28] and too high of an initial xylose concentration also results in lower yields.[72]

The use of heterogeneous catalysts provides a unique opportunity to tailor the catalyst to the reaction. For example, glucose to HMF requires both Lewis and Brønsted acidity for the isomerization and dehydration reactions. Being able to tune the heterogeneous catalyst to have different acid sites and different ratios of acid sites opens the door to many different possibilities. However, chemical stability can be an issue and can lead to acid sites leaching and homogeneous reactions. Due to the benefits of biphasic systems and the ease of separating heterogeneous catalysts, these systems will likely play an important role in producing green chemicals from biomass in the future. However, further research is needed in order to understand the effect liquid systems have on heterogeneous catalysts and how solvent properties affect the reaction.

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Conflict of Interest

The authors declare no conflict of interest.

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CHAPTER THREE

SAPO-34/5A ZEOLITE BEAD CATALYSTS FOR FURAN PRODUCTION FROM XYLOSE AND GLUCOSE

Contribution of Authors and Co-Authors

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Contribution of Authors and Co-Authors—Continued

Co-Author: Stephanie G. Wettstein

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SAPO-34/5A Zeolite Bead Catalysts for Furan Production from Xylose and Glucose

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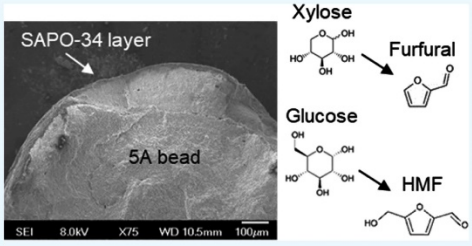
ABSTRACT: SAPO-34 zeolite crystals were grown on zeolite 5A beads, characterized, and then used to produce furfural from xylose and 5-hydroxymethylfurfural (HMF) from glucose. The SAPO-34/5A bead catalysts resulted in moderate furfural and HMF yields of 45% from xylose and 20% from glucose (463 K; 3 h) and were easier to recover than the SAPO-34 powder catalyst. At 463 K, the SAPO-34/5A beads were more selective than 0.02 M sulfuric acid for producing HMF and, unlike the sulfuric acid system, no levulinic acid was formed. The SAPO-34/5A bead catalysts had no significant loss in activity after three rounds of recycle when water washed or heated overnight between reactions; however, the heat-treated beads did show signs of thermal stress after the second reuse. The SAPO-34/5A bead catalysts show promise for dehydration reactions to produce furfural and HMF from xylose and glucose, respectively, and tailoring the catalyst and the support bead could lead to even higher selectivities and yields.



1. INTRODUCTION

Increasing energy demands have motivated research for alternative forms of energy and chemicals derived from non-petroleum sources. Biofuels derived from biomass are recognized as viable alternative energy sources, and the production of bio-based platform chemicals is an area of significant interest. Versatile chemical intermediates, such as furfural, 5-hydroxymethylfurfural (HMF), and levulinic acid (LA), can be derived from lignocellulosic biomass, and any of the aforementioned can deliver a variety of fuels and chemical commodities.[1] For example, furfural, identified as one of the top 12 value-added chemicals from biomass by the DOE,[2] has useful applications as a building block for carbon-rich C_{10}−C_{15} fuel additives and can be upgraded for incorporation into biofuels, which is achieved through hydrogenation, rearrangement, and carbon−carbon coupling.[3,4] HMF is a precursor for 2,5-furan dicarboxylic acid, another top 12 value-added chemical,[2] and can be upgraded for many chemical applications.[5,6]

Existing pathways for furfural and HMF production from lignocellulose are typically energy-intensive and result in only moderate yields.[3] Significant research has been dedicated to producing furfural and HMF using homogeneous acid catalysts such as sulfuric acid and hydrochloric acid;[3,7−9] however, homogeneous acids are corrosive, require special handling, and can have negative effects on downstream catalytic processes. Heterogeneous catalysts are an attractive alternative to homogeneous acids, and many researchers have looked at biomass and sugar conversion to furans and other products, including LA.[10−13]

Different classes of solid acid catalysts have been demonstrated as effective catalysts for both furfural and HMF production, including ion exchange resins, metal oxides, and carbon-based catalysts.[14−19] Of particular interest are zeolites, which are known for their chemical and thermal stability, versatility,[20] and wide range of pore sizes (0.2 nm to over 1.0 nm[21]) that are available. Zeolites have been widely used in biomass conversion.[22−26] For example, research by Gao et al. found that xylose dehydration reactions with ZSM-5 resulted in furfural yields of 51.5% in an aqueous system[25] and Ordomsky et al. used MOR, H-ZSM-5, and H-BEA to convert fructose to HMF with selectivities ranging from 30 to 68% at around 80% conversion (165 °C) in an MIBK/H_2O biphasic system. The high HMF selectivity found with MOR was attributed to its high acid site strength compared to other zeolites tested.[26] Other researchers have looked at the use of powdered silicoaluminophosphates (SAPOs), a class of small-pore zeolites, in various solvent systems to maximize furfural

