Strategies for the Catalytic Conversion of Lignocellulose-Derived Carbohydrates to Chemicals and Fuels

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Biomass, being the only renewable source of carbon, has the potential to serve as a sustainable platform for the production of energy and chemicals, in this era of diminishing supplies of fossil fuels. The conversion of lignocellulose to fuels and chemicals requires the effective utilization of the hemicellulose and cellulose portions. Catalytic processing strategies for these two portions were developed and studied through key platform molecules.

First, catalytic processing of two cellulose-derived intermediates, glucose and levulinic acid, were investigated. As shown previously, glucose (and sorbitol) could be converted over PtRe/C to monofunctional molecules (alcohols, ketones, carboxylic acids and heterocycles), which could then be upgraded by consecutive C-C coupling reaction steps, i.e., ketonization and aldol condensation, to fuel grade alkanes. In this thesis, the aldol condensation step was studied over Pd dispersed ceria-zirconia mixed oxide catalysts. Among the mixed oxides, Pd/ZrO₂ displayed the highest activity, as well as good resistance to inhibition by CO₂ and water, two by-products of ketonization. Therefore, Pd/ZrO₂ allowed for integration of aldol condensation/hydrogenation step with ketonization in a single reactor dual-bed system. As an
alternative, cellulose can be processed through the intermediate formation of levulinic acid. A valuable fuel-precursor, \( \gamma \)-valerolactone, was obtained from levulinic acid via the formation of levulinate and formate esters for improved management of sulfuric acid. The esters were obtained from the corresponding acids by a reactive extraction step using butene.

Two alternative hemicellulose processing strategies were also developed for the production of furfural. In the first strategy, hemicellulose-derived xylose is converted to furfural in a biphasic system with a novel solvent (2-sec-butyl-phenol, SBP) and use of mineral acids. Increased concentrations of furfural compared to the feed could be obtained due to the exceptionally high partition coefficient of furfural in the SBP-water biphasic system. An alternative strategy involves the conversion of xylose in a monophasic system with another novel green solvent (\( \gamma \)-valerolactone) using solid acid catalysts (i.e., H-mordenite) with high yields. Importantly, the furfural degradation reactions were found to be dominated by condensation reactions, rates of which could be decreased significantly when \( \gamma \)-valerolactone was used as the solvent instead of water.
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To My Family
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Yields to levulinic acid starting from furfuryl alcohol solutions in 2-sec-butylphenol (SBP) in a biphasic reactor system with water or in a monophasic system with water at 398 K. All reactions were carried out in a batch reactor system. LA and SA correspond to levulinic acid and 1 M sulfuric acid, respectively. Furfuryl alcohol conversion is complete for all experiments.

Table 7.3

Yields to levulinic acid starting from furfuryl alcohol solutions in 2-sec-butylphenol (SBP), 4-n-hexylphenol (NHP) or 4-propyl guaiacol (PG) in a biphasic reactor system with water or in a monophasic system with water at 398 K. All reactions were carried out in a semi-batch reactor system. LA and SA correspond to levulinic acid and 1 M sulfuric acid, respectively. Furfuryl alcohol conversion is complete for all experiments.

Table 7.4

Furfural conversion, furfuryl alcohol selectivity/yield and production rate over different catalysts. T = 373 K, P= 34 bars in H₂, Feed = 5 wt. % furfural in SBP.

Table 8.1

Composition of monomeric and oligomeric sugars, acetic acid, furfural and 5-hydroxymethylfurfural (HMF) in the dehydration reactor (mixture of evaporated PHL and GVL).

Table 8.2

Results of the distillation simulations (using NRTL) with changing furfural and water concentrations in GVL. In all cases, 99.9 % furfural is recovered in the top stream with 95% mass purity.

Table 8.3

Results of xylose and glucose dehydration experiments carried out at 448 K in a monophasic reactor system, containing 2 wt. % xylose or 0.5 wt. % glucose or both. All the entries contain 10 wt. % H₂O in GVL with H-mordenite. Entries 7 and 8 show the results starting with the concentrated PHL feed (90% of the water is evaporated) in GVL.

Table 8.4

Conversion of glucose and fructose with corresponding furfural yield over acid catalysts in water or 10 wt% water containing GVL (GVL in the solvent column contains 10 wt% water) at 448 K.
Chapter 1: Introduction

1.1. Current Energy Outlook

Fossil fuels are the primary source of energy in the world. For example, in 2008, the global energy consumption was 474 exajoules (1 EJ=1018 J), 88% of which was derived from fossil fuel resources. Following a decrease in 2009 (1.1%), the world energy consumption increased by 5.6% in 2010. As shown in Figure 1.1, renewable resources currently account for only about 7% and 8% of total energy consumption globally and in the U.S. respectively. In the U.S., the primary sources of renewable energy include hydroelectricity (31% of renewables) and traditional biomass (i.e., open combustion; 25% of renewables). Solar, wind, and geothermal energies along with biofuels account for 1%, 11%, 3%, and 21% of the renewable energy used, respectively (1-3). Biofuels include fuel ethanol and biodiesel together with losses and co-products from the production of fuel ethanol and biodiesel.

Residential and commercial energy consumption is primarily in the form of electrical power, and these two sectors consume primarily coal and natural gas. In contrast, transportation energy is derived almost exclusively from oil (95%). Depletion of these finite fossil fuel resources seems unavoidable in the future since these resources are expended faster than can be regenerated. Recent analyses of proven reserves for oil, natural gas, and coal show that these fuels have lifetimes of approximately 46, 59, and 118 years, respectively, at current usage rates (1). In particular, oil is the resource with the shortest expected lifetime, and importantly, oil is the predominant source of transportation energy, one of the largest and fastest growing global energy sectors (28% of energy consumption in U.S.). Additionally, the consumption of fossil fuels leads
to the emission of CO₂, causing detrimental effects on the environment such as accelerated rates of global warming.

![Energy Distribution Chart](image)

**Figure 1.1** Distribution of energy usage A) globally and B) in the United States by resource.(1-3)

Analyses show that renewable energy resources such as solar, wind, geothermal, and hydroelectric are best suited for the generation of electricity and heat (4-6), which makes them (and nuclear energy) ideal for stationary power applications. The transportation industry requires clean burning fuels with high energy densities for efficient storage at ambient
conditions. Currently, these criteria are best met by liquid hydrocarbons derived from crude oil. Therefore, a renewable option would be to utilize resources such as biomass to produce liquid fuels that meet the aforementioned criteria. The liquid biofuels used most widely today for transportation are ethanol and biodiesel. Ethanol is the predominant biomass-derived fuel at the present time, accounting for 90% of total biofuel usage. Fermentation produces a dilute aqueous solution of ethanol and requires an energy-intensive distillation step to completely remove water from the mixture. Low concentration (5%-10%) blends of ethanol with gasoline (i.e. E5-E10) can be employed in current spark ignition engines while ethanol-rich mixtures (E85) require additional engine upgrades (7).

Biodiesel is the second most abundant renewable liquid fuel. It can be used in current injection engines in a wide range of blends with petrol-diesel or as a pure fuel (without petrol-diesel). Esterification of fatty acids or transesterification of oils (triglycerides) with alcohols (normally methanol and ethanol) results in the production of a first generation biodiesel (8, 9). The primary side-product of this reaction is glycerol which is obtained in high concentrations in water. Second generation biodiesel can be formed through hydro-treating of fatty acids and triglycerides (10), which can be carried out in petroleum refineries by co-processing vegetable oils with petroleum-derived feedstocks (11, 12). The main disadvantage of oil-based processes is the unavailability of inexpensive feedstocks. Normally palm, sunflower, canola, rapeseed and soybean oils are used, but they are expensive and can otherwise be used as food sources. Various non-edible oils have been proposed as appropriate feedstocks (e.g., cynara (13), Jatropha, Karanja (14)).
Both of the liquid biofuels presented above are oxygenated fuels with molecular compositions that differ from the petroleum-derived fuels used today. Moreover, these biofuels do not meet the criteria required for liquid transportation fuels, namely to burn cleanly and have high energy densities for efficient storage at ambient conditions. Therefore, in the short term, it is desirable to develop technologies to utilize biomass to generate liquid fuels that meet the physical property requirements of today’s liquid fuels and are compatible with modern internal combustion engines.

The depletion of petroleum reserves has consequences that reach beyond the transportation fuel sector. Currently more than 90% of the chemical industry relies on fossil fuels as a feedstock. The pressing issues discussed above related to depletion of fossil fuels resources and environmental concerns require the development of renewable strategies for production of chemicals as well. However unlike the production of energy, the renewable production of chemicals will solely have to rely on biomass, since among all the renewable resources, biomass is the only source of carbon. A complete transition from petroleum to biomass feedstocks seems feasible for the production of chemicals based on the current production volume of biomass; however, biomass feedstocks, being highly functionalized molecules, are significantly different from petroleum feedstocks that are generally unfunctionalized, presenting significant technological and economic challenges (15, 16).

One of the main concerns in the large-scale production of biofuels and chemicals is the consumption of edible biomass as feedstocks (e.g., sugars, starches and vegetable oils). This issue has motivated researchers around the world to develop technologies for processing non-edible biomass (lignocellulosic biomass) so that a sustainable production of a new generation of
fuels and chemicals can be achieved without affecting food supplies. In this respect, lignocellulosic biomass is attractive since it is abundant (17) and can be grown faster and more economically than food crops (18). Lignocellulosic biomass consists of three major components (Figure 1.2): cellulose (40-50%), hemicellulose (25-35%) and lignin (15-20%) (19, 20). In the following sections, a more detailed description of the major lignocellulose components is presented.

1.2. Research Direction

As discussed earlier, biomass, being the only renewable resource of carbon, has the potential for establishing a sustainable platform for the production of energy as well as chemicals. Similar to development of petroleum-based technologies, the field of catalysis will undoubtedly play a vital role in the development of biomass-based technologies. However, recent research has revealed a new set of challenges for catalysis research to efficiently use lignocellulosic biomass. For example, biomass, being an overfunctionalized starting material, requires selective oxygen removal reactions (i.e., hydrogenation, dehydration, hydrogenolysis etc.) to selectively obtain platform molecules (e.g., alcohols, acids, ketones, furanic species etc.). These platform molecules have diverse and limited functionalities on which biorefining strategies can be established. However, to establish a cost-competitive biorefinery operation, it is important to utilize as few processing steps as possible (e.g. reactors, purifiers and separators). To this end, developing new catalytic processing strategies that achieve the integration of multiple reactions in a single reactor becomes important.

In addition, the presence of an aqueous/condensed phase environment and competing coke-forming side reactions in most biomass conversion reactions presents challenges for
utilizing conventional catalysts. These challenges, among others, create opportunities for scientific and technological advancements to develop efficient biorefining strategies.

This thesis addresses some of the aforementioned challenges by developing catalytic strategies for the conversion of both cellulose and hemicellulose portions of lignocellulose to platform chemicals through successive oxygen removal reactions and upgrading of these platform molecules to obtain fuel and chemical grade products utilizing heterogeneous catalysis. In the rest of this chapter, lignocellulosic biomass and processes developed for its conversion to fuels are introduced. Among different strategies, we focus on the aqueous phase processing of lignocellulose and provide some background on specific strategies for the catalytic conversion of cellulose and hemicellulose portions to chemicals and fuels. Chapter 2 presents the experimental and analytical techniques used throughout the projects. Chapters 3-6 present strategies for the catalytic conversion of cellulose to fuels and chemicals, while Chapters 7-8 focus on the conversion of the hemicellulose portion. More specifically, first, upgrading of monofunctional platform molecules (i.e., ketones, alcohols and carboxylic acids) obtained from hydrodeoxygenation of glucose and sorbitol to liquid fuels is discussed. Chapter 3 focuses on the aldol condensation (a common C-C coupling reaction for the production of fuel grade high molecular weight organics) reaction between ketones in terms of elucidating the reaction network and understanding the effects of reaction conditions and reaction medium on the aldol condensation activity and selectivity. Chapter 4 presents the studies for characterizing and developing a better understanding of the ceria-zirconia mixed oxide catalysts, over which aldol condensation as well as ketonization reactions can be carried out to convert ketones and alcohols as well as carboxylic acids to high molecular weight ketones. Finally, Chapter 5 discusses the
opportunities in the integration of these two upgrading reactions (i.e., ketonization and aldol condensation) as a means of increasing the energy efficiency, decreasing operating and capital costs and streamlining the overall process for the development of a cost competitive biorefining strategy.

Chapter 6 also addresses the conversion of cellulose to fuels and chemicals; however, this time through the formation of another important platform chemical: levulinic acid. A novel strategy for the management of sulfuric acid, which is a significant concern in the upgrading of levulinic acid (after its production from sulfuric acid catalyzed deconstruction of cellulose), is presented. In this strategy, levulinic acid is converted to hydrophobic levulinate esters through a reactive extraction step and consequently separated from the sulfuric acid that remains in the aqueous phase. Levulinic esters can then be catalytically converted to to liquid fuels.

In terms of processing hemicellulose, both Chapters 7 and 8 present studies for the production of furfural. Chapter 7 discusses the furfural production as well as its conversion to levulinic acid (through the formation of furfuryl alcohol) in a biphasic system with a novel solvent (2-sec-butyl-phenol) and use of mineral acids. Chapter 8 presents an alternative strategy in a monophasic system with another novel green solvent (γ-valerolactone) using solid acid catalysts. Finally, Chapter 9 summarizes the conclusions of this work and proposes future research directions.

1.3. Lignocellulosic Biomass

Lignin is an amorphous polymer composed of methoxylated phenylpropane structures such as coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol (21, 22). This compound
provides plants with strength and structural rigidity as well as a hydrophobic vascular system for
the transportation of water and solutes (23). The hemicellulose and cellulose fractions are
surrounded by lignin, which if desired can first be de-polymerized by a pretreatment step so that
the cellulose and hemicellulose portions can be accessed easier for further upgrading (22, 24).
Although lignin can be isolated, it is not readily amenable to upgrading strategies. One option
for lignin utilization is to burn it directly to produce heat and electricity. Process heat and power
obtained from burning lignin and other residual solids are more than enough to drive the biofuel
production process (25, 26). In addition, lignin can serve as a feedstock in the production of
phenolic resins (27). Pyrolysis strategies for lignin have been reported for the production of bio-
oils (28) and aromatics (29, 30).

Hemicellulose is an amorphous polymer generally comprised of five different sugar
monomers: D-xylose (the most abundant), L-arabinose, D-galactose, D-glucose, and D-mannose
(31). If separate processing of cellulose is desired, to increase the effectiveness of the cellulose
hydrolysis steps in the production of glucose, the hemicellulose fraction of biomass can be
removed during pretreatment. The pretreatment process aims to preserve the xylose obtained
from hemicellulose and inhibits the formation of degradation and dehydration products (24).
Compared to hydrolysis of crystalline cellulose, hemicellulose extraction/hydrolysis is an easier
process and allows for high yields of sugar.

Cellulose is a polymer composed of glucose units linked via β-glycosidic bonds,
providing the structure with a rigid crystallinity that inhibits hydrolysis (31). Cellulose is more
accessible to hydrolysis in untreated biomass before the removal of lignin and hemicellulose (22,
24). High yields of glucose (>90% of theoretical maximum) can be achieved by enzymatic
hydrolysis of cellulose after biomass pretreatment (32, 33). Harsher conditions using solutions of mineral acids (H$_2$SO$_4$) at elevated temperatures can be applied to hydrolyze cellulose; however, these conditions lead to the formation of degradation products such as hydroxymethylfurfural (HMF), levulinic acid, and insoluble humins (34, 35).

Figure 1.2 General structures for the three most significant components of lignocellulosic biomass: cellulose, hemicellulose and lignin.

Generally, due to the complexity, the cost of isolating sugars from lignocellulosic biomass, is approximately twice that of isolating sugars from starchy edible biomass (36). Accordingly, research is being conducted worldwide with the aim of simplifying the sugar isolation process so that cost-competitive technologies may be developed for the generation of
liquid fuels from non-edible sources. Experts have identified this challenge as the key bottleneck for the large-scale implementation of a lignocellulose-derived biofuel industry (37).

1.4. Processes Developed for Conversion of Lignocellulosic Biomass to Fuels

Current strategies for the conversion of lignocellulosic biomass into liquid hydrocarbon fuels involve three major primary routes: gasification, pyrolysis and aqueous-phase hydrolysis (Figure 1.3). The first approach involves the conversion of biomass to synthesis gas, a mixture of CO and H₂ which serves as a precursor of liquid hydrocarbon fuels. The second strategy converts solid biomass into a liquid fraction known as bio-oil, which can be further upgraded to gasoline and diesel fuel components. Finally, the third route involves the aqueous phase hydrolysis of biomass to produce sugars and valuable intermediates that can be catalytically processed in the aqueous phase to the full range of liquid hydrocarbon fuels including gasoline, diesel and jet fuels.

Gasification, pyrolysis and liquefaction are mainly referred to as thermochemical conversion strategies. These processes for conversion of lignocellulose are carried out by increasing temperature and/or pressure under controlled atmosphere, usually in the absence of catalysts. In biomass gasification, the plant material is converted to synthesis gas (i.e., a mixture of CO and H₂) at high temperatures (i.e., > 1100 K) via partial combustion due to the presence of an oxidizing agent (i.e., oxygen or air). To obtain alkanes suitable for use as liquid fuels, gasification is followed by Fischer-Tropsch synthesis. Instead of liquid alkanes, H₂ can be obtained as the end product by converting the CO present in the synthesis gas to CO₂ and H₂ via the water gas shift reaction (CO + H₂O → CO₂ + H₂) followed by purification. As another alternative, synthesis gas can be converted to methanol through methanol synthesis.
Unlike gasification, pyrolysis and liquefaction take place under an inert atmosphere and lower temperatures (573-973 K).(19) The result of pyrolysis or liquefaction is a viscous liquid denoted as bio-oil, mixed with solid char. The elemental composition of bio-oil is similar to that of biomass, and it is composed of a complex mixture (more than 300 species) of highly-oxygenated hydrocarbons and a substantial amount of water.(42) Due to its high oxygen content, bio-oil cannot be utilized directly as a fuel and needs further upgrading reactions to lower the oxygen content, such as hydrodeoxygenation reactions.(43)

The aforementioned thermochemical approaches allow for the simultaneous processing of cellulose, hemicellulose and lignin, and these methods are generally preferred due to simplicity of operation and low costs. On the other hand, the simultaneous processing of components of biomass limits flexibility and does not allow us to take full advantage of the different chemical and physical properties of the hemicellulose and cellulose fractions, which is important for establishing biomass-based chemical and fuel industries. Therefore, it is desirable to separate different portions of the biomass through different pretreatment strategies, which are best carried out in the aqueous phase and thus referred to as aqueous-phase processing strategies. By separating the cellulose, hemicellulose and lignin portions of biomass, it becomes possible to combine chemical and biological routes as well. For instance, cellulose-derived C₆ sugars can be processed through established biological routes,(44) whereas hemicellulose-derived C₅ sugars, which are more difficult to process enzymatically, can be converted via chemical routes. In addition, cellulose can be utilized for pulp and paper applications,(45) while hemicellulose can be converted chemically. Finally, it will be shown in this thesis that it is possible to employ chemical methods to process both hemicellulose and cellulose for production of a variety of important platform chemicals and fuel grade compounds.
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Figure 1.3 General processing strategies for the conversion of lignocellulosic biomass to liquid transportation fuels and chemicals.

1.5. Aqueous-Phase Processing of Lignocellulose

As mentioned previously, aqueous-phase processing of lignocellulose allows for the separation of different portions of biomass, i.e. cellulose, hemicellulose and lignin, thereby enabling the separate processing of these different biomass fractions. In this strategy, solid biomass is first subjected to mild pre-treatment in aqueous solution containing dilute acid to solubilize the hemicellulose as xylose. Dilute acid hydrolysis of hemicellulose leads to high amounts of xylose, up to 95% yields from corn stover using a 1 wt% solution of sulfuric acid at 463 K.(46) Other studies have also used sulfuric acid (47), but phosphoric,(48) maleic,(47) and oxalic acids(47) have been successfully used as well for hemicellulose deconstruction. After the
xylose stream is separated, the remaining biomass is then subjected to further treatment to solubilize cellulose as glucose or levulinic acid. Hydrolysis of cellulose may be achieved enzymatically (more selective) or chemically (lower cost).\(49\) The acid-catalyzed hydrolysis of cellulose typically involves a strong mineral acid catalyst, but at concentrations greater than those used for hemicellulose deconstruction. The remaining lignin portion can be used as a source for heat and power generation or can be upgraded to form lignin-derived solvents. As another option, as mentioned earlier, lignin can be depolymerized prior to hemicellulose/cellulose hydrolysis through several pretreatment strategies. Compared to hydrolysis of crystalline cellulose, hemicellulose extraction/hydrolysis is an easier process and allows for high yields of sugar. It is also possible to solubilize hemicellulose through hot water or steam pretreatments to obtain mixtures rich with oligomers of C\(5\) sugar, as carried out in pulp and paper applications.\(45\)

It should be noted that one of the most significant challenges for processing biomass to produce fuels that are currently obtained from petroleum is the overfunctionalized starting materials, i.e., cellulose and hemicellulose. The corresponding sugar molecules (i.e., glucose and xylose, respectively) obtained from deconstruction pretreatment steps are still highly oxygenated species, which makes it difficult to selectively increase the chain length of these molecules through upgrading reactions to obtain high molecular weight alkanes suitable for gasoline, diesel and jet-fuel applications. It is also important to remember for the production of fuels that even though hydrogenation of these oxygenated species is very favorable thermodynamically, the maximum carbon chain length of the alkane hydrogenation product is limited to the carbon number of the sugar or polyol feed, such as glucose or sorbitol \(6\) and xylose or xylitol \(5\). On the other hand, as demonstrated in the previous literature, thermodynamic analysis suggest that
C-C coupling reactions (e.g., aldol condensation, ketonization, and oligomerization) employed to increase the chain length of reactants are favored more when starting from partially oxygenated compounds compared to their fully hydrogenated and thermodynamically more stable counterparts (50). For this reason, a useful strategy for production of liquid fuels from biomass is to start with controlled oxygen removal reactions to produce functional intermediates. These molecules can also be referred to as platform molecules, some examples of which include monofunctional species (i.e., alcohols, ketones and carboxylic acids), levulinic acid, HMF, and furfural. These partially deoxygenated platforms are more stable compared to overfunctionalized sugar molecules and at the same time have sufficient functionality to allow for the production of fuels as well as selective production of a wide range of value-added chemicals.

As mentioned earlier, the fractionation of hemicellulose and cellulose provides increased flexibility of operation as well as a wide range of end products. A small portion of the versatile end products (i.e., chemicals, fuel additives and fuels) obtained from cellulose and hemicellulose, through the formation of glucose and xylose respectively, is demonstrated in Figure 1.4. Accordingly, the following sections outline the production and upgrading of some key platform chemicals from cellulose as well as hemicellulose.
Figure 1.4 Examples of chemical conversions involved in the production of transportation fuels and chemicals from carbohydrate based feedstocks obtained from separate processing of cellulose and hemicellulose portions of lignocellulose. Abbreviations for reactions: Hygn – Hydrogenation; Oxdn – Oxidation; Hygnlys – Hydrogenolysis; Ester- Esterification; Dehydn– Dehydration; Abbreviations for chemical compounds: GA – glycol-aldehyde; DHA – dihydroxyacetone; PDO – propanediol; HMF – Hydroxymethylfurfural; DFF – Diformylfuran; FDCA – 2,5 –Furan-dicarboxylic acid; DHMF – Di(hydroxymethyl)furan; DiMe-THF – Di(methyl)-tetrahydrofuran; THF – Tetrahydrofuran; Me-THF – Methyl-tetrahydrofuran; THFOH – Tetrahydrofurfuryl alcohol; GVL – γ-valerolactone. Adapted from (51).
1.6. Catalytic Conversion Strategies for Cellulose

The conversion of cellulose to chemicals and liquid fuels has been demonstrated through the formation of several platform molecules, such as glucose, HMF, and levulinic acid, utilizing chemical routes as demonstrated in Figure 1.5. [6-9] In the next sections, we focus on the utilization of the two of these platform molecules: glucose and levulinic acid.

![Figure 1.5 Examples of platform molecules that can be obtained from cellulose.](image)

1.6.1. Conversion of Glucose to Liquid Fuels via the Formation of Monofunctional Intermediates

As concluded in the previous sections, the production of heavier liquid fuels from sugars and/or polyols can be accomplished by controlled oxygen removal reactions (controlled C-O and C-C cleavage reactions) to obtain functional intermediates that can undergo C-C bond forming reactions. Kunkes et al. [52] reported a process in which sugars and polyols are converted to monofunctional intermediates over carbon-supported Pt-Re bimetallic catalyst in a single reactor. By operating at moderate temperatures (283-523 K) and pressures (20-30 bar) with concentrated aqueous polyol (60 wt% sorbitol) or sugar (40 wt% glucose) feeds, 80% of the initial oxygen
content of the sugars and polyols is removed by controlling C-C cleavage (leading to CO\textsubscript{2} and H\textsubscript{2}) and C-O cleavage (leading to alkanes) rates. As a result, an organic phase is formed that spontaneously separates from water and consists of a mixture of C\textsubscript{4}-C\textsubscript{6} monofunctional species (carboxylic acids, alcohols, ketones and heterocyclic species). One of the most significant features of this process is that the de-oxygenation (C-O bond cleavage) is accomplished by using the hydrogen generated in situ by the endothermic partial reforming of the carbohydrate feed. The exothermic deoxygenation reactions are balanced with endothermic reforming reactions in the same reactor, such that the overall conversion is mildly exothermic and more than 90\% of the energy content of the carbohydrate feed is stored in the reaction products. The overall process is illustrated schematically for sorbitol in Figure 1.6. The monofunctional species obtained in the organic effluent from the conversion of sugars and polyols over Pt-Re/C catalyst have sufficient functional moieties to undergo various upgrading reactions to form high-molecular weight compounds suitable for gasoline, diesel and jet-fuel applications. Diesel fuels consist primarily of hydrocarbons with linear carbon chain and with minimal branching to achieve high cetane numbers, whereas gasoline typically contains more highly branched hydrocarbons and aromatic compounds having high octane numbers (53, 54). With respect to gasoline components, Kunkes et al.(52) showed that the organic liquid produced from sorbitol/glucose can be converted to aromatic compounds or to a distribution of branched olefins centered at C\textsubscript{12}. The first step for both conversions is the hydrogenation of ketones and carboxylic acids to alcohols. In order to obtain aromatic species, the mixture of alcohols is reacted over HZSM-5 at 673 K and atmospheric pressure. (55) In addition, it is possible to dehydrate secondary alcohols obtained by hydrogenation over an acidic niobia catalyst to form C\textsubscript{4} to C\textsubscript{6} branched olefins. These olefins
can later undergo oligomerization reaction combined with cracking reactions over HZSM-5 to produce a distribution of branched olefins centered at C_{12}.

**Figure 1.6** Schematic representation of the conversion of sugars and polyols over Pt-Re/C to produce an organic liquid consisting of C_4-C_6 monofunctional species (ketones, alcohols, carboxylic acids and heterocyclic species).

To produce C_8 to C_{12} compounds that have minimal branching to be used in diesel fuel applications, C-C coupling by ketonization followed by aldol condensation can be applied to the organic effluent obtained from sorbitol solution over Pt-Re/C. First, the carboxylic acid molecules can be upgraded by coupling through ketonization reactions over CeZrO_x to form higher molecular weight ketones (releasing CO_2 and H_2O), prior to the aldol condensation step resulting in the formation of C_7-C_{11} ketones. During ketonization reaction, the remainder of the
monofunctional species remains unreacted, and therefore, the product stream of this step can be subjected to further C-C coupling by aldol condensation over Pd/CeZrO\textsubscript{x} of ketones and secondary alcohols. When the ketonized organic liquid was reacted over Pd/CeZrO\textsubscript{x} at 573 K and 5 bar pressure with H\textsubscript{2} co-feed, 57% of total carbon in the liquid organic product stream was in the form of C\textsubscript{7+} ketones, with 34% and 23% generated in ketonization and aldol condensation reactions, respectively. Products with carbon chain length greater than C\textsubscript{12} were also observed, due to aldol condensation of C\textsubscript{6} ketones with C\textsubscript{7+} ketones formed during ketonization.\(^{(52)}\)

**1.6.1.1. Aldol Condensation Reaction and Applications**

Carbon-carbon bond formation reactions are very important in organic synthesis; specifically in obtaining many fine commercial chemicals \(^{(56)}\). The base-catalyzed aldol condensation reactions, a type of C-C coupling reaction, is used for synthesis of higher molecular weight ketones and aldehydes from more available low molecular weight homologues \(^{(57)}\). In addition to fine chemical synthesis, as described earlier, aldol condensation reaction followed by oxygen removal steps can be used to obtain branched or linear long carbon chain alkanes suitable for gasoline, diesel and jet fuel from lower molecular weight ketones and aldehydes such as 2-hexanone, acetone, furfural and HMF \((52, 58)\). Aldol-condensation of acetone \((59-67)\), cross-aldol condensation of citral and acetone to synthesize pseudoionone \((68, 69)\), condensation of acetaldehyde \((57)\), butyraldehyde \((70)\), heptanal \((57)\), n-propanol \((71)\) and 2-propanol \((72)\) are examples studied in literature. Examples of solid base catalysts active for aldol condensation reaction are alkali and alkaline earth oxides, anion-exchange resins, phosphates, and hydrotalcites \((73)\). It has also been shown in literature that the aldol condensation can be catalyzed by acid sites as well \((60, 62, 67)\). In addition, several recent studies suggest that acid-
base pairing is crucial for achieving high activities (60, 64, 72, 74, 75). It was also shown in recent literature that coupling the acid-base pairs with metal sites (60, 64, 72) improves overall condensation activity.

**Figure 1.7** A) Main reaction pathways for acetone condensation in the presence of metal coupled with acid/base sites, B) Diacetone alcohol formation mechanism on MgO (base catalyst) and C) Al₂O₃ (acid catalyst). Adapted from (60, 68).
The reasoning behind the synergistic of acid-base pairing is explained in the following section together with the reaction mechanism. Figure 1.7A represents the reaction scheme for acetone self-condensation. Diacetone alcohol (DAA) is the product of aldol condensation, mesityl oxide (MO) is the dehydration product (α,β-unsaturated ketone) and methyl isobutyl ketone (MIBK) is the hydrogenated ketone. It is important to note that there are strong equilibrium limitations to the acetone condensation reaction (59, 60). However, there is a much smaller equilibrium limitation to the overall acetone to MIBK reaction (60). Under the reaction conditions in this project, conversion of acetone to MO is limited by 16%, whereas overall conversion to MIBK has an equilibrium limit of 92%. For this reason, researchers focused on the single step conversion of acetone to MIBK by dispersing hydrogen activating metals on the condensation catalysts (60, 63, 72). Under normal conditions, hydrogenation is a fast step compared to aldol condensation (72). Among different metals, Pd and Pt were favored because of their capability to selectively hydrogenate the C=C bond of unsaturated ketones as opposed to C-C bond cleavage (76). It was also observed in studies of aldol condensation in the presence of metal by Nikolopoulos et al. (60) that, with high metal loadings, the direct hydrogenation reaction of acetone to isopropanol (see Figure 1.7A) was favored more, decreasing the selectivity of MIBK (60, 77). Moreover, Nikolopoulos et al. investigated the effect of acid/base and hydrogenation site proximity and found that metal being close to the acid/base sites resulted in a little higher activity (60). Torres et al. studied MIBK formation directly from 2-propanol (72). They claimed that an additional step for dehydrogenation of the secondary alcohol to acetone was needed and this could happen readily on metal sites via an alkoxide intermediate (‘carbonyl’ mechanism) where the H\(^a\) is removed following the alcohol adsorption (72, 78).
1.6.1.2. Reaction Mechanism of Aldol Condensation of Ketones and Aldehydes

As mentioned previously, condensation of ketones and aldehydes is a typical base catalyzed reaction but can also be carried out over acid sites (61). Figure 1.7 B and C represent the aldol condensation mechanism of acetone to form diacetone alcohol on basic and acidic sites (68). The condensation mechanism on basic sites is initiated by the abstraction of the proton in alpha position to the carbonyl group to form a carbanion intermediate which is stabilized by the enolate resonance isomer. The strength of the basic sites required for abstracting the α-hydrogen depends on the proton acidity. To form the aldol product, the carbanion acts as a nucleophilic reagent and the α-carbon of this donor attacks to the carbonyl carbon of the other molecule which acts as the acceptor (57, 61, 68). On the acid sites, the enol tautomer is activated via the oxygen of the C=O group generating an electrophilic carbonyl carbon. Then, the nucleophilic alpha-carbon of the enol form attacks the acceptor carbonyl carbon to form the aldol product (68). In the case of acid-base pairing on the catalyst, acid sites can interact with the carbonyl group of a ketone or an aldehyde producing a polarization of this group, and increasing the positive charge on the corresponding carbon atom. This favors the nucleophilic attack of the enolate intermediate of the other carbonyl compound produced by basic sites. Also, the lewis acid sites stabilizes the carbanion formed (79, 80). In addition, acid sites are helpful by catalyzing the dehydration step of the aldol product to the corresponding α-β unsaturated ketone (60, 64, 72, 74, 75).

1.6.2. Levulinic Acid and γ-Valerolactone Platforms for the Production of Liquid Fuels

Levulinic acid (LA) is an attractive platform molecule from which a range of fine chemicals (δ-aminolevulinic acid, diphenolic acid, etc.) and fuel additives (levulinate esters,
methyltetrahydrofuran, etc.) can be produced. (81) Levulinic acid can be obtained from the decomposition of HMF or direct hydrolysis of lignocellulosic biomass (82, 83) and cellulose (84) through dilute sulfuric acid hydrolysis. In all of these conversions, equimolar amounts of formic acid are generated with levulinic acid. Levulinic acid production by hydrolysis of cellulose can be carried out through different strategies, such as by using dilute sulfuric acid, (84) concentrated hydrochloric acid, (85) solid acids (86) and ionic liquids. (87) Among these strategies, hydrolysis by dilute sulfuric acid appears to have the optimum balance of cost, yield, and scalability in the preparation of levulinic acid. The Biofine process produces levulinic acid from lignocellulose at a pilot level production via dilute sulfuric acid hydrolysis. (88, 89) Final yields to levulinic acid are around 70-80% of the theoretical maximum, and correspond to 50% of the mass of the C₆ sugars. The remaining mass is collected as formic acid (20%), which is separated from levulinic acid by evaporation, and humins (30%), which are solid polymers produced by degradation reactions of (90).

A specifically valuable derivative of LA is γ-valerolactone (GVL), (90) another platform molecule, from which fine chemicals, fuel additives, gasoline, jet fuel and diesel fuel components can be produced. (84, 91-93) LA can be converted to GVL through consecutive dehydration/hydrogenation reactions. High yields of GVL (97%) can be obtained using a Ru/C catalyst. The reduction of LA to GVL generally takes place in the presence of molecular H₂; however, the use of H₂ generated in situ from the decomposition of formic acid is a promising alternative. The use of formic acid as a hydrogen source in aqueous solutions also eliminates the need for purification of LA. When obtained through mineral acid hydrolysis from cellulose, the separation of levulinic acid from the mineral acid becomes energy intensive. A recent strategy
for production of GVL starting from cellulose, starts with the hydrolysis of cellulose with dilute sulfuric acid solution to generate an equimolar mixture of levulinic and formic acids in water. Levulinic acid is then reduced to GVL over a Ru/C catalyst using the H₂ generated in situ by formic acid decomposition. Even though sulfuric acid inhibits the reduction activity significantly, the Ru/C shows stable activity. The GVL product is more hydrophobic than levulinic acid, and therefore, selective separation of GVL from sulfuric acid becomes possible using a hydrophobic extracting solvent. This way, most of the sulfuric acid can be recycled back to the cellulose deconstruction reactor. For example, using an equal mass of ethyl acetate with aqueous GVL solution, 76% of the GVL can be extracted, while only 3% of the sulfuric acid and 6% of water is transferred into the organic solvent. (84)

In terms of chemicals, some compounds that can be produced from GVL are α-methylene-γ-valerolactone, (94) caprolactone (95) or adipic acid. (95) In terms of fuel applications, GVL itself can be directly used as a fuel additive (i.e., it has a similar capacity to ethanol (96)) or can be converted to methyltetrahydrofuran. In addition to forming fuel additives, two recent strategies have been reported in which GVL can be converted to liquid fuels in the range of diesel and jet fuel. In the first strategy, GVL is converted over bifunctional metal/acid catalysts (e.g., Pd/Nb₂O₅) to form pentanoic acid, which is used to produce 5-nonanone by ketonization at high yields (92%). (93) 5-Nonanone can undergo hydrodeoxygenation to nonane for use in diesel fuel blends, or it can be hydrogenated/dehydrated to produce nonene, which can be converted to C₁₈ olefins through oligomerization reactions. (93, 97) In the second strategy, GVL is converted to butene through decarboxylation over an acidic catalyst, such as SiO₂/Al₂O₃.
Butene can be oligomerized to obtain jet fuel range olefins. These strategies derived from GVL are summarized in Figure 1.8, which includes the production of GVL from levulinic acid.

**Figure 1.8** Reaction pathways for production $\gamma$-valerolactone (GVL) derived from levulinic acid and the production of targeted molecular weight alkanes via the catalytic upgrading of GVL through the formation of pentanoic acid and butene isomers.

### 1.7. Catalytic Conversion Strategies for Hemicellulose: Production of Furfural

Hemicellulose, comprising a substantial amount of biomass (20-35%), needs to be efficiently utilized to establish a cost-competitive biorefining strategy; however, compared to cellulose fewer studies address the conversion of hemicellulose to chemicals and fuels.$^{[10, 11]}$ In this respect, furfural can be obtained through the formation of $C_5$ sugars (mainly xylose), and this furan compound is a key platform chemical for both chemical and fuel industries based on
Furfural can replace crude-oil-based organics for the production of resins, lubricants, adhesives and plastics. It can also be used to produce other valuable chemicals, such as furfuryl alcohol, tetrahydrofurfuryl alcohol, furanoic acid, and tetrahydrofuran (100, 101).

The industrial production of furfural is exclusively from lignocellulosic biomass (pentoses), since there are no synthetic routes available. The first commercial process for furfural production was achieved in 1921 by Quaker Oats. This process uses aqueous sulfuric acid in a batch mode at 443-458 K to achieve only limited (40-50%) furfural yield. Following the Quaker Oats process, other furfural production processes were developed in batch or continuous operation including Westpro-modified Huaxia Technology, Supra yield and Vedernikov’s single step furfural production. However, all these commercial processes utilize mineral acids in single phase operation, which complicates the recovery of the furfural as well as the mineral acid.

In addition to dehydration of the sugar, several other side reactions take place, limiting the furfural yields as shown in Figure 1.9. For example, furfural undergoes several unwanted reactions, such as fragmentation, condensation and resinification. Several smaller molecules, such as formic acid, formaldehyde, acetaldehyde and lactic acid can be produced from furfural fragmentation. Condensation reactions can take place between furfural and pentose molecules or intermediates. In resinification reactions, furfural reacts with another furfural molecule. Products of both condensation and resinification reactions lead to the formation of solid humin products. The reaction conditions need to be optimized to maximize furfural yield, while minimizing humin production.
Figure 1.9 Dehydration of xylose to furfural and side reactions of furfural and pentose intermediates.

Furfural production has been studied using solid acid catalysts as well as biphasic systems as improvement on the current furfural production processes. Even though biomass-derived sugars are typically produced in aqueous solutions, many solid acid catalysts, such as zeolites, do not function well in liquid water, and leaching of acid functionalities at high reaction temperatures in aqueous environments is unavoidable. In addition, water has been found to accelerate side reactions, decreasing furfural selectivity. (104) Therefore, different organic compounds such as toluene, acetone, dimethyl sulfoxide (DMSO) and methyl isobutyl ketone (MIBK) have been studied as solvents for the formation of furfural over solid acid catalysts.
Another challenge with solid acid catalysts is the formation of solid coke on the catalyst and related issues of catalyst stability and regenerability.

Another approach for achieving high yields of furfural in the presence of water is to employ biphasic reactor systems. In this way, furfural is continuously removed from the aqueous acidic phase during reaction, avoiding its acid catalyzed consecutive reactions, including reactions with water. In the presence of an organic phase, homogenous mineral acids can be used to catalyze the reaction in the aqueous phase, and they can be recovered and recycled by separating the aqueous and organic phases after reaction. An important factor in choosing extractive solvents in biphasic systems is the partitioning of furfural between two phases. The partition coefficient, R, is defined as the ratio of the furfural concentration in the organic phase to its concentration in the aqueous phase. Higher values of R correspond to more efficient extraction of furfural to the organic layer, which in turn generally corresponds to higher furfural selectivities (105). The value of R can be altered by using different extractive solvents or saturating the aqueous layer with an inorganic salt, which is referred to as the salting-out effect (105). Xylose dehydration to furfural has been demonstrated with high yields (~90%) in several previous studies using mineral acids and salts in biphasic systems with organic solvents, such as MIBK, 2-butanol and tetrahydrofuran (THF) (106, 107).