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production from xylose, achieving moderate yields.[24] For dehydration reactions that are typically favored at higher temperatures, SAPOs are particularly favorable because of their hydrothermal stability, up to 873 K under steam conditions.[27] Additionally, small-pore zeolites have high versatility because of being able to control the physicochemical functionalities such as acidity and hydrophobic−hydrophilic nature.[28] SAPOs with different acidities, pore sizes, and silica to alumina ratios have been used for furfural synthesis in biphasic systems, achieving yields of up to 63% furfural.[29,30] Other research has shown promising results on powdered catalysts as well.[24,31,32]

Despite the general promise of microporous zeolites for sugar dehydration, prior demonstrations have typically been performed with powdered catalysts having average particle sizes on the micron scale. Unfortunately, these materials are impractical for utilization in industrial flow reactors because of excessive pressure drop and potential for entrainment. For heterogeneously catalyzed sugar dehydration to be feasible industrially, it is important to demonstrate that sugar dehydrations can be performed on macroscale catalysts, which have additional challenges relative to powdered catalysts. Most significantly in the system of interest here, the small zeolite pore size can create a diffusion-limited system. This is particularly true for substrates like sugars, which have large kinetic diameters. Powdered catalysts are able to mitigate this to some extent as their small particle sizes ensure that the bulk of catalytic active sites remain in relatively close proximity to the external particle surface, that is, they have a short diffusion path. In contrast, pelletized catalysts have large particle sizes and diffusion lengths such that mass transfer limitations are generally severe. Often, the small fraction of catalytic active sites at or near the external surface of the pellet participate in the reaction, while the vast majority of the active sites within the interior of the pellet are inaccessible and thus underutilized.

Hybrid, composite materials offer a potential resolution. Specifically, by depositing a micron-scale layer of the catalyst onto the exterior surface of a macrostructure, all of the active sites remain concentrated in the first few microns of the bead diameter. Thus, the short diffusion path of a powdered catalyst is maintained in an industrially relevant material. Despite their promise, active layers of zeolites grown on a bead support remain an unexplored area of solid acid catalyst use, particularly for furan production. In addition to the aforementioned concerns over diffusion limitations, catalysts will typically undergo some form of deactivation during application and thus be subjected to periodic regeneration. Normally, this occurs through thermal cycling in air (calcination) to oxidize surface carbon and regenerate catalytic active sites. It is critical that industrial catalysts retain their macrostructure through repeated catalyst regeneration cycles, and the thermal stability of composite bead catalysts has not been well established.

In this work, we show that novel SAPO-34/5A bead catalysts can be used for the dehydration of xylose and glucose to furans in aqueous systems, exploring the possible diffusion limitations and catalyst recyclability.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. Figure 1 shows representative scanning electron microscopy (SEM) images of a single composite catalyst bead composed of a SAPO-34 layer grown on zeolite 5A. Figure 1a shows the coverage of SAPO-34 crystals, and Figure 1b shows the thickness of the SAPO-34 layer that grew on the surface of the 5A beads, which averaged in the 25−50 μm range. The surface area of the SAPO-34/5A beads was 454 $m^2\ g^{-1}$ compared to 520 $m^2\ g^{-1}$ for the synthesized SAPO-34 powder and 387 $m^2\ g^{-1}$ for the 5A beads (Table 1). Additionally, the SAPO-34/5A and 5A beads had

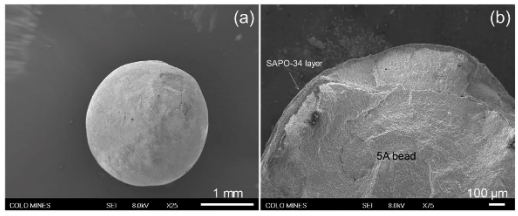

Figure 1. Representative SEM images of SAPO-34/5A beads: (a) single SAPO-34 covered 5A bead and (b) cross-sectional view.

Table 1. Acidity and Textural Properties of the Materials Used in This Study

	Brønsted acid sites (μmol/g_{cat})	surface area (m^2/g)	micropore area (m^2/g)	fraction micropore area
SAPO-34/5A bead	134	454	378	0.83
SAPO-34 powder	400[24]	520[24]	521	1
SAPO-34C powder	1100[24]	510[24]	517	1
5A bead	184	387	332	0.86

significantly less micropore area than the powder, 83 and 86% micropore area, respectively, compared to 100% micropore area that the SAPO-34 powder had. As with the micropore area, the number of acid sites on the bead catalysts was lower than the powders, and in the case of the commercially prepared SAPO-34 (SAPO-34C), the number of acid sites was an order of magnitude higher (Table 1).

Figure 2a shows the X-ray diffraction (XRD) patterns of (i) pure 5A beads, (ii) SAPO-34/5A beads, and (iii) SAPO-34 crystals collected from the autoclave after synthesis of SAPO-34/5A beads. Figure 2i agrees with the known structure of zeolite 5A, which crystallizes in the LTA topology,[33] and after the incorporation of SAPO-34, the XRD pattern of 5A beads is preserved (Figure 2ii). The XRD peak of SAPO-34 (Figure 2iii) overlaps with the XRD peak of the SAPO-34/5A beads (Figure 2ii) at $2\theta \approx 16°$, suggesting the incorporation of

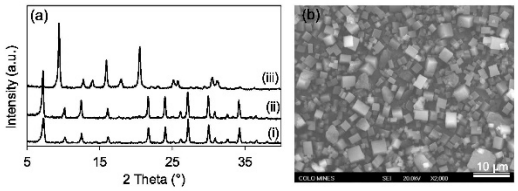

Figure 2. (a) XRD patterns of (i) 5A beads, (ii) SAPO-34/5A beads, (iii) SAPO-34 crystals collected during SAPO-34/5A synthesis; (b) representative SEM image of SAPO-34 crystals collected from the autoclave after SAPO-34/5A synthesis.

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Table 2. Xylose Conversion and Furfural Selectivity and Yield for H_2SO_4 and Heterogeneous Zeolites at Different Temperatures[a]

				furfural	
catalyst	temperature (K)	time (h)	xylose conversion (%)	selectivity (%)	yield (%)
0.02 M H_2SO_4	423	6	35	66	23
	443	6	82	62	51
	463	2	87	69	60
SAPO-34/5A bead	423	6	53	31	16
	443	6*	87	37	32
	463	3	95	47	45
SAPO-34 powder	423	6	27	31	8
	443	6	80	43	34
	463	3	85	46	39
SAPO-34C powder	423	6	17	37	6
	443	6*	53	51	27
	463	3	57	54	31
5A bead	423	6	75	13	10
	443	6	95	20	20
	463	3	97	21	21
no catalyst	423	6	10	69	7
	443	6	41	51	21
	463	3	58	54	31

[a]Reaction conditions: 2 wt % xylose, 4 mL H_2O, and 0.02 M H_2SO_4 or 0.048 g of catalyst. Experimental error is ±4%, based on multiple trials of reactions marked with an asterisk.

SAPO-34 on the surface of 5A beads. Also, it was evident from these XRD patterns that the peaks shift slightly for some of these diffraction peaks. The XRD pattern of the crystals collected in the bottom of the autoclave after synthesis (Figure 2iii) corresponded to the CHA topology characteristic of SAPO-34.[34] The crystal size of SAPO-34 powders collected from the autoclave after synthesis of SAPO-34/5A beads was approximately 1−5 μm (Figure 2b).

2.2. Xylose Reactions. After 6 h at 423 K, all of the catalysts evaluated dehydrated xylose to furfural to some extent. The SAPO-34/5A beads and 0.02 M H_2SO_4 had the highest furfural yields of 16 and 23%, respectively, and the other catalysts had yields less than 10% and were not significantly different than the system that had no catalyst present (7%; Table 2). This was an unexpected result because both SAPO-34 powders had substantially higher acid site densities than the SAPO-34/5A beads (Table 1); therefore, the powdered catalysts would be expected to be more active and result in higher yields at a given time. However, it is important to note that it is impossible to know how many active sites are accessible to the large sugar molecules and therefore, turn-over frequency may not be representative of the actual activity of the catalyst. The average pore diameter of SAPO-34 is in the range of 0.38 nm,[35] which is smaller than the kinetic diameter of xylose (0.68 nm[36,37]); accordingly, xylose dehydration over the powdered SAPO catalyst is likely to be diffusion-limited. This may explain why the powdered SAPO-34 catalysts show little more than background activity at 423 K. However, the SAPO-34/5A beads had twice the furfural yield than the background activity which may be explained by the higher mesoporosity, whereas both SAPO-34 powders were entirely microporous materials (Table 1). For diffusion-limited systems, it stands to reason that introducing mesoporosity into the SAPO-34 structure would substantially improve catalyst activity by facilitating access to interior Brønsted sites. Similar results have been observed previously with modified H-USY zeolites as reported by Pande et al.[38]