1.8. References


Chapter 2: Experimental Techniques

2.1. Catalyst Preparation

2.1.1. Ceria-zirconia Mixed Oxide Catalysts

The CeZrO\textsubscript{x} mixed oxide catalysts with Ce:Zr molar ratios of 2.5, 1, 0.4 as well as pure CeO\textsubscript{x} and ZrO\textsubscript{2} were prepared via co-precipitation of Ce(NO\textsubscript{3})\textsubscript{3} and ZrO(NO\textsubscript{3})\textsubscript{2} with NH\textsubscript{4}OH (Aldrich) as described elsewhere (1). The appropriate amounts of Ce(NO\textsubscript{3})\textsubscript{3} and ZrO(NO\textsubscript{3})\textsubscript{2} to obtain the desired Ce/Zr ratio was mixed in 140 mL H\textsubscript{2}O. This mixture and NH\textsubscript{4}OH were poured in two separate separatory funnels. 400 mL H\textsubscript{2}O was added in a beaker and NH\textsubscript{4}OH was slowly added to obtain a pH of 10. Following this, aqueous Ce(NO\textsubscript{3})\textsubscript{3} and ZrO(NO\textsubscript{3})\textsubscript{2} mixture was added drop wise from the separatory funnel to the pH 10 water. During this precipitation process, pH of 10 was kept constant by adding NH\textsubscript{4}OH as necessary. After the drop wise addition was completed, the resulting slurry was stirred at room temperature for 72 h, while occasionally checking the pH and adding NH\textsubscript{4}OH if required to keep the pH at 10. After the ageing, the solids were separated by filtration, washed with ultra-pure water and ethanol three times each, dried at 383 K overnight, and calcined in air at 723 K for 2 h, with a heating rate of 3 Kmin\textsuperscript{-1}.

2.1.2. Pd/CeZrO\textsubscript{x}, Pd/SiO\textsubscript{2}, Pt/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} and Cu/SiO\textsubscript{2} Catalysts

CeZrO\textsubscript{x} mixed oxide supports were prepared as described in the previous section. SiO\textsubscript{2} (Cab-O-Sil silica gel) and SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} (Grace Davision, MS-25 FCC Catalyst Sample) supports were purchased and calcined in air at 723 K for 2 h, with a heating rate of 3 Kmin\textsuperscript{-1}. The Pd/CeZrO\textsubscript{x} catalyst was prepared via incipient wetness impregnation of CeZrO\textsubscript{x} with an amount of aqueous solution of Pd(NO\textsubscript{3})\textsubscript{2} (Aldrich) necessary to obtain nominal metal
loadings of 0.05, 0.25, 1.45 wt%. The catalyst was dried in air at 373 K overnight and calcined in air at 623 K for 2 h. A 0.5 wt% Pd/SiO₂ catalyst was prepared via the same procedure. Pt/SiO₂-Al₂O₃ catalyst was also prepared by incipient wetness impregnation of SiO₂-Al₂O₃ with an amount of aqueous solution of Pt(NH₃)₄(NO₃)₂ required to obtain a nominal metal loading of 2 wt.% . The catalyst was dried in air at 373 K overnight and calcined in air at 533 K for 2h and reduced in H₂ (180 cm³(STP) min⁻¹ for 2h at 623 K (0.5 K min⁻¹) prior to kinetic measurements. 10 wt% Cu/SiO₂ catalyst was also prepared by incipient wetness impregnation of SiO₂ with an amount of aqueous solution of Cu(NO₃)₂.3H₂O required to obtain a nominal metal loading of 10 wt.%. The catalyst was dried in air at 373 K overnight and reduced in H₂ (180 cm³(STP) min⁻¹ for 8h at 573 K (0.5 K min⁻¹) prior to kinetic measurements.

2.1.3. PtRe/C Bimetallic Catalyst

The Pt-Re/C catalyst was prepared by incipient wetness impregnation of carbon black (Norit-SX1G) with an aqueous solution of H₂PtCl₆·6H₂O and HReO₄ to yield a catalyst with loadings of 5.1 wt% Pt and 4.9 wt% Re. The support was dried in air for 12 h at 373 K prior to impregnation, and 1 g of solution was used for every gram of support. The catalyst was dried at 403 K for 12 h in air after impregnation. Prior to reaction studies, the catalyst was reduced in H₂ (180 cm³(STP) min⁻¹ for 2h at 723 K (0.5 K min⁻¹).

2.1.4. PtSn/SiO₂, PdSn/SiO₂ and RuSn/C Bimetallic Catalysts

SiO₂ supported Pt-Sn catalysts were prepared by sequential impregnation to reach 3:1 molar ratio of Pt:Sn. An aqueous solution of H₂PtCl₆·6H₂O was added to Cab-O-Sil (Cabot) by incipient wetness impregnation to achieve nominal metal loading of 5 wt%. Pt/SiO₂ catalyst was
dried in air at 373 K overnight and reduced in H₂ (180 cm³(STP) min⁻¹ for 2 h at 673 K (0.5 K min⁻¹)), followed by passivation in 2% O₂ in He at room temperature for 3 h. Tin was added to the Pt/SiO₂ catalyst by evaporative impregnation of a solution of tributyltin acetate in pentane being stirred for 2 h at room temperature. After impregnation with tin, the catalyst was dried at 373 K, calcined with flowing air at 573 K (2 h), followed by reduction in flowing hydrogen at 773 K (2 h, 0.5 K min⁻¹). PdSn/SiO₂ catalyst consisting of 5 wt% Pd and 3:1 molar ratio of Pd:Sn was prepared in the same manner. For RuSn/C, the 5 wt% Ru/C was used as received from the vendor (Sigma-Aldrich). The RuSn/C catalyst was prepared by incipient wetness impregnation of the 5 wt% Ru/C catalyst with a solution of SnCl₂·2H₂O, which resulted in a final molar ratio Ru:Sn of 1:3. The catalyst was dried at 353 K for 2 h and reduced for 3 h at 723 K (1 K min⁻¹).

2.1.5. Sulfonated Carbon

Sulfonated carbon was prepared as previously described by Takagaki et al. (2) 20 g of D-glucose (>99.5%, Sigma) was pyrolyzed for 15 h at 673 K under Argon flow. The solid obtained was ground and stirred in 200 mL of fuming sulfuric acid (20% free SO₃, Aldrich) at 423 K for another 15 h. Finally, the mixture was diluted in 1 L of water, filtered, washed with distilled water until no more sulfuric acid was detected in the effluent water and dried in air at 373 K.

2.1.6. Propylsulfonic Acid Functionalized SBA-15

SBA-15 was synthesized as described elsewhere (3). 120.00 g of a 2 mol L⁻¹ aqueous HCl (36.5-38%, Aldrich) solution was added to a solution of 4.00 g of Pluronic P123 (Aldrich) in 30.00 g of distilled water at 308 K. 8.50 g of tetraethyl orthosilicate (TEOS, 98%, Aldrich) was added and the mixture was stirred for 24 h at 308 K and then aged at 373 K for 24 h. The white solid was filtered and washed with 3 L of water. In order to remove the organic template,
SBA-15 was calcined at 823 K in air for 5 h. SBA-15 was functionalized with propyl sulfonic acid groups in a two-step reaction. First 50 mL of dry toluene (99.8%, Aldrich) and 3 g of (3-mercaptopropyl)trimethoxysilane (95%, Aldrich) were added to 1 g of calcined SBA-15 previously dried at 373 K under vacuum. The mixture was refluxed for 15 h under stirring, filtered and washed with hexane (95%, Aldrich) and methanol (99.9%, Aldrich). Finally, the oxidation of the thiol groups was carried out by stirring the material for 24 h with 100 mL of 35% aqueous hydrogen peroxide (Aldrich).

2.1.7. Sn-SBA-15

Sn-SBA-15 was synthesized with a Si/Sn molar ratio of 40, as described by Shah et al. (4) 70 g of a 0.007 mol L⁻¹ aqueous HCl (36.5-38%, Aldrich) solution was added to a solution of 4.00 g of Pluronic P123 (Aldrich) in 30.00 g of distillated water at 313 K. Then, 9.00 g of TEOS (98%, Aldrich) and 0.379 g of tin chloride pentahydrate (SnCl₄·5H₂O, 98%, Aldrich) was added and the mixture was stirred for 24 h at 313 K and aged at 373 K for another 24 h. The white solid was filtered and washed with 3 L of water. In order to remove the organic template, Sn-SBA-15 was calcined at 823 K in air for 5 h.

2.2. Catalyst Characterization

2.2.1. Chemisorption and Physisorption Studies

Adsorption isotherms for CO and BET isotherms (N₂) were collected using a standard volumetric gas handling system employing Baratron capacitance manometers for precision pressure measurement (± 0.5x10⁻⁵ kPa) [4]. For CO chemisorption studies, the supported metal catalysts were reduced under the conditions given section 2.1, and after the reduction, H₂ was
desorbed introducing vacuum \((1 \times 10^{-7} \text{ mbar})\) at pre-treatment temperature for 1 hour, and subsequently cooled to room temperature \((300 \text{ K})\). Following that, small amounts of CO \((1-10 \mu\text{mol})\) were dosed onto the catalyst consecutively until saturation was achieved. The amount of gas adsorbed was determined volumetrically from the dose and equilibrium pressures and system volumes and temperatures. 20-30 minutes were allowed for each dose to reach equilibrium. After saturation, the catalyst was evacuated at 300 K for 1 h to remove weakly bound CO molecules and the reversible isotherm was collected. Irreversible CO uptake was calculated by subtracting the reversible uptake from the total uptake measured in the first isotherm. BET isotherms were recorded at liquid nitrogen temperature \((195 \text{ K})\) through pysisorption of \(\text{N}_2\). The maximum apparent leak rate \((10^{-4} \text{ kPa min}^{-1})\) is negligible compared to the adsorption uptakes of the catalysts.

2.2.2. Temperature Programmed Studies

Temperature–programmed studies were carried out using an apparatus consisting of a mass flow controller (Teledyne-Hastings) and a tube furnace connected to a variable power-supply and PID temperature controller (Love Controls) with a K-type thermocouple (Omega) as shown in Figure 2.1. The effluent was monitored by a mass spectrometer system consisting of a quadruple residual gas analyzer (Stanford Instruments RGA 200) inside a vacuum chamber. Vacuum was provided by a diffusion pump with liquid nitrogen trap connected in series to a rotary pump. The effluent was introduced into the vacuum chamber via a constricted quartz capillary, resulting in a pressure of \(5 \times 10^{-5} \text{ Torr}\) inside the chamber. Dried, unreduced catalyst samples were loaded into a 12.6 mm \((0.5 \text{ inch})\) outer diameter, fritted quartz tube reactor.
Temperature programmed reduction (TPR) measurements were carried out to determine the reduction profiles of CeZrOₓ and Pd/ CeZrOₓ catalysts. TPR measurements were performed by heating 0.2-0.3 g of calcined catalyst at 10 K min⁻¹ under a 5 mol % H₂ in N₂ mixture (50 cm³(STP) min⁻¹) to 973 K, and measuring hydrogen consumption with the MS system described above. H₂ was tracked by the ion with m/z ratio of 2.

Figure 2.1 Schematic representation of the apparatus used for temperature programmed studies.
Temperature programmed desorption (TPD) measurements of CO$_2$ and NH$_3$ were performed to quantify the total surface base and acid sites, respectively. Prior to desorption experiments, 0.3 to 1 g of catalyst was reduced in flowing hydrogen (100 cm$^3$(STP) min$^{-1}$) for 2 h at 623K. The catalyst was degassed for 1 h in flowing helium (200 cm$^3$(STP) min$^{-1}$) at the reduction temperature, and then cooled to 300 K for CO$_2$ adsorption and 423 K for NH$_3$ adsorption, respectively. Carbon dioxide was adsorbed onto the reduced catalysts by exposure to flowing 10 mol % CO$_2$ in helium (100 cm$^3$(STP) min$^{-1}$) for 30 min. Residual CO$_2$ was removed by purging the catalyst with helium (200 cm$^3$(STP) min$^{-1}$) at 300 K for 2 h. Ammonia adsorption was performed in a similar manner as CO$_2$ adsorption, except that both adsorption and purging steps were performed at 423 K, and a 1 mol % NH$_3$ in He gas mixture was used. Desorption of CO$_2$ or NH$_3$ was performed by heating the catalyst at a rate of 10 K min$^{-1}$ under flowing helium (50 cm$^3$(STP) min$^{-1}$) from room temperature to 1073 K for NH$_3$ or 1123 K for CO$_2$. Ions with m/z ratios of 44 and 16 were tracked for CO$_2$ and NH$_3$, respectively.

Temperature programmed surface reactions (TPSR) experiments were performed to investigate the interaction between CO$_2$ and CeZrO$_x$ and Pd/CeZrO$_x$ catalysts especially when the catalysts were regenerated under H$_2$ flow. TPSR experiments followed the same procedure as those involving TPD of CO$_2$, except that the desorption of CO$_2$ was performed in flowing hydrogen (50 cm$^3$(STP) min$^{-1}$).

2.2.3. X-Ray Diffraction

X-Ray diffraction (XRD) was used to investigate the phase structure of the Pd/Ce$_a$Zr$_b$O$_x$ catalysts. A Scintag PAD V X-ray diffractometer with a monochromated CuK$_\alpha$ X-ray tube was used in the diffraction studies. The tube voltage and current were 45 kV and 40 mA,
respectively. Diffraction patterns were collected in the $20^\circ$ to $65^\circ$ $2\theta$ range, with 0.01$^\circ$ intervals and a dwell time of 2 s. The diffractometer with the $0:2\theta$ goniometer, the X-ray tube is stationary, the sample moves by the angle $\theta$ and the detector simultaneously moves by the angle $2\theta$ as shown in Figure 2.2. For powder diffraction, samples were prepared by first grinding to very fine particles and then smeared and pressed on a sample slide.

![Figure 2.2 Schematic representation of the X-ray diffractometer with the $0:2\theta$ goniometer.](image)

**2.2.4. Fourier Transform Infrared (FTIR) Spectroscopy**

FTIR analysis was carried out using a Thermo Nicolet 6700 spectrophotometer equipped with a pyroelectric detector (DTGS type) (see Figure 2.3) using a resolution of 4 cm$^{-1}$ for the identification of Lewis and Brønsted acid sites by adsorption of pyridine. Self-supported pellets
of calcined H-mordenite and γ-alumina were placed in an IR cell equipped with CaF$_2$ windows and dried under air flow at 573 K for 2 h. The pellets were then contacted with helium saturated with pyridine at room temperature for 30 min. Finally, the cell was flushed with helium at 373 K for 1 h to remove hydrogen-bonded pyridine.

Figure 2.3 A) Set-up and B) Schematic of the spectrophotometer equipped with a pyroelectric detector (DTGS type) (5).
2.3. Reaction Studies

2.3.1. Flow Reaction Studies

A fixed bed, down-flow reactor (see Figure 2.4) consisting of a half-inch or quarter-inch stainless steel tube was used for aldol condensation, reforming, ketonization, hydrogenation and dehydration/hydrogenation experiments. Quartz wool was used in the lower end of the reactor to keep the catalyst bed in place. The catalyst was mixed with crushed fused SiO$_2$ granules (Aldrich) in a 2:1 volumetric ratio to maintain bed height. The reactor was heated with an aluminum block that was heated externally by a well-insulated furnace (Applied Test Systems). Type-K thermocouples (Omega) were used to measure the reaction temperature, which was controlled by a PID controller (Love controls) connected to a variable transformer (Tesco). Mass flow controllers (Brooks 5850E) were used to regulate the flow of H$_2$, He and other gases during the experiments. The liquid feed was pumped from a graduated cylinder by an HPLC pump (Lab Alliance series 1) to a needle located at the entrance of the catalyst bed. A back-pressure regulator (GO model BP-60) was used to control the total pressure, which was measured by two gauges at the entrance and the exit of the bed. A gas-liquid separator at room temperature was used to collect the liquid phase for analysis. Before starting the catalyst pretreatment, the reaction system (including the separator) was pressurized with He to the reaction pressure to check for leaks and depressurized back to atmospheric pressure after the leak check was completed. The gas effluent could be directed to measure the flow rate (by a bubble flow meter), to the venting system, to a gas chromatograph (GC) equipped with a flame ionization detector (FID) or to a GC equipped with a thermal conductivity detector (TCD) by the use of a 5-way valve.
Figure 2.4 Schematic representation of the flow reaction system.

2.3.2. Batch and Semi-batch Reaction Studies

Experiments for dehydration of xylose with 2-sec-butylphenol (Chapter 7) and γ-valerolactone (Chapter 8) and hydrolysis/alcoholysis of furfuryl alcohol (Chapter 7) in monophasic and biphasic systems were carried out in 10 mL thick-walled glass reactors rated for ~8 bar (Alltech) using a triangular magnetic stir bar as shown in Figure 2.5. Reactors were tightly sealed with PTFE-Silicon septa placed in the caps and placed in an oil bath at the desired
temperature. Xylose dehydration reactions were carried out at 443-448 K and furfuryl alcohol conversion reactions were carried out at 398 K. The oil bath contained silicone oil and was heated with an Isotemp digital hotplate (Fisher Scientific), which was also used for stirring at 1100 rpm (see Figure 2.5). Reactors were removed at the desired times and cooled by air and in ice-water bath. For biphasic reactions, after the reactors were cooled down, they were centrifuged for 4 min at 4000 rpm for complete separation of the phases.

Figure 2.5 10 mL glass reactors and the reactor set-up with the silicone oil bath kept at constant temperature by a hot plate with magnetic stirring.

In addition to glass reactors, 50-450 mL batch reactors were used for hemicellulose deconstruction (Chapters 7-8) and furfuryl alcohol hydrolysis/alcoholysis (Chapter 7). The batch reactors were purchased from Parr Instruments. The reactors ranged in size from 50 mL capacity to 450 mL and in materials of construction (e.g. stainless steel, Hastelloy). A graphical schematic of the typical pressure vessel used is shown in Figure 2.6. For experiments carried out
in 50 mL Parr reactors, the feed solution and the desired amount of catalyst were added into the reactor at room temperature and atmospheric pressure. The vessel was then sealed, and the air was flushed out by pressurizing with He to 300 psig and depressurizing for three times. Later on, the reactor was pressurized if desired with the gas of choice and heated to reaction temperature with an external heating mantle connected to a temperature controller while stirring with a magnetic stir bar (the reactor was placed on a stirring plate). After the reaction was completed, the reactor was cooled with air flow and depressurized before opening the vessel. 450 mL reactors were set up in a similar manner; however, an internal impellor was used for stirring and the reactor was cooled with cooling water (internal cooling line).

Figure 2.6 Schematic representation of the Parr reactors used for batch reaction studies.(6)

A semi-batch reactor set-up with a 50 mL Parr reactor and an HPLC pump connected to an input line into the reactor head was used for furfuryl alcohol hydrolysis experiments in monophasic and biphasic (with use of 2-sec-butylphenol as the organic solvent) systems
(Chapter 7). For a monophasic reaction system, the reactor was first loaded with solvent and catalyst as described above and heated to reaction temperature. Following that, the feed solutions were slowly pumped into the reactor using an HPLC pump (Lab Alliance series 1) to reach the weight hourly space velocity (WHSV) and feed concentration desired. For biphasic reactions, the reactor was loaded with aqueous solution with the catalyst and heated to the reaction temperature. When the reaction temperature was reached, feed solutions in the organic solvents were pumped into the reactor using an HPLC pump (Lab Alliance series 1) to reach the weight hourly space velocity (WHSV) and volume ratio of organic to aqueous layer desired.

2.3.3. Analytical Techniques and Data Analysis

2.3.3.1. Gas Chromatography (GC)

As described earlier, the gas effluent form the flow reactor system was connected online to two gas chromatographs, one being HP GC5890 gas chromatograph, equipped with a Haysep DB 100/120 column (Alltech) with a thermal conductivity detector (TCD) to quantify CO and CO\textsubscript{2} and the other being Agilent GC6890, equipped with an Rtx column (Agilent) and a flame ionization detector (FID), to quantify gas-phase light alkanes, alkenes and other organics. The organic liquid samples collected from the separator of the flow reactor or batch reactors were analyzed with a Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID detector. Unknown species in the organic samples were identified with a Shimadzu 2060 GC/MS with a NIST library of spectra.
2.3.3.2. High-Performance Liquid Chromatography (HPLC)

Aqueous samples collected from the separator of the flow reactor or batch reactors were analyzed using liquid chromatography. A Waters e2695 HPLC system equipped with a 2998 PDA UV detector and a 2414 refractive index detector was used for quantification of reactants and products. The system was equipped with an Aminex HPX-87H column (Bio-Rad) at 353 K, using 0.005 M H$_2$SO$_4$ solution as the mobile phase at a flow rate of 0.6 mL min$^{-1}$ or with an Aminex HPX-87P (Bio-Rad) column at a temperature of 358 K using Mili-Q (pH 7) water as the mobile phase at a flow rate of 0.6 mL min$^{-1}$. Non-UV active species (e.g. sugars) were quantified using the refractive index detector (Waters 410). UV active species were quantified using the UV detector (Waters PDA 990) at appropriate absorbance wavelengths.

2.3.3.3. Data Analysis

The conversions of various reactants were defined by equation 1, where $R_{in}$ and $R_{out}$ represents the molar flow rate of the reactant in and out of the flow reaction system, respectively or molar amounts in batch reaction systems. Selectivities to reaction products were calculated on a molar carbon basis as shown in equation 2, where $R_{j,\text{out}}$ represents the molar flow rate of product $j$ and $N_j$ is the number of moles of carbon in one mole of product $j$ in a flow reactor, while molar amounts were used for batch systems. Yields of reaction products were calculated as shown in equation 3.
Conversion (%) = \left(\frac{R_{in} - R_{out}}{R_{in}}\right) \times 100 \quad (1)

Selectivity_j (%) = \left(\frac{R_{j\_out}N_j}{\sum_j (R_{j\_out}N_j)}\right) \times 100 \quad (2)

Yield_j (%) = \left(\frac{R_{j\_out}N_j}{R_{in}N_{in}}\right) \times 100 \quad (3)

Weight hourly space velocities (WHSV) were calculated by dividing the total mass flow-rate of a feed (on a diluent-free bases) by the mass of catalyst inside the reactor.

2.4. References

Chapter 3: Vapor-Phase C-C Coupling Reactions of Biomass-Derived Oxygenates over Pd/CeZrO$_x$ Catalysts

As described in Chapter 1, petroleum currently supplies more than 95% of the energy requirements for the U.S. transportation sector (1). This non-renewable fossil fuel resource is in diminishing supply, and its combustion contributes to the accumulation of CO$_2$ in the atmosphere, leading to global climate change. However, petroleum-derived fuels possess optimal physical properties with respect to energy density, volatility and hydrophobicity that allow for efficient storage, distribution and combustion. Biomass-derived fuels have attracted considerable attention as alternatives to petroleum, because they are derived from abundant, renewable resources, and because combustion of these fuels is CO$_2$ neutral. However, obtaining biomass-derived fuels with the appropriate physical and combustion properties to integrate into the current transportation infrastructure has presented numerous challenges. For example, utilization of the most successful biomass derived fuel, ethanol, necessitates modifications to the internal combustion engine of the vehicle and the use of bio-diesel requires special precautions in cold climates (2, 3).

Previously in our group, a catalytic process that can be tuned to convert biomass derived carbohydrates to a variety of fuel-grade products, such as light alkanes (C$_1$-C$_4$), benzene, substituted aromatics, branched alkanes (C$_6$-C$_{12}$), and linear or singly-branched alkanes (C$_7$-C$_{12}$) was developed. As described in Chapter 1, this process consists of an initial de-oxygenation step that converts concentrated aqueous solutions of sugars and polyols (40-60%) over a carbon-supported Pt-Re catalyst into hydrophobic mixtures of mono-functional C$_4$-C$_6$ alcohols, ketones, carboxylic acids and heterocyclic compounds(4). The carbon chain length of these
monofunctional species is limited to six by the chain length of the parent carbohydrate, i.e., glucose and sorbitol. To produce higher molecular weight species required for gasoline, diesel and jet fuel applications, the mixture of monofunctional species is subsequently subjected to catalytic C-C coupling processes. These coupling processes include (i) ketonization, in which two carboxylic acid molecules react to form a linear ketone, CO$_2$ and water(5), and (ii) aldol condensation/hydrogenation, in which two ketone or alcohol molecules react to form a heavier branched ketone(6). The combination of ketonization and aldol condensation/hydrogenation yields C$_7$-C$_{12}$ linear and branched ketones, that can be converted into fuel grade alkanes via dehydration/hydrogenation over solid acid supported noble metal catalysts, such as Pt/NbOPO$_4$ (7).

Ketonization of carboxylic acids has been investigated in the literature using a variety of basic, acidic and amphoteric oxide catalysts, and occurs at temperatures near or higher than 623 K (6, 8, 9). It was demonstrated that the carboxylic acids found in the aforementioned carbohydrate-derived mixture of monofunctional species can be ketonized with nearly 100% yield over a CeZrO$_x$ mixed oxide catalyst at temperatures from 623 to 673 K(4). The combined aldol condensation/hydrogenation of alcohols and ketones has been studied in the literature on metals (Cu and Pd) supported on mixed oxides such MgAlO$_x$ (5, 10) and anion-exchange resins(11) in the temperature range from 423 to 473 K in the presence of hydrogen. This reaction consists of metal-catalyzed dehydrogenation of alcohol groups, followed by base-catalyzed aldol condensation, acid-catalyzed dehydration and subsequent metal-catalyzed hydrogenation of the $\alpha$-$\beta$ unsaturated aldol adduct. Hydrogenation of the C=C bond in the dehydrated aldol adduct improves the overall thermodynamics for the process, allowing a greater
extent of C-C coupling than aldol condensation/dehydration alone (5, 10, 12). For example, under the reaction conditions in this project, conversion of acetone to mesityl oxide (α-β unsaturated aldol adduct) is limited by 16%, whereas overall conversion to methyl isobutyl ketone (MIBK, the hydrogenated ketone) has an equilibrium limit of 92%. Several investigators report that the presence of intermediate strength acidic and basic sites in close proximity results in optimal catalytic performance(10, 13-15), and the presence of strong acid or basic sites leads to undesirable side reactions that may also lead to coking (16).

Most studies of aldol condensation/hydrogenation have focused on self-condensation of acetone or isopropanol to form MIBK(5, 12, 17-21), and few reports have been published regarding self-condensation of higher ketones(22) (such as the ones produced from the conversion of carbohydrates on Pt-Re/C). In contrast to acetone, C₄+ methyl ketones posses a single set of reactive α-hydrogen atoms, resulting in a substantial decline in reactivity when compared to acetone. As a result, higher reaction temperatures are required to achieve appreciable conversion, and appropriate catalysts must be used that are resistant to coking and sintering at these conditions. In this respect, it has been reported that the self-condensation/hydrogenation of 2-hexanone on a CuMg₁₀Al₇Oₓ catalyst at 573 K and have shown that even small amounts of carboxylic acids are detrimental to the self-condensation reaction (23). For this reason, the ketonization reaction provides an efficient means of removing carboxylic acids from the feed prior to aldol condensation/hydrogenation, and it has been demonstrated that a catalyst consisting of Pd-supported on CeZrOₓ is effective at 623 K for the condensation of ketones present in the ketonized mixture of monofunctional species derived from glucose(4). The CeZrOₓ support was selected because it possesses high lattice oxygen
mobility and the ability to interact strongly with supported metals – properties that have been associated with resistance to the formation of carbonaceous species that lead to deactivation(24, 25). Additionally, CeZrO\textsubscript{x} contains a combination of acidic and basic functionalities for aldol condensation(26). Thus, we suggest that ketonization and aldol condensation/hydrogenation can be carried out at comparable operating conditions, and can potentially be integrated into a single reactor system, containing a catalytic bed consisting of CeZrO\textsubscript{x} to perform ketonization, followed by a downstream bed of Pd/CeZrO\textsubscript{x} to perform aldol condensation/hydrogenation.

In this chapter, we explore the possibility of the aforementioned integration between ketonization and aldol condensation/hydrogenation by elucidating the reaction pathways for aldol condensation of a representative ketone (2-hexanone) on Pd/CeZrO\textsubscript{x} by varying reaction conditions, such as temperature, pressure and space velocity. We show that in addition to the expected C\textsubscript{12} condensation product (7-methyl-5-undecaone), the catalyst produces C\textsubscript{18} and C\textsubscript{9} secondary species. We investigate the effect of metal loading and proximity of metal and support on catalytic activity, and we find that low metal loadings lead to optimal activity and selectivity. Additionally, we investigate the effect of other monofunctional oxygenates present in the carbohydrate-derived hydrophobic mixture, such as primary and secondary alcohols, carboxylic acids, heterocyclics, and 3-ketones on the self-condensation of 2-hexanone. Furthermore, we study the effects of the ketonization by-products, CO\textsubscript{2} and water, on the downstream condensation reaction, and we probe the interaction of CeZrO\textsubscript{x} with CO\textsubscript{2} using temperature programmed desorption (TPD), temperature programmed reduction (TPR), and temperature programmed surface reaction (TPSR) of CO\textsubscript{2}. We observe that the addition of oxygenates as well as water and CO\textsubscript{2} all lead to reversible inhibition of the self-condensation activity, and this inhibition is strongest when CO\textsubscript{2} is present in the feed. Through these observations we conclude
that it is beneficial to remove water and CO$_2$ prior to the aldol/condensation hydrogenation step over Pd/CeZrO$_x$.

3.1. Experimental

3.1.1. Catalyst Preparation

The CeZrO$_x$ support with a 1:1 Ce:Zr molar ratio was prepared via co-precipitation of Ce(NO$_3$)$_3$ and ZrO(NO$_3$)$_2$ with NH$_4$OH (Aldrich) according to Serrano-Ruiz, et al. (27) as described in Chapter 2. The Pd/CeZrO$_x$ catalyst was prepared via incipient wetness impregnation of CeZrO$_x$ with an amount of aqueous solution of Pd(NO$_3$)$_2$ (Aldrich) necessary to obtain nominal metal loadings of 0.05, 0.25, 1.45 wt%. The catalyst was dried in air at 373 K overnight and calcined in air at 623 K for 2 h. A 0.5 wt% Pd/SiO$_2$ catalyst was prepared via the same procedure, using a Cab-O-Sil silica gel support.

3.1.2. Reaction Kinetics Studies

2-hexanone, 1-butanol, tetrahydrofuran, heptane, 3-pentanone and butanoic acid were purchased from Sigma-Aldrich and used without further purification. Hydrogen (99%), helium (99.9%) and 10 mol % CO$_2$ in helium were purchased from Airgas and used without further purification. The conversions of oxygenated species over Pd/CeZrO$_x$ were carried out at temperatures between 573 and 673 K, pressures of 5 to 26 bar, and liquid flow rates between 0.02 and 0.08 mL/min. The molar ratio of the gas flow rate to the liquid flow rate was maintained at 5.5, with the exception of reaction order studies. A fixed bed, down-flow reactor consisting of a half-inch stainless steel tube was used for all experiments as described in Chapter 2. The catalyst was reduced in-situ at 623 K (ramp rate of 0.5 K min$^{-1}$) for 2 h in flowing H$_2$ (200 cm$^3$(STP) min$^{-1}$). After the reduction was completed, the temperature and pressure were adjusted and the feed flow was started with flowing H$_2$ or H$_2$-He or H$_2$-CO$_2$ mixtures. The weight hourly
space velocity (WHSV) was calculated for experiments using the mass flow rate of the liquid flow into the reactor and the mass of the catalyst used (2 g, except for reaction order studies).

The rate of gas production was measured with a bubble flow meter. An HP GC5890 gas chromatograph, equipped with a Haysep DB 100/120 column (Alltech) and thermal conductivity detector (TCD), was used to quantify CO and CO₂, and an Agilent GC6890, equipped with an Rtx column (Agilent) and a flame ionization detector (FID), was used to quantify gas-phase alkanes. Liquid phase analysis was performed with a Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID detector. Unknown species were identified with a Shimadzu 2060 GC/MS with a NIST library of spectra. Some species could not be identified definitively using the library, and their identification was based on the atomic mass of the molecular ion fragment and analogous species reported for acetone condensation. Liquid and gas analysis points were collected every 2-3 h, and steady state was usually achieved after 6 h time-on-stream. At our reaction conditions on Pd-containing catalysts, 2-hexanol was always in equilibrium with 2-hexanone. Therefore, the conversion of 2-hexanone to 2-hexanol was not factored into the total conversion calculation, as given by equation 4. The selectivities to reaction products were calculated on a molar carbon basis, as given by equation 2 (Chapter 2). In equations 2 and 4, R represents the molar flow rate, f represents reactant conversion, S represents the carbon selectivity, and N is the carbon number of a given species. All carbon balances closed to within 10%.

\[
f_{2\text{-hexanone}} = \left(1 - \frac{R_{2\text{-hexanone\_out}}}{R_{2\text{-hexanone\_in}}} + \frac{R_{2\text{-hexanol\_out}}}{R_{2\text{-hexanone\_in}}}\right) \times 100\%
\]  (4)
3.1.3. Catalyst Characterization

3.1.3.1. CO Chemisorption and BET Measurements

The adsorption uptakes of carbon monoxide at 300 K were measured on a standard gas adsorption apparatus described elsewhere (28) and Chapter 2. The number of surface metal sites was taken to be the irreversible CO uptake. The BET surface area was measured by nitrogen adsorption at liquid nitrogen temperature on the same apparatus.

3.1.3.2. X-Ray Diffraction

X-Ray diffraction (XRD) was used to investigate the phase structure of the Pd/CeZrOₓ catalyst. A Scintag PAD V X-ray diffractometer with a monochromated CuKα X-ray tube was used in the diffraction studies. The tube voltage and current were 45 kV and 40 mA, respectively. Diffraction patterns were collected in the 20° to 65° 2θ range, with 0.01° intervals and a dwell time of 2 s.

3.1.3.3. Temperature Programmed Desorption of NH₃ and CO₂

Carbon dioxide and ammonia temperature–programmed desorption (TPD) experiments were carried out using an apparatus as described in Chapter 2. Dried, unreduced catalyst samples were loaded into a 12.6 mm (0.5 inch) outer diameter, fritted quartz tube reactor. Prior to desorption experiments, 0.3 to 1 g of catalyst was reduced in flowing hydrogen (100 cm³(STP) min⁻¹) for 2 h at 623K. The catalyst was degassed for 1 h in flowing helium (200 cm³(STP) min⁻¹) at the reduction temperature, and then cooled to 300 K for CO₂ adsorption and 423 K for NH₃ adsorption, respectively. Carbon dioxide was adsorbed onto the reduced catalysts by exposure to flowing 10 mol % CO₂ in helium (100 cm³(STP) min⁻¹) for 30 min. Residual CO₂ was removed by purging the catalyst with helium (200 cm³(STP) min⁻¹) at 300 K for 2 h. Ammonia adsorption
was performed in a similar manner as CO$_2$ adsorption, except that both adsorption and purging steps were performed at 423 K, and a 1 mol % NH$_3$ in He gas mixture was used. Desorption of CO$_2$ or NH$_3$ was performed by heating the catalyst at a rate of 10 K min$^{-1}$ under flowing helium (50 cm$^3$(STP) min$^{-1}$) from room temperature to 1073 K for NH$_3$ or 1123 K for CO$_2$.

3.1.3.4. Temperature Programmed Reduction and Surface Reaction Measurements

Temperature programmed surface reaction (TPSR) experiments followed the same procedure as those involving TPD of CO$_2$, except that the desorption of CO$_2$ was performed in flowing hydrogen (50 cm$^3$(STP) min$^{-1}$). Temperature programmed reduction (TPR) measurements were performed by heating 0.2-0.3 g of calcined catalyst at 10 K min$^{-1}$ under a 5 mol % H$_2$ in N$_2$ mixture (50 cm$^3$(STP) min$^{-1}$) to 973 K, and measuring hydrogen consumption with the MS system described above.

3.2. Surface and Bulk Characterization

The desorption profiles of NH$_3$ and CO$_2$ from CeZrO$_x$ and several Pd/CeZrO$_x$ catalysts of various loadings are shown in Figure 3.1. These profiles were integrated to obtain the quantities of acidic and basic surface sites, which are reported in Table 3.1. The values of the irreversible CO uptake and BET areas are also listed in Table 3.1. The NH$_3$ desorption profiles of all catalysts show a single, uniform desorption peak, centered at 570-600 K, suggesting a narrow distribution of acidic sites on the surface. These results are consistent with those obtained by Zhu, et al. for NH$_3$ TPD from Pt/CeZrO$_x$ (29). The 1.45 wt% Pd catalyst contains nearly 50% more NH$_3$ adsorption sites than CeZrO$_x$ and the lower loading catalysts. Pokrovski and Bell showed that the presence of a hydrogen-dissociating metal on CeZrO$_x$ causes the reduction of Ce$^{4+}$ into Ce$^{3+}$ via hydrogen spillover, and the presence of Ce$^{3+}$ is shown to increase the acidity of the CeZrO$_x$ surface (30). In this respect, the 1.45 wt% Pd/CeZrO$_x$ catalyst may contain
sufficient concentrations of Ce$^{3+}$ to influence the acidic site properties, as measured by NH$_3$ TPD.

Figure 3.1 NH$_3$ desorption profiles (A) and CO$_2$ desorption profiles (B) from CeZrO$_x$ and Pd/CeZrO$_x$ catalysts.

Table 3.1 Quantification of metal (CO), basic (CO$_2$) and acidic sites (NH$_3$), and BET surface areas of selected catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO (irreversible) ($\mu$mol/g)</th>
<th>CO$_2$ (TPD) ($\mu$mol/g)</th>
<th>NH$_3$ (TPD) ($\mu$mol/g)</th>
<th>BET area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeZrO$_x$</td>
<td>0</td>
<td>370</td>
<td>56</td>
<td>130</td>
</tr>
<tr>
<td>0.05 % Pd/CeZrO$_x$</td>
<td>8</td>
<td>390</td>
<td>50</td>
<td>135</td>
</tr>
<tr>
<td>0.25 % Pd/CeZrO$_x$</td>
<td>18</td>
<td>380</td>
<td>54</td>
<td>133</td>
</tr>
<tr>
<td>1.45 % Pd/CeZrO$_x$</td>
<td>76</td>
<td>395</td>
<td>77</td>
<td>139</td>
</tr>
<tr>
<td>0.5% Pd/SiO$_2$</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The CO₂ desorption profiles show the presence of basic sites of varying CO₂ adsorption strength. These profiles can be divided into three distinct regions representing weak adsorption sites (300-500 K), medium strength adsorption sites (500-700 K), and strong adsorption sites (700-1000 K). Di Cosimo, et al. have correlated TPD and FTIR studies of CO₂ adsorbed on MgAlOₓ and have associated the CO₂ desorption temperature with different types of CO₂ binding sites. The weakly binding sites are associated with surface OH⁻ groups and the formation of bicarbonate, while the medium-strength sites are associated with M²⁺-O²⁻ pairs and the formation of bridged and bidentate carbonates. The strongly binding sites are associated with low coordination O²⁻ ions and the formation of more strongly bound unidentate carbonates (14). Several of the aforementioned species have been observed on ZrO₂ (31), and it is probable that the correlation found by Di Cosimo, et al. for MgAlOₓ may be extended to other oxides such as CeZrOₓ.

Di Cosimo, et al. and Bianchi, et al. observed weak CO₂ adsorption sites on CeO₂ and weak and medium strength sites on ZrO₂, respectively (21, 32). The presence of strong CO₂ binding sites on CeZrOₓ surface likely results from the surface heterogeneity introduced by substituting Ce ions with Zr⁴⁺ ions. The addition of Zr to Ce is known to increase the mobility of O²⁻ ions in the lattice (27, 33), and is therefore likely to cause higher concentrations of low coordination O²⁻ (associated with surface defects) that strongly bind CO₂. The number and strength of CO₂ binding sites are not influenced significantly by metal loading. This observation contradicts that of Nikolopoulous, et al. who observed that the surface basicity decreases with increasing Pd loading on MgAlOₓ. Nikolopoulous, et al. suggest that residual chlorine from the metal precursor (PdCl₂) is responsible for this effect (5). This detrimental effect on basicity was
not observed in the present investigation, probably due to the use of a nitrate precursor (Pd(NO$_3$)$_2$) that decomposed to PdO upon calcination.

The BET surface area is not affected by metal loading in the loading range studied here, suggesting that there is no modification to the pore structure upon metal deposition. The BET surface area (130-140 m$^2$/g) is consistent with measurements obtained by other investigators on CeZrO$_x$ prepared by the co-precipitation method (27).

Measurements of irreversible CO adsorption show that the CO uptake increases with metal loading. When a reducible oxide support is present (such as CeO$_2$), reduced sites on the support can contribute to the CO uptake, which normally occurs only on metal sites(34). This phenomenon is particularly evident in the case of 0.05 wt% Pd/CeZrO$_x$, where the amount of chemisorbed CO appears to exceed the number Pd atoms in the catalyst. TPR studies in the present work and by others show that hydrogen spillover is responsible for the reduction of surface Ce$^{4+}$ into Ce$^{3+}$, and this reduction takes place at the interface of the metal and the support (27). For smaller particles, the ratio of these interfacial sites to metal sites is higher than for large particles, leading to a greater normalized CO uptake (apparent dispersion). In this respect, we conclude that the Pd particle size decreases with lower Pd loadings.

The XRD pattern of calcined 0.25 wt% Pd/CeZrO$_x$ (the predominate catalyst studied in this work) shows broad reflections at 2θ=29.2°, 33.8°, 48.6° and 57.5°. This pattern (Figure 3.2) is consistent mainly with the CeO$_2$ fluorite-cubic structure, as observed by other investigators (27, 33, 35).
All peaks in the pattern displayed a small shift to higher values of 2θ, as compared to fluorite cubic CeO$_2$ (JCPDS # 43-1002), and this shift is associated with lattice contraction caused by the introduction of smaller Zr$^{4+}$ ions in the CeO$_2$ lattice. No reflections corresponding to palladium or palladium oxide phases were detected, indicating the presence of small (< 4nm) particles.

The TPR profiles of calcined 0.25 wt% Pd/CeZrO$_x$ and CeZrO$_x$ are shown in Figure 3.3. The profile of 0.25 wt% Pd/CeZrO$_x$ contains two reduction peaks: a sharp peak at 480 K and a broad peak centered at 720 K.
Figure 3.3 TPR profiles of CeZrO\textsubscript{x} and 0.25 wt\% Pd/CeZrO\textsubscript{x}.