Increasing the temperature to 443 K significantly increased the furfural yields for all systems (Figure 3). The SAPO-34/5A

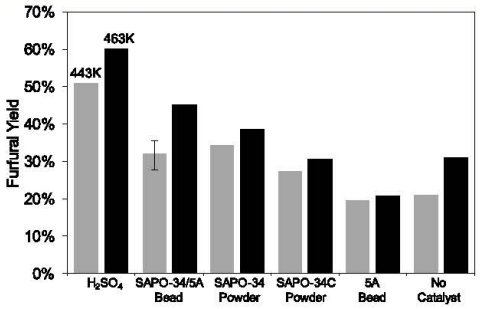

Figure 3. Effect of temperature on furfural yield at 443 K (6 h; gray) and 463 K (3 h for all except H_2SO_4 at 2 h; black). Reaction conditions: 2 wt % xylose, 4 mL H_2O, and 0.02 M H_2SO_4 or 0.048 g of catalyst.

bead catalyst had a significantly lower furfural yield (32%) than 0.02 M H_2SO_4 (51%) at similar conversions and was within error of the SAPO-34 (34%) and SAPO-34C (27%) powder catalysts (Table 2). Because the powder and the bead yields were similar, the increased mesoporosity of the beads did not seem to affect the reaction at 443 K as much as it may have at 423 K. Further increasing reaction temperature to 463 K led to the highest furfural yield with the SAPO-34/5A beads which was 45% at 95% xylose conversion (Table 2). The furfural selectivities of the SAPO-34 catalysts were in the range of 46−54%, which was at least double that of the 5A beads (21%). The 5A beads had similar Brønsted acidity and micropore area fraction (Table 1) as the SAPO-34/5A bead catalysts, but resulted in significantly lower furfural yields at all temperatures evaluated. One difference between zeolite 5A and SAPO-34 is

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the framework structure. The 5A zeolites have an LTA framework with a pore size of 0.41 nm and interior cages that can include molecules up to 1.1 nm, while SAPO-34 has a CHA framework with 0.38 nm pores and cages that can include molecules up to 0.74 nm.[21] This may affect the product selectivity[39] because furfural degradation generally occurs through condensation,[3] which may be more facile in the more open cages of LTA.

The effect the catalysts had on the reaction kinetics was more evident when conversion was compared with time at 443 K (Figure 4). The xylose conversion of all catalysts systems

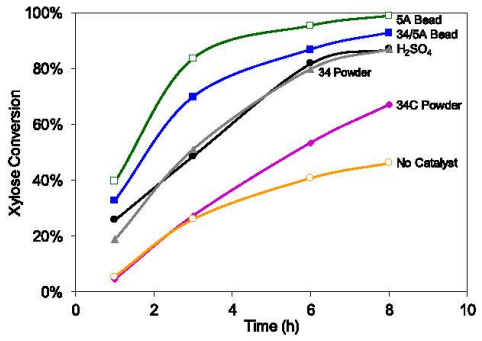

Figure 4. Effect of reaction time on conversion at 443 K with 2 wt % xylose, 4 mL H_2O, 0.02 M H_2SO_4 or 0.048 g of catalyst. Lines have been added to guide the eye for the H_2SO_4 (●), SAPO-34/5A bead (blue ■), SAPO-34 powder (gray ▲), SAPO-34C powder (pink ♦), 5A bead (green □), and no catalyst (orange ○) systems.

was at least double that of the no catalyst system at a given time, excluding the SAPO-34C powder. With the exception of 5A beads, for which furfural selectivities range from 15 to 20%, the heterogeneous catalysts had furfural selectivities generally in the 30−55% range over the reaction times presented (Table 2), which resulted in furfural yields of approximately half of the xylose conversion (Figure 5). The SAPO-34/5A bead and SAPO-34 powder catalysts showed similar kinetic trends to the 0.02 M H_2SO_4 system where the furfural yield increased