The reduction profile of CeZrO\textsubscript{x} only displays a broad peak at 860 K. The 860 K reduction peak in the TPR of CeZrO\textsubscript{x} has been assigned to the reduction of surface Ce\textsuperscript{4+}(35). The low temperature reduction peak in the TPR of Pd/CeZrO\textsubscript{x} has been assigned to the reduction of the metal, and of ceria species in intimate contact with the metal(27). This interpretation is supported by hydrogen consumption measurements, which show that ten times the amount of hydrogen is consumed for the 480 K reduction peak, than is required to reduce all of the Pd\textsuperscript{2+} in the calcined catalyst to metallic Pd. The broad peak at 720 K observed for 0.25 wt\% Pd/CeZrO\textsubscript{x} has been assigned to the reduction of surface ceria species that are not in contact with the metal(27), and this reduction is shifted to lower temperature (as compared to 860 K on the support alone) due to spillover of hydrogen from the metal. In summary, characterization results show that the Pd/CeZrO\textsubscript{x} catalysts used in this work consist of a reducible mixed oxide of Ce and
Zr, containing both acidic and basic surface sites, and that the addition of Pd to CeZrO₃ promotes the reduction of ceria surface species in contact with Pd particles.

3.3. Reaction Network

The conversion of 2-hexanone over 0.25 wt% Pd/CeZrO₃ was studied to probe the pathways for aldol condensation and related reactions catalyzed by metal, acidic and basic surface sites. The conversion of 2-hexanone was subsequently carried out at identical conditions on CeZrO₃ to address the effects of removing the metal sites for hydrogen dissociation. For brevity, the reaction products are grouped by carbon number, and the product distributions obtained at space velocities of 0.48 and 1.92 h⁻¹ are summarized in Table 3.2. The temperature dependence of the product distributions resulting from 2-hexanone conversion over 0.25 wt% Pd/CeZrO₃ is shown in Table 3.3.

**Table 3.2** Product distributions from conversion of 2-hexanone over 0.25 wt% Pd/CeZrO₃ and CeZrO₃, at 623 K and 5 bar total pressure.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>WHSV (h⁻¹)</th>
<th>Conversion</th>
<th>C₁₂</th>
<th>C₁₈</th>
<th>C₁₁</th>
<th>C₉</th>
<th>Alkanes (≤C₇)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 wt%Pd CeZrO₃</td>
<td>1.92</td>
<td>58%</td>
<td>83%</td>
<td>2%</td>
<td>2%</td>
<td>5%</td>
<td>8%</td>
</tr>
<tr>
<td>0.25 wt%Pd CeZrO₃</td>
<td>0.48</td>
<td>77%</td>
<td>69%</td>
<td>3%</td>
<td>3%</td>
<td>11%</td>
<td>13%</td>
</tr>
<tr>
<td>CeZrO₃</td>
<td>1.92</td>
<td>21%</td>
<td>66%</td>
<td>25%</td>
<td>-</td>
<td>7%</td>
<td>2%</td>
</tr>
<tr>
<td>CeZrO₃</td>
<td>0.48</td>
<td>33%</td>
<td>46%</td>
<td>31%</td>
<td>-</td>
<td>18%</td>
<td>5%</td>
</tr>
</tbody>
</table>

The major organic liquid-phase product formed during the conversion of 2-hexanone over 0.25 wt% Pd/CeZrO₃ was the self aldol condensation product, a C₁₂ ketone (7-methyl-5-undecanone). Additionally, C₉ ketones (M/Z =142), C₁₈ ketone (M/Z=268) and a C₁₁ ketone (5-undecanone) were detected. Liquid phase alkane products included hexane, with smaller amounts of 2-methyl-hexane and 5-methyl-undecane. Lighter alkanes (C₁-C₆) were detected in the gas phase, with methane, butane and hexane being the predominant gas phase species. As mentioned previously, 2-hexanone was observed to be in equilibrium with 2-hexanol, and a 9:1
ketone to alcohol ratio was measured experimentally at standard reaction conditions (5.5:1 H\textsubscript{2}:2-hexanone ratio, 623 K, 5 bar). The experimentally measured ketone/alcohol ratio was consistent with the calculated ratio for the equilibrium conversion of acetone into 2-propanol at the aforementioned conditions.

**Table 3.3** Effect of reaction temperature on the conversion of 2-hexanone over 0.25 wt% Pd/CeZrO\textsubscript{x} at 5 bar and WHSV=1.92 h\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Conversion</th>
<th>C\textsubscript{12}</th>
<th>C\textsubscript{18}</th>
<th>C\textsubscript{11}</th>
<th>C\textsubscript{9}</th>
<th>Alkanes (≤C\textsubscript{7})</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>42%</td>
<td>96%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>598</td>
<td>49%</td>
<td>93%</td>
<td>1%</td>
<td>1%</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>623</td>
<td>60%</td>
<td>83%</td>
<td>2%</td>
<td>2%</td>
<td>5%</td>
<td>8%</td>
</tr>
</tbody>
</table>

The activity of CeZrO\textsubscript{x} towards 2-hexanone conversion was a factor of 3 lower than that of 0.25 wt% Pd/CeZrO\textsubscript{x} at 1.92 h\textsuperscript{-1} (Table 3.2). The major organic products formed in this conversion were unsaturated C\textsubscript{12} ketones (M/Z=182), C\textsubscript{9} ketones, and a doubly-unsaturated C\textsubscript{18} ketone (M/Z=264). Additionally, significant amounts of C\textsubscript{18} aromatic species (1,3,5-tributyl benzene and its isomers) were detected. Conversion to light alkane species was less than 5% at all reaction conditions.

The selectivities to C\textsubscript{9} and C\textsubscript{18} species for both catalysts increased with decreasing space velocity, suggesting that these species are secondary reaction products resulting from the decomposition of C\textsubscript{12} ketones and/or further reactions of C\textsubscript{12} ketones with 2-hexanone. Similarly, the selectivity towards light alkanes (on the Pd containing catalyst) increased by a factor of ~2 with decreasing space velocity. The combined selectivities to C\textsubscript{9} and C\textsubscript{18} products also decreased with decreasing reaction temperature, and decreased by a factor of ~3 at 0.48 h\textsuperscript{-1} when adding Pd to CeZrO\textsubscript{x} to form the 0.25 wt% PdCeZrO\textsubscript{x} catalyst. A reaction network is presented in Figure 3.4 for Pd/CeZrO\textsubscript{x}, based on the observed product distributions and results from studies.
of acetone condensation (36, 37). Species marked with an asterisk are reaction intermediates that were not detected in the reaction effluent. These intermediates are believed to react rapidly, leading to undetectable steady-state concentrations.

The primary reaction pathway involves the self-coupling of 2-hexanone (0) to yield 7-methyl-5-undecanone (3). In this pathway, 2-hexanone undergoes self aldol condensation on basic sites to form an aldol alcohol (1), which then undergoes dehydration on acidic (or basic) sites to form an $\alpha$-$\beta$ unsaturated ketone (2), followed by hydrogenation on metal sites to yield a saturated ketone (3). Neither the aldol alcohol nor the $\alpha$-$\beta$ unsaturated ketone were observed in the reaction effluent, suggesting that the dehydration and hydrogenation reactions are fast in comparison to aldol condensation. 7-methyl-5-undecanone undergoes further aldol condensation with 2-hexanone (in the pathway described above) to yield a C$_{18}$ ketone (4). Similar observations were reported by Di Cosimo for the self-coupling of 2-propanol on Cu/MgAlO$_x$(21).

Thermodynamic analysis shows that C-C coupling steps involving aldol condensation and dehydration are equilibrium limited (such as (0)→(2)). In contrast, the hydrogenation of $\alpha$-$\beta$ unsaturated ketones such as (2) is not equilibrium limited at these conditions (5, 23). This hydrogenation reaction prevents reverse-aldol reactions, and therefore drives C-C coupling reactions towards higher conversions. Therefore, the absence of a hydrogenation functionality on CeZrO$_x$ limits the yields of C$_{12}$ condensation products.
The equilibrated hydrogenation of the C=O group of 2-hexanone yields 2-hexanol, which can undergo dehydration over acidic sites to yield hexene. Hexene is not observed among the reaction products, because it is rapidly hydrogenated to form hexane. By analogy, 7-methyl-5-undecanone undergoes dehydration and hydrogenation steps to form 5-methyl undecane (7). Alcohols have been shown to undergo reforming (cleavage of C-C bonds adjacent to the –COH group) over metal catalysts to yield CO\textsubscript{x} species and alkanes. In this respect, 2-hexanol
undergoes reforming to form methane, butane and CO\(_x\) (38, 39). As we will show in subsequent sections, CO\(_x\) species are hydrogenated to methane over 0.25 wt% Pd/CeZrO\(_x\), and only small amounts of CO\(_x\) species (<1% of total carbon) are detected in the gas phase. Similarly, 7-methyl-5-undecanol (5) undergoes reforming to yield methane and 2-methyl hexane (6). These reforming and dehydration steps remove the C=O functionality, and they are therefore detrimental to C-C coupling processes.

The reaction temperature was varied to determine activation energies of reactions forming the C\(_{12}\), C\(_{18}\) and C\(_{9}\) species resulting from the conversion of 2-hexanone over 0.25 wt% Pd/CeZrO\(_x\). The activation energies were calculated from Arrhenius plots in Figure 3.5. The activation energy for C\(_{12}\) formation was found to be 15 kJ/mol, in agreement with the value obtained by Al-Wadaani (40) for the conversion of acetone to MIBK over Pd/ZnCrO\(_x\), a similar reducible amphoteric oxide.

![Figure 3.5](image)

**Figure 3.5** Arrhenius plots and calculated activation energies for the formation of C\(_9\) and C\(_{18}\) species (A) and C\(_{12}\) species (B) from the conversion of 2-hexanone on 0.25 wt% Pd/CeZrO\(_x\).
The activation energy of C\textsubscript{18} formation (28 kJ/mol) was comparable to that of C\textsubscript{12} formation, suggesting that both species form through similar bond-making processes (aldol condensation). In contrast, the activation energy for the formation of C\textsubscript{9} species is an order of magnitude higher (140 kJ/mol). The C\textsubscript{9} ketones could not have been formed by aldol condensation, because this process would yield oligomers with carbon numbers that are multiples of six. The high activation energy associated with C\textsubscript{9} formation suggests that a bond-breaking step decreases the carbon number in the products. Furthermore, the absence of significant amounts of C\textsubscript{3} species suggests that the C\textsubscript{9} products are not formed via degradation of C\textsubscript{12} ketones, and that the cleavage of C\textsubscript{18} products may be involved.

One possible pathway for the formation of C\textsubscript{9} ketones proceeds through C=C double bond migration in the \(\alpha\)-\(\beta\) unsaturated aldol product (2) followed by Michael addition with 2-hexanone on basic catalytic sites to produce a C\textsubscript{18} dione (9). Migration of the C=C double bond in \(\alpha\)–\(\beta\) unsaturated ketones has been observed by Mussolino et al. over Pd/TiO\textsubscript{2} (41). The conversion of 2-butanone over CeZrO\textsubscript{x} in the present study showed the existence of double bond migration, because \(\alpha\)–\(\beta\) unsaturated condensation products (C\textsubscript{8} ketones) with the C=C double bond in different positions were identified by GC/MS analysis. These products included 5-methyl-4-hepten-3-one, 5-methyl-5-hepten-3-one and 5-methylene-3-heptanone. The resulting unsaturated ketone (8) contains a less substituted double bond, that is more susceptible to Michael addition with 2-hexanone to form a dione (9). The C\textsubscript{18} dione then undergoes retro-Michael reaction (42) to form the two different C\textsubscript{9} ketones (10) identified in the effluent. Finally, small amounts (~2% selectivity) of a C\textsubscript{11} ketone (5-undecanone), may be obtained from C-C
hydrogenolysis of the methyl branch of 7-methyl-5-undecanone, also yielding methane (not shown in the figure).

Reactions involving $\alpha$-β unsaturated ketones become more significant over CeZrO$_x$, because these species are not stabilized against further reaction by hydrogenation. The selectivity towards C$_9$ and C$_{18}$ secondary products is enhanced substantially compared to that on 0.25 wt% PdCeZrO$_x$. Furthermore, the $\alpha$-β unsaturated ketone (2) can undergo cross-aldol condensation with 2-hexanone followed by a 1,6-aldol addition or aromatization to form 1,3,5-tributylbenzene, a C$_{18}$ species. This reaction is analogous to the formation of mesitylene from acetone (36, 37). It is also important to note that C=O hydrogenation (that produces alcohols), reforming, and hydrogenolysis reactions are minimized in the absence of Pd.

3.4. Effects of Partial and Total Pressures

Reaction kinetic studies were conducted to determine the reaction orders with respect to 2-hexanone and H$_2$. These studies were performed using an inert species (heptane for 2-hexanone, He for H$_2$) to change the partial pressures of 2-hexanone and hydrogen independently, while keeping the total pressure constant. The space velocity of the reaction system was adjusted to achieve conversions of <30%. At these conversions, secondary products were produced in negligible yields. The logarithm of the reaction rate ($\mu$mol C$_{12}$ min$^{-1}$ g cat$^{-1}$) was plotted against the logarithm of the partial pressure of the species, with the slopes yielding the reaction orders, as shown in Figure 3.6. For both hydrogen and 2-hexanone, the reaction orders were fractional and decreased with increasing partial pressures. For 2-hexanone, the reaction order was 0.9 for low partial pressures (0.08-0.16 bar), whereas it decreased to 0.5 as partial pressure was
increased (0.31-0.63 bar). For hydrogen, the order decreased from 0.8 to 0.6 going from low to higher partial pressures (0.9 to 3.5 bar).

**Figure 3.6** Rate versus partial pressure, and calculated reaction orders with respect to 2-hexanone pressure at $P_{\text{H}_2} = 4.2$ bar (A) and with respect to hydrogen pressure at $P_{\text{2-hexanone}} = 0.8$ bar (B).

Several investigators have studied the aldol condensation of acetone with citral on basic oxides. Diez, et al. showed that the rate determining step in the reaction is the abstraction of an $\alpha$-hydrogen from acetone over a Li-doped MgO catalyst (43). However, Abello, et al. showed the slow step to be the surface reaction in which the enolate ion generated from an acetone molecule attacks a citral molecule over MgAlO$_x$ (44). Either rate-determining step is possible for 2-hexanone self-condensation. If it is abstraction of an $\alpha$-hydrogen atom, then the reaction order with respect to 2-hexanone in the numerator of a Langmuir-Hinshelwood type rate expression should be 1, and if the rate-determining step is the surface reaction, the reaction order in the numerator would be 2. However, under the partial pressures used here, inhibition due to surface coverage by reactant or product species reduces the apparent reaction order, as observed by both previous investigators, and it is possible that either first order or second order kinetics is
approached in the limit of low 2-hexanone partial pressures. The apparent reaction orders for 2-hexanone conversion observed in the present study are similar to ones found by Torres, et al. and Melo, et al. for acetone condensation reaction. (10, 45) Torres, et al. calculated an apparent order in 2-propanol of 0.35 for the MIBK formation rate for partial pressures of 2-propanol around 0.4 bar. Melo, et al. found that the apparent order with respect to acetone was 0.3. Also Melo, et al. reported an apparent reaction order in hydrogen of 1.3 for partial pressures up to 0.8 bar, which is in accordance with the values found in the present study for a higher partial pressure range.

The effects of total reactor pressure on the condensation activity and selectivity are shown in Table 3.4. The conversion of 2-hexanone is increased significantly upon increasing the total pressure, while the selectivity to primary and secondary products remained approximately constant. This behavior results from a combination of the effects of increasing H₂ and 2-hexanone partial pressures that were documented above.

### Table 3.4 Effect of total pressure on the conversion of 2-hexanone over 0.25 wt% Pd/CeZrOₓ at 623 K and WHSV= 1.92 h⁻¹.

<table>
<thead>
<tr>
<th>P&lt;sub&gt;total&lt;/sub&gt; (bar)</th>
<th>Conversion</th>
<th>C&lt;sub&gt;12&lt;/sub&gt;</th>
<th>C&lt;sub&gt;18&lt;/sub&gt;</th>
<th>C&lt;sub&gt;11&lt;/sub&gt;</th>
<th>C&lt;sub&gt;9&lt;/sub&gt;</th>
<th>Alkanes (≤C&lt;sub&gt;7&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>58%</td>
<td>83%</td>
<td>2%</td>
<td>2%</td>
<td>5%</td>
<td>8%</td>
</tr>
<tr>
<td>16</td>
<td>75%</td>
<td>80%</td>
<td>3%</td>
<td>2%</td>
<td>4%</td>
<td>10%</td>
</tr>
<tr>
<td>25</td>
<td>84%</td>
<td>79%</td>
<td>5%</td>
<td>2%</td>
<td>4%</td>
<td>9%</td>
</tr>
</tbody>
</table>

### 3.5. Effects of Metal Loading and Metal-Support Proximity

The activity and selectivity data for the conversion of 2-hexanone over Pd/CeZrOₓ catalysts with different metal loadings are given in Table 3.5. The selectivity towards saturated C<sub>12</sub> product decreases with increasing metal loadings. The decline in selectivity towards the major condensation product is accompanied by an increase in selectivity towards light alkanes. This result demonstrates that higher metal loadings promote hydrogenolysis reactions to form
hexane and reforming reactions leading to the formation of butane and methane. These reactions take place in parallel with the condensation reaction pathway leading to the C\textsubscript{12} ketone. It is important to note that hydrogenation of the α-β unsaturated ketone is complete for all metal loadings, as unsaturated C\textsubscript{12} species were not detected in the effluent. This observation shows that the hydrogenation step of the overall ketone coupling process is a fast step in the reaction network. Therefore, the rates of the side reactions, such as hydrogenolysis and reforming, can be minimized by avoiding the use of excess metal functionality.

**Table 3.5** Product distributions from conversion of 2-hexanone over Pd/CeZrO\textsubscript{x} with different metal loadings, and a physical mixture of 0.5 wt% Pd/SiO\textsubscript{2} and CeZrO\textsubscript{x} at 623 K and 5 bar total pressure.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>WHSV (hr\textsuperscript{-1})</th>
<th>Conversion</th>
<th>C\textsubscript{12}</th>
<th>C\textsubscript{18}</th>
<th>C\textsubscript{11}</th>
<th>C\textsubscript{9}</th>
<th>Alkanes (≤C\textsubscript{7})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 wt% Pd/CeZrO\textsubscript{x}</td>
<td>1.92</td>
<td>68%</td>
<td>85%</td>
<td>3%</td>
<td>2%</td>
<td>4%</td>
<td>3%</td>
</tr>
<tr>
<td>0.25 wt% Pd/CeZrO\textsubscript{x}</td>
<td>1.92</td>
<td>58%</td>
<td>83%</td>
<td>2%</td>
<td>2%</td>
<td>5%</td>
<td>8%</td>
</tr>
<tr>
<td>1.45 wt% Pd/CeZrO\textsubscript{x}</td>
<td>1.92</td>
<td>85%</td>
<td>57%</td>
<td>2%</td>
<td>1%</td>
<td>4%</td>
<td>36%</td>
</tr>
<tr>
<td>0.5 wt% Pd/SiO\textsubscript{2}</td>
<td>2.84</td>
<td>6%</td>
<td>12%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>87%</td>
</tr>
<tr>
<td>0.5 wt% Pd/SiO\textsubscript{2} + CeZrO\textsubscript{x}</td>
<td>1.92*</td>
<td>48%</td>
<td>77%</td>
<td>10%</td>
<td>4%</td>
<td>5%</td>
<td>3%</td>
</tr>
</tbody>
</table>

The importance of the proximity of metal sites to acid/base sites was investigated by comparing the conversion of 2-hexanone over a physical mixture of Pd/SiO\textsubscript{2} and CeZrO\textsubscript{x} to that over 0.25 wt% Pd/CeZrO\textsubscript{x}, and the results are presented in Table 3.5. Due to the weak acid/base properties of Si-OH groups on the surface, the SiO\textsubscript{2} support can be considered to be inert (5). In this respect, 0.5 wt% Pd/SiO\textsubscript{2} was tested alone, and a very low conversion of 2-hexanone (6%) was observed, with a low selectivity towards the C\textsubscript{12} ketone (12%). A physical mixture of 0.5 wt% Pd/SiO\textsubscript{2} with CeZrO\textsubscript{x} was then prepared to give the same amount of acid, base and metal functionality as 0.25 wt% Pd/CeZrO\textsubscript{x}, and this physical mixture was studied for 2-hexanone condensation at the same reaction conditions. A lower (~ 10%) activity was obtained in the case of the physical mixture. Even though the selectivity towards the C\textsubscript{12} ketone did not vary
considerably from that on 0.25 wt% Pd/CeZrO$_x$, the selectivity towards higher molecular weight products, such as C$_{18}$ aromatics was increased at the expense of light alkanes on the physical mixture. This change in selectivity suggests that a metal-support interaction is responsible for reforming reactions and dehydration/hydrogenation reactions. In addition, because the $\alpha$–$\beta$ unsaturated aldol condensation product cannot be hydrogenated on the physical mixture unless it desorbs from the CeZrO$_x$ surface, it has a higher probability to undergo further condensation reactions (e.g., Michael or aldol) to produce the higher molecular weight species using the pathways described earlier.