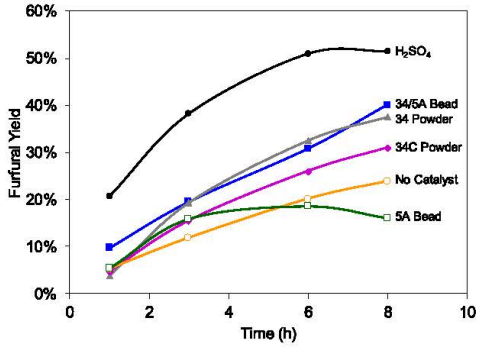

Figure 5. Effect of reaction time on furfural yield at 443 K with 2 wt % xylose, 4 mL H_2O, 0.02 M H_2SO_4, or 0.048 g of catalyst. Lines have been added to guide the eye for the H_2SO_4 (●), SAPO-34/5A bead (blue ■), SAPO-34 powder (gray ▲), SAPO-34C powder (pink ♦), 5A bead (green □), and no catalyst (orange ○) systems.

through 8 h and then the yield decreased at 24 h (not shown). For these systems, the xylose conversion was above 80% at 8 h, and the decrease in furfural yield at 24 h was likely due to degradation reactions, which lead to formation of humins and other by-products. The 5A bead catalyst had the highest xylose conversion at a given time, but had the lowest furfural yields. The increased activity of the 5A bead catalyst relative to all other systems may have several causes. First, the slightly larger pore size and increased mesoporosity (Table 1) of the 5A catalyst may decrease mass transfer resistance relative to the SAPO-34 based systems. In addition, after reaction, the 5A beads showed signs of partial and sometimes complete disintegration. Because the 5A beads were held together using a binder and not composed of a single crystal, partial dissolution of the bead may have created a suspension of fine LTA particles in solution, which would, generally, increase access to active sites relative to intact beads.

2.3. Recyclability. The retention of the SAPO-34/5A bead structure in multiple use recycle reactions is critical to the demonstration of the feasibility of the composite catalysts. Recyclability experiments were performed after catalyst regeneration by (1) only washing catalysts with water and (2) not washing the catalyst and only heating it overnight at 523 K. The catalysts showed good performance after three times recycling with the water washing (Figure 6; gray bars)

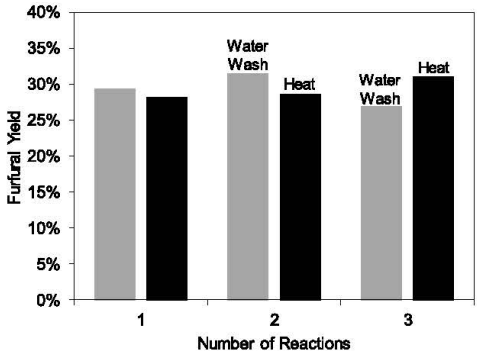

Figure 6. Furfural yields from recycle reactions with SAPO-34/5A with water washes (gray bars) and heating (black bars) between runs. Reaction conditions: 2 wt % xylose, 443 K, 6 h.

and overnight heating led to a slight increase in furfural yield during the third reuse compared to the nonheated sample (Figure 6; black bars). The decrease in catalyst activity seen for SAPO-34/5A with the second water washing was within experimental error but may be attributed to the blocking of acid sites from surface deposition of carbonaceous species. Similar conclusions have been previously reported for SAPO-34 in other research studies.[24,40] Suprun et al. hypothesized that the relatively high acidity and small pores of SAPO-34 are both factors that lead to accumulation of carbonaceous deposits blocking its surface.[40] The overnight heating process could remove some of these species, regenerating more acid sites than with just water washing thus, maintaining activity.

The water-washed beads maintained their structure and after the third reuse, the beads still had a spherical shape with no significant mass loss; however, after the second reuse, several of the heat regenerated SAPO-34/5A beads had cracked,

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resulting in nonspherical beads with approximately 38% mass loss (Figure 7a). This damage likely occurred because of

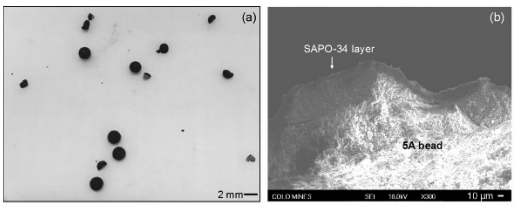

Figure 7. Heat-treated SAPO-34/5A beads (a) after one heat-treatment and two reactions and (b) cross-section of a representative bead after two heat treatments and three reactions.

thermal stressing since the water-washed beads did not show signs of cracking. In a third reuse, the heat-regenerated SAPO-34/5A beads still showed good activity, and the SAPO-34 layer remained intact and was a similar thickness (Figure 7b) to the starting beads (Figure 1b).

2.4. Glucose Reactions. Starting with glucose led to a moderate amount of HMF formed at 443 K (6 h) and 463 K (3 h) for all heterogeneous catalysts tested (Figure 8). The

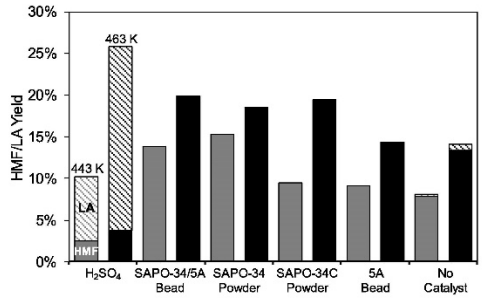

Figure 8. LA (patterned bars) and HMF (solid bars) yields from glucose. Reaction conditions: 2 wt % glucose, 4 mL H_2O, 0.02 M H_2SO_4 or 0.048 g of catalyst, 443 K (gray bars) reactions for 6 h, and 463 K (black bars) reactions for 3 h.

SAPO-34/5A bead catalyst resulted in the highest HMF yield (20%) with no detectable amount of LA formed, while the SAPO-34C and SAPO-34 powders had HMF yields within the experimental error (19 and 18%, respectively). The reaction solutions from all SAPO-34 catalysts also had fructose peaks present after reaction, indicating that the acid sites isomerized the glucose to fructose, whereas no fructose peak was present for the H_2SO_4 system. Although the yields with the SAPO catalysts were low to moderate, it is worth noting that they were obtained directly from glucose in an aqueous phase, which is a notoriously difficult reaction for selectivity control. Further, these SAPO-34-based catalysts perform comparably to other zeolites when they are tested under similar conditions.[23] Particularly compelling was the observation that SAPO-34-based materials did not appear to catalyze the hydration of HMF to form LA, whereas H_2SO_4 was primarily selective to LA and the no catalyst system at 463 K did have some LA present (Figure 8). The focus of this study was to probe the activity, stability, and recyclability of these hybrid materials for sugar dehydration, so we do not have a definitive explanation for this enhanced selectivity; however, we speculate that the microporous material appears to be beneficial to selectivity. That said, these observations suggest that SAPO-34 may be a platform for rational design of solid catalysts that offer improved HMF selectivity relative to conventionally employed mineral acids.

3. CONCLUSIONS

We have demonstrated for the first-time the synthesis of zeolite bead catalysts consisting of SAPO-34 zeolite grown on zeolite 5A beads and their ability to convert sugars to furans in an aqueous system with significantly higher HMF selectivities than H_2SO_4 systems and no LA formation. The SAPO-34/5A beads heterogeneously catalyzed dehydration reactions and resulted in moderate yields of furfural from xylose and HMF from glucose. The bead structure made recovery and reuse of the catalysts significantly easier and the structure was not affected by water washes. The catalysts were able to be recycled three times for xylose reactions with only a slight decrease in the furfural yield. We believe that the rational design of these new catalysts for biomass upgrading could successfully lead to the production of platform chemicals from biomass.

4. METHODS

4.1. Catalyst Preparation. The SAPO-34 synthesis gel had a molar composition of 1.0 Al_2O_3:1.0 P_2O_5:0.3 SiO_2:1.0 tetraethylammonium hydroxide (TEAOH):1.6 dipropylamine (DPA):300 H_2O, similar to that reported elsewhere.[41] To prepare the gel, aluminum isopropoxide [$Al(i\text{-}C_3H_7O)_3$, Sigma-Aldrich 98% (all U.S. suppliers)] and deionized water were stirred for 1 h to form a homogeneous solution. Then, phosphoric acid (H_3PO_4, Sigma-Aldrich 85 wt % aqueous solution) was added to the aluminum solution for another 2 h under stirring. Ludox AS-40 colloidal silica was added (Sigma-Aldrich, 40 wt % suspension in water) and the resulting solution was stirred for another 3 h. Finally, TEAOH (35 wt % in water, Sigma-Aldrich) and DPA (Acros 99%) were added. The final gel was stirred at ~323 K for 4 days. The resultant solution was transferred into a 45 mL Teflon-lined stainless-steel autoclave containing 5 g of pure zeolite 5A beads. Zeolite 5A beads were selected because of their chemical, thermal, and mechanical stability.[33,42] Hydrothermal synthesis was carried out in a conventional oven at 503 K for 6 h. After the autoclave was cooled to room temperature using a cold water bath, the SAPO-34-covered 5A beads were taken out from the autoclave, washed with deionized water, and dried at 373 K overnight. To remove the templates, the SAPO-34/5A beads were calcined using an oven at 673 K for 4 h with heating and cooling rates of 0.8 K/min.