3.6. Effects of Oxygenated Additives and Water

The influence of oxygenated compounds such as primary alcohols, secondary alcohols, 3-ketones, heterocyclics and carboxylic acids on the aldol condensation of ketones was studied, because these species represent classes of compounds (together with 2-ketones) present in the hydrophobic organic mixture derived from the conversion of sugars or polyols over a Pt-Re/C catalyst(4). One representative species was selected from each group to facilitate the analysis, and the results are given in Table 3.6. An experiment with 10 mol % inert species (heptane) serves as a benchmark for the additives study (entry 2), because although heptane is expected to be inert, it may act as a diluent and therefore decrease the overall rate of a positive order reaction. Results (entry 2) show that heptane has little effect on the activity and selectivity of 2-hexanone conversion.

The effect of a primary alcohol on the self-condensation of 2-hexanone was studied by feeding a mixture of 10 mol % 1-butanol in 2-hexanone (entry 3). At the reaction conditions used in this study, primary alcohols are readily equilibrated (through dehydrogenation) with the
corresponding aldehydes, in this case butanal (46). The aldehydes can undergo self aldol condensation reactions or cross aldol condensation reactions with ketones, where the ketones act as the nucleophilic species.

Table 3.6 Effects of monofunctional oxygenates and water on the conversion of 2-hexanone and 2-butanone over 0.25 wt% Pd/CeZrO₃ at 623 K, 5 bar and WHSV=1.92h⁻¹.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Feed</th>
<th>Conversion</th>
<th>Primary product(s)</th>
<th>Secondary product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ketone</td>
<td>Additive</td>
<td>Species</td>
<td>Selectivity</td>
</tr>
<tr>
<td>1</td>
<td>2-hexanone</td>
<td>58%</td>
<td>-</td>
<td>7-methyl-5-undecanone (C₁₂ ketone)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkane (≤C₇)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁₁ ketones</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁₈ ketones</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₉ ketones</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkane (≤C₇)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁₁ ketones</td>
</tr>
<tr>
<td>2</td>
<td>90% 2-hexanone and 10% heptane</td>
<td>56%</td>
<td>0%</td>
<td>7-methyl-5-undecanone (C₁₂ ketone)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7-methyl-5-undecanone (C₁₂ ketone)</td>
</tr>
<tr>
<td>3</td>
<td>90% 2-hexanone and 10% 1-butanol</td>
<td>29%</td>
<td>100%</td>
<td>5-decanone (C₁₀ ketone)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkane (≤C₇)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁₁ ketones</td>
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<td></td>
<td></td>
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<td>CO+CO₂</td>
</tr>
<tr>
<td>4</td>
<td>90% 2-hexanone and 10% 2-butanol</td>
<td>53%</td>
<td>65%</td>
<td>3-methyl-5-nonanone and 5-methyl-3-nonanone (C₁₀ ketones)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkane (≤C₇)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁₁ ketones</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7-methyl-5-undecanone (C₁₂ ketone)</td>
</tr>
<tr>
<td>5</td>
<td>90% 2-hexanone and 10% butanoic acid</td>
<td>8%</td>
<td>100%</td>
<td>4-heptanone (C₇ ketone)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkane (≤C₇)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁₁ ketones</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO+CO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁₈ ketones</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₉ ketones</td>
</tr>
<tr>
<td>6</td>
<td>90% 2-hexanone and 10% THF</td>
<td>48%</td>
<td>12%</td>
<td>7-methyl-5-undecanone (C₁₂ ketone)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7-methyl-5-undecanone (C₁₂ ketone)</td>
</tr>
<tr>
<td>7</td>
<td>75% 2-hexanone and 25% 3-pentanone</td>
<td>50%</td>
<td>27%</td>
<td>7-ethyl-5-nonanone (C₁₁ ketone)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkane (≤C₇)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5-undecanone</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>C₁₂ ketones</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>C₉ ketones</td>
</tr>
<tr>
<td>8</td>
<td>2-butanol</td>
<td>70%</td>
<td>-</td>
<td>5-methyl-3-heptanone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkane (≤C₇)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>C₁₈ ketones</td>
</tr>
<tr>
<td>9</td>
<td>Water – saturated 2-butanol (12 wt% water)</td>
<td>39%</td>
<td>-</td>
<td>5-methyl-3-heptanone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alkane (≤C₇)</td>
</tr>
</tbody>
</table>
A reaction scheme for the conversion of primary alcohols is illustrated in Figure 3.7(A). Condensation of butanal with 2-hexanone yields 5-decanone, and this product accounted for 26% of the product carbon. The self-condensation product of butanal, 2-ethyl hexanal, was not observed due to the low concentration of butanal. Butanal can also undergo decarbonylation reaction to produce CO and propane (47), which were both detected in the effluent. A significant decrease in the activity of 2-hexanone self-condensation (70%) was caused by the addition of the primary alcohol, which was almost completely converted. This loss of activity was completely reversed upon a 12 h treatment in flowing H₂ and removal of the primary alcohol from the feed. Possible causes for inhibition by primary alcohols include strongly bound aldehyde species (33) or oligomers of butanal that can act as coke precursors (48, 49) and which can be removed by H₂ treatment. Microcalorimetric studies have shown that primary alcohols and aldehydes bind more strongly to metal and basic sites compared to secondary alcohols and ketones (50, 51). Therefore, it is likely that the catalytic sites required for coupling of ketones are preferentially occupied by primary alcohols or aldehydes under reaction conditions, leading to inhibition of ketone coupling. Lowering the WHSV to 0.48 h⁻¹ increased 2-hexanone conversion to 65% and the C₁₂ selectivity to 60%, showing that the detrimental effect of primary alcohols on condensation activity can be overcome if the inhibiting species are reacted to completion.

The effect of secondary alcohols on the self-condensation of 2-hexanone was studied by feeding a mixture of 10 mol % 2-butanol in 2-hexanone (entry 4). Secondary alcohols are dehydrogenated to quasi-equilibrium with the corresponding ketones (2-butanone in this case), the latter of which can undergo either self or cross condensation, as illustrated in Figure 3.7(B). The observed products are the self-condensation product of 2-hexanone and the cross-condensation product of 2-butanone and 2-hexanone (3-methyl-5-nonanone and/or 5-methyl-3-
nonanone). If $\alpha$-hydrogen atoms of the methyl group are abstracted from 2-butanol, and the resulting carbanion attacks the carbonyl group of 2-hexanone, then 3-methyl-5-nonanone is formed. In the opposite case, 5-methyl-3-pentanone is formed. The 2-butanol self-condensation product was not observed due to the low 2-butanol concentration, resulting in preferential cross condensation. The overall ketone conversion was 55%, showing that secondary alcohols do not significantly affect the condensation activity.

The effect of carboxylic acids was investigated using a 10 mol % butyric acid in 2-hexanone feed (entry 5). The butyric acid was found to ketonize to 4-heptanone and also undergo a coupling reaction with 2-hexanone to form 5-decanone. The 5-decanone results from the aldol condensation of 2-hexanone with butanal, which is formed upon the partial reduction of butanoic acid. The reactions involved in the conversion of butanoic acid are illustrated in Figure 3.7(C). The addition of acid causes a significant loss in activity for 2-hexanone self-condensation, such that the 2-hexanone conversion decreased from 58% to 8%. However, complete deactivation was not observed and the activity could be regained as described for primary alcohols. Poisoning of the basic catalytic sites by carboxylic acids is the most probable cause for the loss of activity (49, 52). Further poisoning of the basic sites may be caused by the CO$_2$ released from the ketonization reaction of butyric acid. The effect of CO$_2$ was investigated separately and will be explained in the following sections. Decreasing the space velocity to 0.48 h$^{-1}$ increased the 2-hexanone conversion and C$_{12}$ selectivity to 48% and 56%, respectively. It should be noted that selectivities to light alkanes are substantially higher in the presence of either primary alcohols or carboxylic acids as compared to secondary alcohols or ketones. The production of additional alkanes results from the more facile reforming of the terminal functionalized carbon in comparison to internal C-C cleavage.
A slight decrease of 2-hexanone self-condensation activity resulted with the addition of 10 mol % THF (2-hexanone conversion declined from 58% to 48%, entry 6). Product analysis revealed that 10% of the THF was converted, and the amount of propane detected approximately matched the amount of THF converted. This result suggests a ring opening reaction yielding a linear oxygenated intermediate species, n-butanol, which undergoes further decarbonylation to produce propane as observed by Kreuzer, et al.(47). Therefore, the decrease of activity can be attributed to partial conversion of THF to n-butanol, for which the deactivating effects of primary alcohols were explained above.

The effect of 3-ketones was investigated (entry 7) via the reaction of a 25 mol% mixture of 3-pentanone in 2-hexanone. The self-condensation of 3-pentanone was not observed, and the cross condensation of 3-pentanone with 2-hexanone was slower relative to the self-condensation of 2-hexanone. The methyl group in 2-ketones contains \( \alpha \)-hydrogen atoms that upon abstraction lead to a more stable carbanion, than the secondary carbanions that form upon abstraction of \( \alpha \)-hydrogen atoms from 3-ketones. Furthermore, the methyl carbanion is less sterically hindered than internal carbanions. The aforementioned properties make the methyl carbanion a better nucleophile than secondary carbanions. Additionally, the carbonyl group of 3-ketones is more sterically hindered than that of 2-ketones, making it less susceptible to nucleophilic attack (53). In this respect, the self-condensation of 2-hexanone is favored over cross condensation with 3-pentanone, which is favored substantially over the self-condensation of 3-pentanone. Accordingly, a single cross condensation product (where 2-hexanone acts as the nucleophile) would be expected, as illustrated in Figure 3.7(D). These results are observed experimentally.
Figure 3.7 Reactions of selected oxygenates—primary alcohols (A), secondary alcohols (B), carboxylic acids (C) and 3-ketones (D). For aldol-type reactions, the source of the carbanion is indicated by ‡, and the attacked carbonyl group is indicated by *.
In addition to containing alkanes and oxygenated hydrocarbon species, organic streams derived from the conversion of sugars over Pt-Re/C are saturated with water, resulting from contact with an aqueous phase. Water is also formed as a by-product of aldol condensation, and associated secondary hydrogenolysis reactions. Furthermore, water is produced during ketonization. Accordingly, it is important to study the effects of water on the self-coupling of ketones, and in this respect we have investigated the effects of water on the self-aldol condensation of 2-butanone into 5-methyl-2-heptanone (Entries 8 and 9). In these studies, 2-butanone was chosen as the reactant, because it can be saturated with a larger amount of water (~12 wt%) than 2-hexanone, and this water content is representative of the products of ketonization. The addition of water decreased the condensation activity by 40%, and this activity loss was reversible, suggesting inhibition.

The inhibition of the aldol condensation activity by water may be responsible for the fractional H₂ and 2-hexanone reaction orders described previously. In this respect, Gammara, et al. report that the presence of relatively large amounts of molecularly adsorbed water on ceria is responsible for inhibition of CO oxidation on Cu/CeOₓ catalysts(54). Moreover, Gutierrez- Ortiz, et al. showed by H₂O-TPD experiments that the hydrophilicity of ceria is increased by addition of ZrO₂(55). In addition to inhibition by site blocking, the presence of water may also shift the aldol condensation equilibrium to the reactants side by inhibiting dehydration of the aldol-alcohol product.

3.7. Effect of CO₂ Co-feeding

Carbon dioxide is produced as a by-product of the ketonization of carboxylic acids. Therefore, it is necessary to understand the effects of the by-product CO₂ on the self-coupling of ketones to accomplish the integration of ketonization and aldol condensation/hydrogenation in a
single reactor system. To that end, we have substituted the pure hydrogen gas co-feed used above with H₂-CO₂ gas mixtures. The results of CO₂ co-feeding at various conditions are shown in Table 3.7. Co-feeding a 10 mol % CO₂ in H₂ stream resulted in almost complete loss of self-condensation activity on 0.25 wt% Pd/CeZrOₓ, decreasing the conversion of 2-hexanone from 60% to 5%. Under these conditions, 63% of the CO₂ was converted to CO by the reverse water-gas shift reaction and to CH₄ by methanation, and 2-hexanone was observed to be in equilibrium with 2-hexanol. Carbon monoxide adsorbs more strongly than hydrogen on the Pd surface, and CO poisoning has been reported in hydrogenation reactions (56, 57). However, the observation of quasi-equilibration of 2-hexanone with 2-hexanol in the presence of CO (derived from reduction of CO₂) suggests that hydrogenation is still fast in the presence of CO, possibly because of the high reaction temperatures.

Table 3.7 Effects of CO₂ on the conversion of 2-hexanone on CeZrOₓ and Pd/CeZrOₓ at 623 K and 5 bar total pressure.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% CO₂ in H₂</th>
<th>WHSV (h⁻¹)</th>
<th>Conversion</th>
<th>Carbon Selectivities</th>
<th>Alkanes (C₅-C₇)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 wt%Pd CeZrOₓ</td>
<td>10%</td>
<td>1.92</td>
<td>5%</td>
<td>63%</td>
<td>22%</td>
</tr>
<tr>
<td>0.25 wt%Pd CeZrOₓ</td>
<td>10%</td>
<td>0.48</td>
<td>17%</td>
<td>45%</td>
<td>12%</td>
</tr>
<tr>
<td>0.25 wt%Pd CeZrOₓ</td>
<td>5%</td>
<td>1.92</td>
<td>7%</td>
<td>44%</td>
<td>26%</td>
</tr>
<tr>
<td>CeZrOₓ</td>
<td>10%</td>
<td>1.92</td>
<td>7%</td>
<td>0%</td>
<td>45%</td>
</tr>
</tbody>
</table>

A decrease in the concentration of CO₂ in the co-feed to 5% did not improve the self-coupling yield. Similarly, decreasing the space velocity of the ketone feed was not effective in overcoming the effects of CO₂. The self-coupling of 2-hexanone was also significantly suppressed on CeZrOₓ, suggesting that CO₂ influences aldol condensation sites on the support. For all conditions listed in Table 3.7, the activity loss associated with CO₂ was observed to be completely reversible upon removal of CO₂ from the gas co-feed stream. Kamimura, et al.
showed that co-feeding of CO$_2$ suppresses the aldol condensation activity of CeFeO$_x$ catalysts, and they attribute this effect to the blocking of basic catalytic sites by acidic CO$_2$ (58). The suppression of basic catalytic sites by CO$_2$ causes the product selectivity to be substantially altered by reactions taking place on other functionalities such as metal and acidic sites, thereby leading to higher selectivities to alkanes for all conditions in Table 3.7. The alkanes are formed by dehydration/hydrogenation, and reforming of 2-hexanol.

3.8. Interaction of CO$_2$ with Pd/CeZrO$_x$ and CeZrO$_x$

The carbon dioxide desorption profiles described in section 3.1 show that CO$_2$ desorption from Pd/CeZrO$_x$ persists at temperatures up to 1000 K. It is therefore, interesting to note that the loss of activity resulting from CO$_2$ co-feeding was completely reversible on 0.25 wt% Pd/CeZrO$_x$ and CeZrO$_x$ at a temperature of 623 K, because a fraction of the adsorbed CO$_2$ may still be blocking active basic sites, even after desorption at this reaction temperature. Due to the setup of our reactor system we were not able to obtain a transient reaction profile needed to establish the relationship between the rate of CO$_2$ desorption at 623 K and the return of aldol condensation activity; however, activity was returned after 6-12 h treatment in H$_2$ at reaction temperature.

Strongly binding sites may become irreversibly covered by tightly bound spectator species that prevent catalytic turnover. Since these site do not participate in the overall reaction, their deactivation by CO$_2$ will not be reflected in catalytic activity measurements. However, the catalyst regeneration studies carried out in the present work employed flowing H$_2$, whereas CO$_2$-TPD studies were carried out using an inert carrier gas. Therefore, studies employing TPSR of CO$_2$ under flowing H$_2$ were carried out. Figure 3.8 shows the desorption profiles of CO$_2$ and associated products (CO and methane) for 0.25 wt% Pd/CeZrO$_x$ and CeZrO$_x$. On 0.25 wt%
Pd/CeZrOₓ, the desorption of CO₂ was complete by 620 K, and was accompanied by the production of CO and methane, which peaked at 550 and 650 K, respectively. Palladium is a poor catalyst for the methanation of CO₂ and CO(59). However, the presence of a reducible support such as CeO₂ has been shown to substantially promote the activity of Pd for CO₂ activation. Leitenberg, et al. propose a mechanism in which Ce⁴⁺ is reduced to Ce³⁺ by hydrogen, which is activated via dissociation over a metal, followed by spillover onto the support(60). The resulting Ce³⁺ reacts with CO₂ to form CO and regenerates Ce⁴⁺. The formation of Ce³⁺ is required for the activation of CO₂. In agreement with this behavior, we observe that the onset temperature of CO formation (450 K) in TPSR corresponds to the reduction temperature (obtained from TPR) of Ce⁴⁺ in intimate contact with Pd. At higher temperatures (>600 K), CO is hydrogenated to methane. Accordingly, the activation of CO₂ by a hydrogen-reduced ceria permits the removal of CO₂ from the surface at substantially lower temperatures than in the absence of hydrogen. Figure 3.8B shows that even in the absence of metal, desorption of CO₂ from CeZrOₓ is facilitated by the presence of hydrogen, with CO₂ desorbing completely at 850 K. This observation may explain the fact that even CeZrOₓ regains catalytic activity after regeneration with hydrogen, and suggests that hydrogen interacts with the surface in the absence of a metal. In this respect, Kondo, et al. have observed the dissociation of hydrogen on ZrO₂ to form Zr-OH surface species at temperatures above 373 K(61). These species may drive the conversion of surface carbonates into more labile species, thereby facilitating the desorption of CO₂. Furthermore, the desorption of CO₂ above ~700 K is accompanied by the production of CO, which subsides at a temperature near 900 K. As with the presence of metal, the production of CO appears to be associated with the reduction of surface CeO₂ species observed in TPR.
Figure 3.8 TPSR of adsorbed CO\(_2\) under H\(_2\) for 0.25 wt% Pd/CeZrO\(_x\) (A) and CeZrO\(_x\) (B).

3.9. Conclusions

The self-coupling of 2-hexanone to form C\(_{12}\) species via aldol condensation/hydrogenation was studied over Pd/CeZrO\(_x\) catalysts. XRD studies show that the CeZrO\(_x\) support consists of a cerium-zirconium solid solution. TPR studies of these catalysts indicate that the presence of palladium causes reduction of neighboring ceria species. Ammonia and CO\(_2\) TPD spectra indicate the presence of both acidic and basic functionalities. TPRS studies in flowing H\(_2\) for catalysts containing adsorbed CO\(_2\) indicate that CO\(_2\) is converted to CO over Ce\(^{3+}\) sites that are formed during reduction of Ce\(^{4+}\) to Ce\(^{3+}\). Reaction kinetics studies show
that the primary product of aldol condensation/hydrogenation is C_{12} ketone, with the formation of C_{9} and C_{18} ketones as secondary products, as well as the production of light alkanes (C_{1}-C_{7}). The high activation energy of C_{9} formation (140 kJ/mol) compared to the formation of C_{12} and C_{18} species (15 and 28 kJ/mol, respectively), and the increase in the selectivity towards C_{9} species in the absence of Pd, indicate that these species may be formed as a result of the decomposition of unsaturated C_{18} condensation products. The light alkane species are formed as a result of dehydration/hydrogenation and reforming of 2-hexanol. The self-coupling of 2-hexanone was found to be positive order in both 2-hexanone and hydrogen, and consequently the yield to C_{12} products was found to increase with total reaction pressure. Lower metal loadings resulted in enhanced selectivity to C_{12} products and suppressed de-oxygenation side reactions. Metal-support proximity was not found to substantially influence catalyst performance, although it had a measureable effect on the formation of secondary products.

Monofunctional oxygenated additives such as primary alcohols and carboxylic acids were found to reversibly inhibit the self-coupling activity of 2-hexanone. The detrimental effects of these species could be overcome by increasing the overall reaction residence time. Water (the product of both aldol condensation and ketonization) and carbon dioxide (a product of ketonization) were also observed to reversibly inhibit 2-hexanone self-coupling. These observations lead us to conclude that it may be difficult to integrate efficiently the ketonization of carboxylic acids and the aldol condensation/hydrogenation of ketones integrated in a single reactor system. However, because water and CO_{2} can easily be separated from the organic reaction mixture, the operation of a cascade system consisting of separate ketonization and aldol condensation reactors appears to be preferred.
3.10. References

Chapter 4: Integration of C-C Coupling Reactions of Biomass-Derived Oxygenates to Fuel-Grade Compounds

Two important coupling reactions for the upgrading of mono-functional oxygenated compounds for transportation fuel applications, ketonization and aldol condensation/hydrogenation were discussed in Chapter 3. In ketonization reactions, two carboxylic acid molecules combine to form a higher molecular weight linear ketone, CO$_2$ and water (1), whereas in aldol condensation/hydrogenation reactions, two ketone or secondary alcohol molecules couple to form a heavier branched ketone (2). These ketones obtained can then be converted into corresponding fuel grade alkanes by dehydration/hydrogenation over bi-functional solid-acid supported noble metal catalysts such as Pt/NbOPO$_4$ (3). It was found in our previous work that ketonization must be performed prior to aldol condensation/hydrogenation, because the active basic sites in the aldol condensation catalyst are poisoned by the presence of carboxylic acids (4, 5). Carboxylic acids in the hydrophobic mixture can be ketonized with nearly 100% yield over a Ce$_1$Zr$_1$O$_x$ mixed oxide catalyst at temperatures from 623 to 673 K (4). The aldol condensation/hydrogenation was carried out over Pd/Ce$_1$Zr$_1$O$_x$ with H$_2$ co-feed. Metal catalyzed hydrogenation of the unsaturated dehydrated aldol condensation product is required to overcome the equilibrium limitation of aldol condensation reaction and obtain high yields (2). In addition, metal functionality is needed to catalyze the dehydrogenation reaction of alcohols to form ketones for coupling reactions (6).