4.2. Catalyst Characterization. The synthesized SAPO-34/5A beads were inspected by XRD using a Siemens Kristalloflex 810 diffractometer operating at 30 kV and 25 mA with Cu Kα1 radiation (λ = 1.54059 Å). The morphology of the samples was inspected by SEM model JEOL JSM-7000F.

Specific surface areas were determined from Brunauer–Emmett–Teller analysis of N_2 physisorption isotherms at 77 K. *t*-Plot analysis of the same isotherms was used to determine the micropore area for each sample. N_2 uptake isotherms were obtained using Micromeritics ASAP 2020. Each experiment

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used roughly 75 mg of catalyst, and all samples were outgassed under vacuum at 623 K for 4 h prior to N_2 dosing.

Brønsted site densities were determined from molar quantities of ethylene evolved between 470 and 870 K during temperature-programmed desorption of ethylamine.[15] Approximately 70 mg of catalyst was loaded into a quartz tube (1/2″) on top of a quartz wool plug, and the tube was positioned in a high-temperature furnace (Omega) and connected to a gas flow manifold. Prior to analysis, catalysts were calcined in situ at 673 K for 4 h under 50 mL min^{-1} of air (Airgas, Ultra Zero). Subsequently, samples were cooled to 423 K and purged with 100 mL min^{-1} of He that was dried over molecular sieves. After pretreatment, the samples were held at 423 K and contacted with ethylamine (99%, Sigma). Ethylamine was introduced into the He stream (60 mL min^{-1}) by vaporization of liquid ethylamine through a 50 μm capillary tube. The point of ethylamine surface saturation was determined by monitoring the off-gas with a mass selective residual gas analyzer (Stanford Instruments RGA 100). After ethylamine saturation, the cell was purged with He (423 K, 400 mL min^{-1}) for 1 h and subsequently ramped to 973 K (10 K min^{-1}). The sweep gas for this experiment contained 1.0 mol % Ar, which was used as an internal standard to facilitate quantitative analysis. During the temperature ramp, the cell effluent was monitored using a mass selective residual gas analyzer (Stanford Instruments RGA 100). Signals corresponding to ethylamine (m/z = 30), ethylene (m/z = 27), and Ar (m/z = 40) were monitored continuously. Brønsted site densities were calculated from evolved ethylene based on the assumption that one molecule of ethylene forms at one accessible Brønsted site.

4.3. Catalytic Reactions. Reactions were performed in 15 mL pressure tube reactors with magnetic stirring. Reactors were heated in a silicone oil bath held at the reaction temperature by a heated stir plate. For a typical reaction, 2 wt % xylose (Sigma-Aldrich, X1500) or glucose (Fisher Scientific, D16-500), 4 mL H_2O, and the catalyst were added to the reactors with a stir bar and sealed. SAPO-34 powder was purchased commercially (ACS Material) and used as received. To differentiate between the SAPO-34 powder that was synthesized (SAPO-34 powder) and the commercial SAPO-34 (SAPO-34C), a "C" will be used for the commercial SAPO-34 powder. The heterogeneous catalysts were stored in a 403 K oven overnight to remove water prior to reaction. Either 0.02 M sulfuric acid (H_2SO_4) or 0.048 g of catalyst was added to the pressure tube, and the sealed pressure tubes were placed in the heated oil bath. The mass of the heterogeneous catalyst was the same for both the powder and bead catalysts. After the reaction, external airflow was used to cool the reactors to room temperature. Products were analyzed by high-performance liquid chromatography (Agilent 1100, Bio-Rad Aminex HPX-87H column, trifluroacetic acid mobile phase) with a refractive index detector and diode array detector.

For the recyclability experiments, two methods were used to regenerate the SAPO-34/5A bead catalysts. A fresh catalyst was used in 6 h xylose reactions that were run as described previously, and for both methods, the catalysts were recovered after reaction using tweezers. For the first method, the recovered catalyst was washed with water five times and then used for a 6 h xylose reaction and the process was repeated. For the second method, no washing occurred, but the catalyst was placed in a 523 K oven overnight. The regenerated catalysts were then used again for a 6 h xylose reaction as described above.

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Notes

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CHAPTER FOUR

CONCLUSIONS

The efficient production of platform chemicals from biomass and model sugars for use as intermediates in fuel, chemical, and material applications has been a major focus of research. Furfural and HMF, derived from sugars in biomass feedstocks, are important building blocks for many value-added products. The recent drive towards heterogeneous catalysts for furan production provides a viable alternative to homogeneous acids, which require additional material and safety considerations. Additionally, the exploration of different solvent systems has demonstrated increased yields in biphasic systems with all classes of heterogeneous catalysts. In particular, zeolites, with their unique physical and chemical properties, provide a new avenue to further tune and control catalyst properties that contribute to their activity.

Although biphasic systems and carefully designed zeolite catalysts have achieved moderate to high yields, challenges for industrial realization of these systems remain. As outlined in Chapter 2, solvent selection in biphasic systems should also consider downstream separations and product recovery. Additionally, the recyclability of expensive organic solvents must be considered, as well as if the increased product offsets the increased cost. Despite these challenges, biphasic solvent systems achieve high furan yields from biomass. Organic solvents, such as toluene and MIBK, have shown furfural yields greater than 70% and HMF yields as high as 50% for multiple heterogeneous catalysts. Compared to aqueous and monophasic systems, biphasic systems present an advantageous approach to furan production.

Zeolite bead catalysts, as demonstrated for the first time in Chapter 3, are an unexplored area of heterogeneous catalysts for sugar upgrading. Although only producing moderate furfural and HMF yields, the SAPO-34/5A catalysts had excellent recyclability and good selectivity to HMF. Careful design of zeolite bead catalysts could lead to high yields of furfural and HMF from model sugars and biomass. Additionally, exploration of biphasic solvent systems could increase product yields with the SAPO-34/5A zeolite beads.

Achieving high furan yields from biomass and model sugars requires the consideration of both catalyst and solvent system, in addition to reaction conditions. The current literature reporting the use of biphasic systems for furfural and HMF production shows promise for maximizing yields in heterogeneous catalyzed systems. In a step towards increasing yields with carefully tuned catalysts, the zeolite SAPO-34/5A beads have shown good activity and stability in aqueous systems. However, beyond extensive kinetic studies, complex molecular modeling, and “trial and error” selection there is no clear method to optimize catalyst, solvent, and reaction conditions. The path forward to realizing the potential of platform chemical production from biomass should seek to simplify the development of catalytic reaction systems, which could include relating attributes of high yield systems to fundamental properties. Nevertheless, platform chemicals derived from biomass have considerable potential to replace petroleum precursors in the production of fuels, chemicals, and materials.

CHAPTER FIVE

RECOMMENDATIONS

This thesis lays the foundation for further research to actualize the industrial potential of platform chemical production of furfural and HMF from lignocellulosic biomass. Continuing research must seek to simplify the optimization of catalytic reaction systems by increasing reaction yields and selectivities with rational catalyst design and solvent system selection. One possible avenue to better inform solvent selection would be to determine correlations between conversions, yields, selectivities, and solvent properties, such as density, water solubility, or polarity, as mentioned in the section on solvent selection of Chapter 2. With a comprehensive knowledge of how a particular solvent property benefits or impedes high furan yields, a systematic approach to solvent selection could be developed.

Additionally, heterogeneous catalyst development should continue to relate physical and chemical properties to furan yields, such as has been demonstrated in the zeolite section of Chapter 2. The SAPO-34/5A zeolite bead catalysts showed moderate furan yields from xylose and glucose, however, due to the small pore size of the chabazite framework of the SAPO-34, dehydration of sugars is likely diffusion limited. Other classes of zeolites, such as mordenite, have larger frameworks which could more easily accommodate xylose and glucose molecules. Furthermore, treatments introducing mesoporosity into the surface structure could increase furan yields, as was demonstrated with the mesoporosity of the SAPO-34/5A beads in Chapter 3. Considering the demonstrated success of the zeolite bead catalysts for recyclability, increased

mesoporosity, and product selectivity, the concept could be extended to investigate different zeolite frameworks, such as mordenite synthesized on 5A bead supports.

Additionally, further research into what is happening on a fundamental level within the zeolite structure could provide insight into zeolite selection as well. As mentioned in Chapter 2, the sugar molecules are much larger than the SAPO-34 pores, which leads to the question of where the dehydration reaction takes place. Does it occur within the zeolite structure or on external active sites? Exploring different atomistic techniques, such as NMR, may elucidate the active sites participating in the reaction on the zeolite.

A focus on the fundamental properties of both solvent and catalyst in reaction systems for furan production from lignocellulosic biomass and model sugars will aid in the development of simple, high yield reaction systems. In addition to new experimental exploration, further comprehensive review of the literature is needed that brings together common trends in multiple catalytical systems. With a planned path forward for continued research, furan production from lignocellulosic biomass has great potential as an alternative for global chemical production.

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