In the previous chapter, we have suggested that ketonization and aldol condensation/hydrogenation reactions could be integrated in a single reactor with a double bed system, because the reaction conditions for both reactions are similar. Integrating the aldol
condensation and ketonization steps into a single reactor system would streamline the overall C-C coupling process. However, the CO₂ produced in the ketonization reaction is a known poison for basic sites active in aldol-condensation (7, 8). We have shown previously (9) that the presence of 5% CO₂ in the feed is detrimental to aldol condensation activity (~90% decrease in activity) over Pd/Ce₁Zr₁Oₓ. Accordingly, we concluded that it was beneficial to remove CO₂ prior to the aldol condensation/hydrogenation step over Pd/Ce₁Zr₁Oₓ.

It has been shown in literature that the nature of the interaction of CO₂ with the oxide surface can be modified by changing the composition of mixed oxides (10, 11). In this chapter, we study the possibility of modifying the composition of ceria-zirconia mixed oxide to formulate an aldol condensation catalyst that is not severely inhibited by CO₂, so as to permit the integration of ketonization and aldol condensation reactions in a single reactor. In addition to CO₂ inhibition, inhibition by water also needs to be investigated, because water is a by-product of ketonization as well as aldol condensation. For example, we have shown in the previous chapter that a 40% decrease in activity takes place for aldol condensation of 2-butanone over Pd/Ce₁Zr₁Oₓ when a mixture containing 12 wt% water in 2-butanone is used as the feed (9).

4.1. Experimental

4.1.1. Catalyst Preparation

Ceria-zirconia mixed oxides with different molar compositions were prepared via coprecipitation of Ce(NO₃)₃ and ZrO(NO₃)₂ with NH₄OH (Aldrich) according to Serrano-Ruiz, et al. (12) with appropriate concentrations to obtain desired Ce/Zr ratios. The Pd/CeₓZr₅Oₓ catalysts were prepared via incipient wetness impregnation of CeₓZr₅Oₓ with an amount of aqueous solution of Pd(NO₃)₂ (Aldrich) necessary to obtain the nominal metal loading of 0.25 wt%. The catalysts were dried in air at 373 K overnight and calcined in air at 623 K for 2 h.
4.1.2. Reaction Kinetics Studies

2-hexanone and butanoic acid were purchased from Sigma-Aldrich and used without further purification. Hydrogen (99%) and 10 mol% CO\textsubscript{2} in H\textsubscript{2} were purchased from Airgas and used without further purification. The conversions of 2-hexanone over Pd/\text{Ce}\text{\textsubscript{3}}\text{Zr}\text{\textsubscript{2}}\text{O}_{\text{x}} were carried out at 598 and 623 K, pressure of 5 bar, and liquid flow rates of 0.08 and 0.16 mL/min. The molar ratio of the gas flow rate to the liquid flow rate was maintained at 5.5. A fixed bed, down-flow reactor consisting of a half-inch stainless steel tube was used for all experiments as described in Chapter 2. The catalysts were reduced in-situ at 623 K (ramp rate of 0.5 K min\textsuperscript{-1}) for 2 h in flowing H\textsubscript{2} (200 cm\textsuperscript{3}(STP) min\textsuperscript{-1}). After the reduction was completed, the temperature and pressure were adjusted and the feed flow was started with flowing H\textsubscript{2} or H\textsubscript{2}-CO\textsubscript{2} mixtures. The weight hourly space velocity (WHSV) was calculated for experiments using the mass flow rate of the liquid flow into the reactor and the mass of the catalyst used.

Experiments employing a double bed, single reactor configuration were performed in a fixed bed, down-flow reactor system consisting of a half-inch stainless steel tube. In contrast to the single bed experiments, two different catalysts (2 g each) were loaded in the same reactor, separated by whole fused SiO\textsubscript{2} granules. Pd/ZrO\textsubscript{2} catalyst was placed on the quartz wool and fused SiO\textsubscript{2} granules were placed on top of this bed. Ce\textsubscript{3}Zr\textsubscript{2}O\textsubscript{x} catalyst was then placed on the silica chips, so that the feed could pass through the ketonization catalyst first and the aldol condensation/hydrogenation catalyst second. Both catalysts were mixed with crushed fused SiO\textsubscript{2} granules (Aldrich) in a 1:1 volumetric ratio.

The rate of gas production was measured with a bubble flow meter. An HP GC5890 gas chromatograph, equipped with a Haysep DB 100/120 column (Alltech) and thermal conductivity detector (TCD), was used to quantify CO and CO\textsubscript{2}, and an Agilent GC6890, equipped with an
Rtx column (Agilent) and a flame ionization detector (FID), was used to quantify gas-phase alkanes. Liquid phase analysis was performed with a Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID detector and a Shimadzu 2060 GC/MS with a NIST library of spectra. Liquid and gas analysis points were collected every 2-3 h, and steady state was usually achieved after 6 h time-on-stream. At our reaction conditions, 2-hexanol was in equilibrium with 2-hexanone; therefore, the conversion of 2-hexanone to 2-hexanol was not factored into the total conversion calculation, as given by equation 4 in Chapter 3. The selectivities to reaction products were calculated on a molar carbon basis, as given by equation 2 (Chapter 2).

4.1.3. Catalyst Characterization

4.1.3.1. BET and XRD measurements

The BET surface area was measured by nitrogen adsorption at liquid nitrogen temperature using a standard volumetric apparatus (13). X-Ray diffraction (XRD) was used to investigate the phase structure of the Pd/CeₓZrᵧOₙ catalysts as described in Chapter 2. Diffraction patterns were collected in the 20° to 65° 2θ range, with 0.01° intervals and a dwell time of 2 s.

4.1.3.2. Temperature-Programmed Desorption Experiments

Carbon dioxide and ammonia temperature–programmed desorption (TPD) experiments were carried out using an apparatus described in Chapter 2 and procedure in the previous chapter.

4.2. Surface and Bulk Characterization

The desorption profiles of NH₃ and CO₂ from several Pd-supported ceria-zirconia catalysts of varying compositions, as well as pure CeOₓ and ZrO₂, are shown in Figure 4.1 and
Figure 4.2, respectively. These profiles were integrated to obtain the quantities of acidic and basic surface sites per gram of catalyst, which are reported in Table 4.1. The BET surface areas are also listed in Table 4.1. The surface area increases significantly upon the addition of zirconia to ceria, and remains nearly constant when comparing the mixed oxides with pure zirconia. Figure 4.1 and Table 4.1 show that the number of surface acidic sites increases with zirconia content. Pd/CeO$_x$ shows no appreciable surface acidity, as measured by TPD, while Pd/ZrO$_2$ has the maximum number of surface acid sites (212 μmol/g-cat or 1.4 μmol/m$^2$). Furthermore, the NH$_3$ desorption profiles of all catalysts display a single uniform peak in the range of 560-600 K. These results suggest that surface acidity is associated primarily with ZrO$_2$.

The CO$_2$ desorption profiles in Figure 4.2 show the presence of basic sites of varying CO$_2$ adsorption strength for different ceria/zirconia molar ratios. These profiles can be divided into three distinct regions representing weak adsorption sites (300-500 K), medium strength adsorption sites (500-700 K), and strong adsorption sites (700-1000 K) (14). The total numbers of CO$_2$ binding sites are given in Table 4.1 and the distributions of weak, medium and strong CO$_2$ binding sites are given in Table 4.2. According to the literature (10, 14), the weak sites for CO$_2$ binding are associated with the formation of hydroncarnonates due to surface OH$^-$ groups; the medium-strength sites are associated with M$^{x+}$--O$^{2-}$ pairs and the formation of bridged and bidentate carbonates; and the strong binding sites are associated with low coordination O$^{2-}$ ions and the formation of more strongly bound carbonates. All these species have been identified by FTIR studies of CO$_2$ adsorbed on ceria-zirconia mixed oxide catalysts together with pure ceria and zirconia by Daturi et al. (15).
According to our TPD results, strong CO$_2$ binding sites are associated with ceria only, since these sites gradually disappear as the ZrO$_2$ content increases, as shown in Table 4.2, whereas ZrO$_2$ possesses only weak and medium strength adsorption sites associated with OH$^-$ and M$^{x+}$--O$^2$ pairs.
The mixed-oxide catalysts show similar desorption profiles, and possess a mixture of weak, medium and strong (low coordination O\textsuperscript{2-} ions) binding sites. It is interesting to note that the mixed-oxide catalysts possess a greater number of intermediate strength binding sites than either Pd/CeO\textsubscript{2} or Pd/ZrO\textsubscript{2}. The presence of the aforementioned distribution of CO\textsubscript{2} binding sites on Ce\textsubscript{2}Zr\textsubscript{5}O\textsubscript{x}, Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x} and Ce\textsubscript{5}Zr\textsubscript{5}O\textsubscript{x} surfaces likely results from surface heterogeneity introduced by substituting Ce ions with Zr\textsuperscript{4+} ions. The addition of Zr to Ce increases the mobility of O\textsuperscript{2-} ions in the lattice (12, 16), and is therefore likely to cause a higher number of O\textsuperscript{2-} sites that bind CO\textsubscript{2} more strongly.

Figure 4.2 TPD of CO\textsubscript{2} on Pd/CeO\textsubscript{x}, Pd/Ce\textsubscript{5}Zr\textsubscript{2}O\textsubscript{x}, Pd/Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x}, Pd/Ce\textsubscript{5}Zr\textsubscript{5}O\textsubscript{x} and Pd/ZrO\textsubscript{2}. Site counts are presented with increasing offsets for clarity.
Table 4.1 Quantification of basic and acidic sites and BET surface areas of 0.25 wt. % Pd/CeO$_x$, Pd/Ce$_5$Zr$_2$O$_x$, Pd/Ce$_1$Zr$_1$O$_x$, Pd/Ce$_2$Zr$_5$O$_x$ and Pd/ZrO$_2$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO$_2$ (TPD) (µmol/g)</th>
<th>NH$_3$ (TPD) (µmol/g)</th>
<th>BET area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 wt. %Pd /CeO$_x$</td>
<td>266</td>
<td>0</td>
<td>88</td>
</tr>
<tr>
<td>0.25 wt. %Pd /Ce$_5$Zr$_2$O$_x$</td>
<td>414</td>
<td>27</td>
<td>131</td>
</tr>
<tr>
<td>0.25 wt. %Pd /Ce$_1$Zr$_1$O$_x$</td>
<td>380</td>
<td>54</td>
<td>133</td>
</tr>
<tr>
<td>0.25 wt. %Pd /Ce$_2$Zr$_5$O$_x$</td>
<td>350</td>
<td>86</td>
<td>141</td>
</tr>
<tr>
<td>0.25 wt. %Pd /ZrO$_2$</td>
<td>296</td>
<td>212</td>
<td>149</td>
</tr>
</tbody>
</table>

It is important to note that acid and base properties were attributed to metal oxide supports only, since we have shown in our previous work with TPD experiments that the presence of 0.25 wt% Pd doesn’t change the acid or base properties of Ce$_1$Zr$_1$O$_x$. (9)

Table 4.2 Quantification of weak, medium-strength and strong CO$_2$ binding sites over 0.25 wt. % Pd/CeO$_x$, Pd/Ce$_5$Zr$_2$O$_x$, Pd/Ce$_1$Zr$_1$O$_x$, Pd/Ce$_2$Zr$_5$O$_x$ and Pd/ZrO$_2$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO$_2$ (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak (T &lt; 500K)</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>0.25 wt. %Pd /CeO$_x$</td>
<td>95</td>
</tr>
<tr>
<td>0.25 wt. %Pd /Ce$_5$Zr$_2$O$_x$</td>
<td>131</td>
</tr>
<tr>
<td>0.25 wt. %Pd /Ce$_1$Zr$_1$O$_x$</td>
<td>142</td>
</tr>
<tr>
<td>0.25 wt. %Pd /Ce$_2$Zr$_5$O$_x$</td>
<td>129</td>
</tr>
<tr>
<td>0.25 wt. %Pd /ZrO$_2$</td>
<td>195</td>
</tr>
</tbody>
</table>

The XRD patterns collected after calcination of catalysts consisting of 0.25 wt. % Pd supported on ceria-zirconia mixed oxides with different compositions are shown in Figure 4.3. The fluorite cubic structure for pure ceria and a mixture of monoclinic and tetragonal phases for pure zirconia could be identified from these XRD patterns. For the ceria-rich solid solutions, only the cubic structure was detected, whereas a mixture of tetragonal and cubic phases was detected for zirconia-rich mixed oxides. As the zirconia content in the mixed oxide catalyst samples was increased, the XRD patterns displayed a small shift to higher values of 2θ, as compared to fluorite cubic CeO$_2$ (JCPDS # 43-1002), and this shift is associated with the lattice contraction caused by the introduction of smaller Zr$^{4+}$ ions into the CeO$_2$ lattice. No reflections
corresponding to palladium or palladium oxide phases were detected, indicating the presence of small (<4nm) particles. The XRD patterns obtained are similar with the measurements obtained by Serrano-Ruiz et al. and Solinas et al. (12, 17).

![XRD patterns for Pd/CeOₓ, Pd/CeₓZr₀.₅Oₓ, Pd/CeₓZr₁Oₓ, Pd/CeₓZr₅Oₓ and Pd/ZrO₂. Counts are presented with increasing offsets for clarity.](image)

**Figure 4.3** XRD patterns for Pd/CeOₓ, Pd/CeₓZr₀.₅Oₓ, Pd/CeₓZr₁Oₓ, Pd/CeₓZr₅Oₓ and Pd/ZrO₂. Counts are presented with increasing offsets for clarity.

### 4.3. Aldol Condensation/Hydrogenation Activity and Selectivity over 0.25 wt. %

**Pd/CeₓZr₃Oₓ Catalysts**

To study the effect of CO₂ and water on aldol condensation activity, experiments with pure 2-hexanone as the feed were first carried out for all catalysts. The activity and selectivity data for the conversion of 2-hexanone over Pd/CeₓZr₃Oₓ catalysts with different ceria to zirconia
ratios are given in Table 4.3, and these results are shown graphically in Figure 4.4. The 2-hexanone conversion increases with increasing ZrO$_2$ content, pure ZrO$_2$ having the highest conversion of 90%. The main product for all catalysts is the primary condensation product, 7-methyl-5-undecanone. The C$_{12}$ entry in Table 4.3 also includes 5-methyl-undecane, resulting from the deoxygenation of 7-methyl-5-undecanone. For all catalysts, C$_9$ and C$_{18}$ ketones could be observed. As the quantity of acid sites is increased with increasing zirconia content, the formation of 1,3,5-tributylbenzene becomes more significant, increasing the total selectivity to C$_{18}$ species. For Pd/Ce$_2$Zr$_5$O$_x$ and Pd/ZrO$_2$, very small amounts (1-3% selectivity) of even higher molecular weight species are observed.

**Table 4.3** Product distributions from conversion of 2-hexanone over 0.25 wt. % Pd/CeO$_x$, Pd/Ce$_5$Zr$_2$O$_x$, Pd/Ce$_2$Zr$_1$O$_x$, Pd/Ce$_2$Zr$_3$O$_x$ and Pd/ZrO$_2$ at 623 K and 5 bar, WHSV= 1.92 h$^{-1}$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Carbon Selectivities (%)</th>
<th>Alkanes (≤C$_7$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 wt.% Pd/CeO$_x$</td>
<td>40</td>
<td>77 - 1 2 4 16</td>
<td></td>
</tr>
<tr>
<td>0.25 wt.% Pd/Ce$_5$Zr$_2$O$_x$</td>
<td>58</td>
<td>79 - 3 5 3 10</td>
<td></td>
</tr>
<tr>
<td>0.25 wt.% Pd/Ce$_2$Zr$_1$O$_x$</td>
<td>58</td>
<td>83 - 5 2 2 8</td>
<td></td>
</tr>
<tr>
<td>0.25 wt.% Pd/Ce$_2$Zr$_3$O$_x$</td>
<td>84</td>
<td>77 3 5 6 1 8</td>
<td></td>
</tr>
<tr>
<td>0.25 wt.% Pd/ZrO$_2$</td>
<td>90</td>
<td>57 5 11 10 4 13</td>
<td></td>
</tr>
</tbody>
</table>

The total selectivity of all these species is reported in the entry C$_{18+}$. Furthermore, for these two catalysts, C$_{15}$ ketones were detected, resulting from the aldol condensation of 2-hexanone with C$_9$ ketones. Some of these species could not be identified definitively using the NIST library of the GC-MS, and their identification was based on the atomic mass of the molecular ion fragment and analogous species reported for acetone condensation (18, 19). Small amounts of C$_8$ and C$_{11}$ ketones may be obtained from C-C hydrogenolysis of the methyl branch of C$_9$ and C$_{12}$ ketones.
Figure 4.4 2-hexanone conversion and yields for product species over Pd/CeO$_x$, Pd/Ce$_5$Zr$_5$O$_x$, Pd/Ce$_7$Zr$_7$O$_x$, Pd/Ce$_2$Zr$_2$O$_x$ and Pd/ZrO$_2$ at 623 K and 5 bar, WHSV = 1.92 h$^{-1}$. C$_{12+}$ species consists of C$_{12}$ and higher molecular weight species (C$_{15+}$). See Table 4.3 for detailed carbon distribution among C$_{12+}$ as well as remaining product species.

The selectivity towards the C$_{12}$ products remains approximately constant for all the catalysts except for pure ZrO$_2$. It is possible to compare the selectivities over Pd/Ce$_2$Zr$_2$O$_x$ and Pd/ZrO$_2$ as the conversion values for the two catalysts are very similar. For pure ZrO$_2$, the selectivity shifts about 8% towards higher molecular weight species, mainly C$_{18}$ ketones and aromatics. This increase in the yield of C$_{18}$ aromatic species is due to the acidic nature of pure ZrO$_2$. The aromatization reaction is catalyzed by acid sites (19), and ZrO$_2$ has by far the highest number of acid sites as demonstrated by NH$_3$ TPD results in Table 4.1. Also, 2-hexanone conversion on Pd/ZrO$_2$ catalyst produces higher amounts of C-C cleavage products, such as C$_8$-C$_{11}$ ketones and lighter alkanes, at the expense of C$_{12}$ species. The large number of surface acid
sites for Pd/ZrO$_2$ is responsible for the increase in selectivity towards light alkanes, mainly hexane, as the dehydration of 2-hexanol to hexene is mainly catalyzed by acid sites. As shown in the earlier chapter, a double-bond shift or isomerization is a part of the pathway for the production of C$_9$ ketones and this isomerization can also be catalyzed by acid sites (20) which are more abundant on Pd/ZrO$_2$ as compared to Pd/Ce$_2$Zr$_3$O$_x$. The increased activity of C-C hydrogenolysis to produce C$_8$ and C$_{11}$ ketones on Pd/ZrO$_2$ may result from the absence of strong metal-support interactions (SMSI). In particular, it is known in the literature that ceria exhibits strong metal-support interactions (21), and the rate of C-C hydrogenolysis can be suppressed by the presence of SMSI (22). We have shown in our previous work (9) with temperature programmed reduction (TPR) experiments that reduction of ceria occurs at our reduction temperatures, which is required for the onset of SMSI.

Pd dispersions were not measured for the catalysts except for Pd/Ce$_1$Zr$_1$O$_x$ shown in the previous chapter. We saw from this previous work that it is hard to quantify accessible Pd sites by irreversible CO adsorption measurements with the presence of a reducible oxide support, i.e. CeO$_2$, as reduction of Ce$^{4+}$ to Ce$^{3+}$ also takes place due to the hydrogen spillover effect and contribute to CO adsorption. Serrano-Ruiz et al. studied atomic Pt/(Ce+Zr) ratios for Pt/Ce$_x$Zr$_y$O$_x$ catalysts with XPS as a representation of dispersion and found that platinum dispersion decreases slightly with decreasing ceria content. (12) Applying the results of the authors for Pt to the Pd/Ce$_x$Zr$_y$O$_x$ catalysts we prepared, highest dispersion is expected for Pd/CeO$_2$. The probable low metal dispersions for zirconia-rich mixed oxide catalysts do not seem to be an issue in terms of limiting hydrogenation rate of α-β unsaturated ketone, which is an important step to overcome the equilibrium limitation of aldol condensation reaction and reach high conversion. This is demonstrated by complete conversion of α-β unsaturated ketone (aldol condensation product) to
the saturated ketone for all experiments, proving that hydrogenation is a fast step in the reaction network. However, metal dispersion might be important in terms of side reactions such as hydrogenolysis and hydrogenation to yield light alkanes. This might be the reason for higher selectivity towards light alkanes over Pd/CeO$_x$ even at low conversion. It is interesting to note that at the same conversion (~40%), Pd/ZrO$_2$ only generates high molecular weight species, as shown in Table 4.4.

Table 4.4 2-hexanone conversion and product distribution for Pd/ZrO$_2$ and Pd/Ce$_x$Zr$_1$O$_x$ at 598 K, WHSV=256 h$^{-1}$ and 5 bar.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>2-hexanone conversion (%)</th>
<th>Carbon Selectivites (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C$_{12}$</td>
</tr>
<tr>
<td>0.25 wt.% Pd/Ce$_x$Zr$_1$O$_x$</td>
<td>5</td>
<td>99</td>
</tr>
<tr>
<td>0.25 wt.% Pd/ZrO$_2$</td>
<td>39</td>
<td>98</td>
</tr>
</tbody>
</table>

The high activities displayed by Pd/Ce$_x$Zr$_5$O$_x$ and Pd/ZrO$_2$ compared to our original catalyst Pd/Ce$_x$Zr$_1$O$_x$ are promising in terms of improving the C-C coupling yield. The conversion values for both of these catalysts are similar (84 and 90%), and the selectivity for Pd/ZrO$_2$ shows a significant shift towards higher molecular weight ketones and aromatic species and C-C cleavage products. Figure 4.4 demonstrates the trend in 2-hexanone conversion, C$_{12}$ yield and C$_{12+}$ yield as the zirconia content in the mixed oxides is changed. It can be seen that while the 2-hexanone conversion and the C$_{15+}$ yield continuously increase with increasing zirconia content, the C$_{12}$ and total C$_{12+}$ yield pass through a maximum with Pd/Ce$_x$Zr$_5$O$_x$. Pd/ZrO$_2$ is the second best catalyst in terms of C$_{12}$ and total C$_{12+}$ yields. This variation in the product selectivity brings flexibility to the process, in which Pd/Ce$_x$Zr$_5$O$_x$ can be used to obtain high yields of the primary condensation product, whereas Pd/ZrO$_2$ would be preferred to increase the content of higher molecular weight species or aromatics in the product stream. It is likely that
side reactions are more significant over Pd/ZrO₂ due to the high density of acid sites and C₁₂ selectivity can be increased if a higher WHSV is used. The increase in activity with increasing zirconia content in the mixed oxide catalyst can be attributed to changes in the intrinsic properties of the catalyst, i.e. acid-base properties, and/or increased resistance to water inhibition (that is generated in aldol condensation and dehydration steps in the reaction network). These two possibilities are discussed further in the following sections.

In terms of acid-base properties, CeOₓ possesses weak CO₂ binding sites (surface OH⁻ groups)(23), as well as a second peak observed in the desorption profile at about 1000 K due to the formation of stable carbonates. As the ceria content decreases, these carbonates gradually disappear, and for all the mixed oxides, a distribution among weak, medium and strong CO₂ binding sites is achieved, corresponding to surface OH⁻, M⁺⁻O²⁻ pairs, and low coordination O²⁻ sites. These mixed oxides show higher activity than pure CeOₓ. Therefore, it is probable that both surface OH- ions and M⁺⁻O²⁻ pairs contribute to aldol condensation activity, and the mixed oxides contain more of these sites per gram of catalyst compared to pure CeOₓ. In addition, it has been reported that low coordination O²⁻ sites show low activity for C-C bond formation (14, 23). This behavior is also supported by the fact that Pd/ZrO₂ shows high aldol condensation activity in the absence of the strong CO₂ binding O²⁻ sites. These isolated O²⁻ sites lack the acid-base site pairing that can more easily activate the C-H bond for carbanion formation (14). Pure ZrO₂, on the other hand, has only surface OH⁻ sites and M⁺⁻O²⁻ pairs, as shown by Bianchi et al. and Daturi et al. (15, 24). It is also possible that aldol coupling proceeds via an acid catalyzed mechanism on zirconia and zirconia-rich mixed oxides, and the high content of acidic sites contributes to the overall activity. For example, Chen et al. achieved reasonable conversions for self condensation of acetone over Pd/(Nb₂O₅/SiO₂) (25).
4.4. Effect of CO\textsubscript{2} and Water Co-feeding

To explore the effect of CO\textsubscript{2} on condensation activity over the catalysts with different compositions, we have substituted the pure hydrogen gas co-feed used above with H\textsubscript{2}-CO\textsubscript{2} gas mixtures. All ceria-containing catalysts displayed significant inhibition by CO\textsubscript{2}, showing yields of less than 20\% to C-C coupling products. The decrease in activity for these catalysts can be correlated with the abundance of isolated O\textsuperscript{2-} sites that strongly bind CO\textsubscript{2}, as shown in CO\textsubscript{2} TPD profiles. On the other hand, Pd/ZrO\textsubscript{2} showed significant resistance to CO\textsubscript{2} poisoning (20\% decrease in condensation activity), and this catalyst does not contain strong CO\textsubscript{2} binding sites. The effect of CO\textsubscript{2} co-feeding on activity and selectivity to condensation products are shown in Table 4.5 for all the catalysts.

Table 4.5 2-hexanone conversion and product distribution over 0.25 wt. \% Pd/CeO\textsubscript{x}, Pd/Ce\textsubscript{5}Zr\textsubscript{2}O\textsubscript{x}, Pd/Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x}, Pd/Ce\textsubscript{2}Zr\textsubscript{5}O\textsubscript{x} and Pd/ZrO\textsubscript{2} with co-feeding 10mol\% CO\textsubscript{2} in H\textsubscript{2} stream at 623 K and 5 bar, WHSV=1.92h\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>2-hexanone conversion (%)</th>
<th>Carbon Selectivities (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 wt.% Pd/CeO\textsubscript{x}</td>
<td>4</td>
<td>34</td>
</tr>
<tr>
<td>0.25 wt.% Pd/Ce\textsubscript{5}Zr\textsubscript{2}O\textsubscript{x}</td>
<td>5</td>
<td>36</td>
</tr>
<tr>
<td>0.25 wt.% Pd/Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x}</td>
<td>5</td>
<td>22</td>
</tr>
<tr>
<td>0.25 wt.% Pd/Ce\textsubscript{2}Zr\textsubscript{5}O\textsubscript{x}</td>
<td>19</td>
<td>55</td>
</tr>
<tr>
<td>0.25 wt.% Pd/ZrO\textsubscript{x}</td>
<td>72</td>
<td>62</td>
</tr>
</tbody>
</table>

In addition to CO\textsubscript{2}, water is another by-product of ketonization, which we showed previously to cause a decrease by 40\% in the activity for aldol condensation of 2-butanone over Pd/CeZrO\textsubscript{x} when a mixture containing 12 wt\% water in 2-butanone was used as the feed. (9) This inhibition by water is an additional obstacle to integrating ketonization and aldol condensation/hydrogenation steps. Therefore, we have studied the effect of water on the aldol condensation activity over Pd/ZrO\textsubscript{2} by co-feeding water with 2-butanone. In these studies, 2-
butanone was chosen as the reactant, because it can be saturated with a larger amount of water (~12 wt%) than 2-hexanone, and this water content is representative of the products of ketonization. The effect of water co-feeding over Pd/ZrO₂ is compared in Table 4.6 with the effect of water addition over Pd/Ce₁Zr₁Oₓ. It can be seen that the catalytic activity decreases by about 10% for the case of Pd/ZrO₂ compared to a 40% decrease for Pd/Ce₁Zr₁Oₓ. The selectivity shifts slightly towards the primary condensation product, 5-methyl-3-heptanone, at the expense of secondary reaction products for both catalysts. The diminished inhibition of aldol condensation reaction by water and CO₂ over Pd/ZrO₂ makes this catalyst suitable for the integration of ketonization and aldol condensation/hydrogenation.

**Table 4.6** 2-butanol conversion and product distribution over Pd/ZrO₂ and Pd/Ce₁Zr₁Oₓ with and without the presence of water in the feed at 623 K and 5 bar, WHSV= 1.92 h⁻¹.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Feed</th>
<th>2-butanol conversion (%)</th>
<th>Carbon Selectivities (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 wt.% Pd/Ce₁Zr₁Oₓ</td>
<td>2-butanol</td>
<td>69</td>
<td>91 5</td>
</tr>
<tr>
<td>0.25 wt.% Pd/Ce₁Zr₁Oₓ</td>
<td>12 wt.% water in 2-butanol</td>
<td>37</td>
<td>93 3</td>
</tr>
<tr>
<td>0.25 wt.% Pd/ZrO₂</td>
<td>2-butanol</td>
<td>88</td>
<td>77 11</td>
</tr>
<tr>
<td>0.25 wt.% Pd/ZrO₂</td>
<td>12 wt.% water in 2-butanol</td>
<td>78</td>
<td>80 9</td>
</tr>
</tbody>
</table>

We now consider whether the higher activity of Pd/ZrO₂ might be partially or completely due to the resistance of this catalyst to water inhibition, because water is a product of aldol-condensation/hydrogenation. To investigate this possibility, the activity for 2-hexanone coupling was measured over both Pd/ZrO₂ and Pd/Ce₁Zr₁Oₓ at low conversions, where water generation is minimal. The reaction conditions were adjusted to 598 K, 5 bar and WHSV=256 h⁻¹, such that the 2-hexanone conversion remained under 40%, and the results are presented in Table 4.4.

The 2-hexanone conversion over Pd/ZrO₂ at these conditions was 39% whereas it was only 5% over Pd/Ce₁Zr₁Oₓ. At these low conversions both catalysts showed high selectivities
towards the primary condensation product, 7-methyl-5-undecanone. These results demonstrate that Pd/ZrO$_2$ is still significantly more active compared to Pd/Ce$_i$Zr$_j$O$_x$ when water inhibition is minimized. Even though the resistance to water inhibition might play a role for the performance of Pd/ZrO$_2$ at high conversions, it is not the only cause for the enhanced activity of Pd/ZrO$_2$ as compared to Pd/Ce$_i$Zr$_j$O$_x$.

4.5. Integration of Ketonization and Aldol Condensation/Hydrogenation Reactions in a Single Reactor, Double Bed System for a Simulated Feed Mixture

The results of this study involving different compositions of ceria-zirconia mixed oxide catalysts indicate that Pd/ZrO$_2$ is the preferred catalyst to be used for integration of ketonization and aldol condensation/hydrogenation reactions in a single reactor system. Pd/ZrO$_2$ has high activity and it is resistant to inhibition by CO$_2$ and water. To test the applicability of a double bed system, a 20 mol% mixture of butanoic acid in 2-hexanone was used as the feed. Before using the double bed set up, the following conditions for complete conversion of butanoic acid over Ce$_i$Zr$_j$O$_x$ in the ketonization step were found: 623 K and 5 bar, and WHSV= 1.92 h$^{-1}$. Under these conditions, butanoic acid reacted with 100% conversion to the ketonization product, 4-heptanone, and 6% of the 2-hexanone was converted to yield the primary aldol condensation product – an unsaturated C$_{12}$ ketone - and C-C cleavage products (C$_{11}$ and C$_9$ ketones). The double bed system was then set up by adding a downstream Pd/ZrO$_2$ catalyst to achieve aldol condensation/hydrogenation following the ketonization step. The reaction system was carried out at 623 K and 5 bar, with H$_2$ co-feed for a liquid feed of 2-hexanone containing 20 mol% butanoic acid, compared to a liquid feed of 2-hexanone containing 20 mol% heptane (as an inert species). Results obtained for these two runs are presented in Table 4.7. The heptane containing mixture
was used in a control experiment to test for the effects of CO$_2$ generated by ketonization. C$_{12}$ species include 7-methyl-5-undecanone and 5-methyl-undecane. C$_{18+}$ species include the condensation product of 7-methyl-5-undecanone and 2-hexanone, 1,3,5-tributylbenzene and a small fraction of higher molecular weight species. C$_{15}$ ketone is the condensation product of 2-hexanone and C$_9$ ketone. C$_8$ and C$_{11}$ ketones are obtained from C-C hydrogenolysis reactions as discussed previously. Finally, lighter alkanes are obtained from dehydration/hydrogenation of the feed, and reforming reactions of the alcohols formed within the reaction network. It can be seen that there is little difference between the activity and selectivity values for the two runs. These results show that Pd/ZrO$_2$ is resistant to the CO$_2$ and water generated in the ketonization step for this simulated feed mixture and that the double bed system can be successfully implemented.

**Table 4.7** 2-hexanone and butanoic acid conversions and product selectivities for reaction of 2-hexanone containing 20 mol% butanoic acid or 20 mol% heptane over the double-bed system at 623 K and 5 bar.

<table>
<thead>
<tr>
<th>Feed (balance 2-hexanone)</th>
<th>Conversion (%)</th>
<th>Carbon Selectivities (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-hexanone</td>
<td>Butanoic acid</td>
</tr>
<tr>
<td>20 mol% heptane</td>
<td>76</td>
<td>-</td>
</tr>
<tr>
<td>20 mol% butanoic acid</td>
<td>75</td>
<td>100</td>
</tr>
</tbody>
</table>

**4.6. Conclusions**

Production of liquid transportation fuels by catalytic upgrading of hydrophobic mixtures of mono-functional intermediates obtained from carbohydrates over Pt-Re/C can be achieved by the integration in a single reactor of ketonization and aldol condensation/hydrogenation steps. With this integration of steps, the energy consumption as well as reactor infrastructure associated with cooling and re-heating the products obtained from ketonization prior to the aldol condensation/hydrogenation step can be eliminated. For this integration to be realized, the catalyst for aldol condensation must be resistant to inhibition by the CO$_2$ and water produced in
the ketonization step. We have found that Pd/Ce\textsubscript{2}Zr\textsubscript{5}O\textsubscript{x} and Pd/ZrO\textsubscript{2} show high activity for aldol condensation of 2-hexanone, a representative ketone produced from carbohydrates over Pt-Re/C. Formation of C\textsubscript{12} products was predominant on both catalysts, and secondary reaction products, such as C\textsubscript{18} ketones and aromatic species, were produced with higher selectivities over Pd/ZrO\textsubscript{2}, likely due to the high surface acidity of this catalyst. The inhibiting effect of CO\textsubscript{2} on the rate of aldol condensation was significant over all compositions of ceria-zirconia mixed oxide catalysts, as well as pure CeO\textsubscript{2}. However, Pd/ZrO\textsubscript{2} was found to be substantially more resistant to CO\textsubscript{2} inhibition. The effect of water co-feeding was investigated over Pd/ZrO\textsubscript{2}, in comparison with Pd/Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x}, and it was found that Pd/ZrO\textsubscript{2} was also more resistant to water inhibition compared to Pd/Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x}. With these promising catalytic properties of Pd/ZrO\textsubscript{2}, a double bed system consisting of Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x} (for ketonization) followed by Pd/ZrO\textsubscript{2} (for aldol condensation) was successfully implemented to achieve the combined C-C coupling of carboxylic acids and ketones, as illustrated with a simulated mixture of 20 mol% butanoic acid in 2-hexanone.

4.7. References

Chapter 5: Dual-bed catalyst system for C-C coupling of biomass-derived oxygenated hydrocarbons to fuel-grade compounds

As mentioned in the previous chapters, a promising strategy for catalytic upgrading of mono-functional intermediates to produce liquid transportation fuels is to carry out C-C coupling of carboxylic acids by ketonization processes, forming higher molecular weight linear ketones plus CO\textsubscript{2} and H\textsubscript{2}O\textsuperscript{,}(1) followed by additional C-C coupling reactions of ketones and alcohols by aldol condensation/hydrogenation to produce heavier branched ketones.(2) The ketonization processing must be carried out up-stream of aldol-condensation/hydrogenation reactions, because this latter processing step requires basic catalyst sites, and these sites are poisoned by carboxylic acids.(3) Similar reaction conditions should allow the integration of these two processes in a single reactor. However, an important issue that must be addressed is the extent to which the catalyst employed for aldol-condensation/hydrogenation is inhibited by the CO\textsubscript{2} and water by-products of ketonization reactions. In the present chapter, we show that Pd/ZrO\textsubscript{2} catalysts are effective for aldol-condensation/hydrogenation in the presence of CO\textsubscript{2} and water, allowing for the integration of ketonization and aldol-condensation/hydrogenation processes for achieving C-C coupling of mono-functional intermediates in a single reactor, dual-bed catalyst system, thereby streamlining the overall catalytic upgrading process. The novelty of this process lies in the integration of two separate C-C coupling processes such that an alkane stream highly suitable for diesel fuel can be obtained only in a two stage process, latter being a dehydration/hydrogenation step to convert long-carbon chain ketones to alkanes, starting from biomass-derived mono-oxygenated streams. This combined process can be used for any
oxygenate stream that contains carboxylic acids, carbonyl and alcohol species and has a very high potential for application in a bio-refinery industry that is in immediate need for development of new and efficiently streamlined processes.

In our previous work, we studied a Pd/Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x} catalyst for the aldol condensation of 2-hexanone (a representative ketone) in the presence of CO\textsubscript{2} and water. These experiments showed a decrease by 90% and 40% in catalytic activity with the introduction into the feed stream of CO\textsubscript{2} and water, respectively, and we concluded that it would be difficult to integrate ketonization with aldol-condensation in a single reactor.\((3)\) In the previous chapter, we investigated the extent of CO\textsubscript{2} inhibition on aldol condensation over catalysts prepared by depositing Pd on different compositions of ceria-zirconia mixed oxides (Ce\textsubscript{a}Zr\textsubscript{b}O\textsubscript{x}), including pure ceria and zirconia, and we found that Pd/ZrO\textsubscript{2} showed the best resistance towards CO\textsubscript{2} inhibition. In addition to this important feature, Pd/ZrO\textsubscript{2} also showed higher activity compared to Pd/Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x} catalyst, as well as good resistance to water inhibition. The feasibility of a dual-bed catalyst system was studied using a mixture of a carboxylic acid and a ketone (20 mol\% butanoic acid in 2-hexanone), and the integrated process showed high activity as well as selectivity to C-C coupling products.\((4)\) Following these promising results, this chapter presents a detailed comparison of catalytic upgrading processes for a mixture of mono-functional intermediates obtained by conversion of an aqueous solution of 60 wt\% sorbitol over a PtRe/C catalyst. Specifically, we compare the performance of two separate reactors for ketonization over Ce\textsubscript{1}Zr\textsubscript{1}O\textsubscript{x} followed by aldol condensation/hydrogenation over 0.25 wt\% Pd/ZrO\textsubscript{2}, with removal of CO\textsubscript{2} and water between reactors, versus the performance of a dual-bed of these two catalysts in a single reactor.
5.1. Experimental

5.1.1. Catalyst Preparation

The Pt-Re/C catalyst was prepared by incipient wetness impregnation of carbon black (Norit-SX1G) with an aqueous solution of H₂PtCl₆·6H₂O and HReO₄ to yield a catalyst with loadings of 5.1 wt% Pt and 4.9 wt% Re. (5) The CeZrOₓ support with a 1:1 Ce:Zr molar ratio was prepared via co-precipitation of Ce(NO₃)₃ and ZrO(NO₃)₂ with NH₄OH (Aldrich) and ZrO₂ support was prepared via precipitation of ZrO(NO₃)₂ with NH₄OH (Aldrich) according to Serrano-Ruiz, et al. (6) The Pd/ZrO₂ catalyst was prepared via incipient wetness impregnation of ZrO₂ with an amount of aqueous solution of Pd(NO₃)₂ (Aldrich) necessary to obtain a nominal metal loading of 0.25 wt. %. The catalyst was dried in air at 373 K overnight and calcined in air at 623 K for 2 h. Pt/SiO₂-Al₂O₃ catalyst was prepared by incipient wetness impregnation of SiO₂-Al₂O₃ (Grace Davision, MS-25 FCC Catalyst Sample) with an amount of aqueous solution of Pt(NH₃)₄(NO₃)₂ required to obtain a nominal metal loading of 2 wt.% The catalyst was dried in air at 373 K overnight and calcined in air at 533 K for 2 h.

5.1.2. Reaction Kinetics Studies

The conversion of 60 wt% sorbitol solution over Pt-Re/C was carried out at 18 bar and at 503 K with a flow rate of 0.04 mL/min. (5) The ketonization reaction of the organic liquid obtained from sorbitol feed was carried out over Ce₁Zr₁Oₓ at 623 K, pressure of 5 bar, and a liquid flow rate of 0.02 mL/min with 4 g catalyst. The aldol condensation reaction was carried out over Pd/ZrO₂ at 623 K and 5 bar with 0.02 mL/min liquid flow (2 g catalyst). The molar ratio of the gas flow rate to the liquid flow rate was maintained at 5.5 for both
reactions. The hydrodeoxygenation reactions were carried out over 2 wt. % Pt/SiO$_2$-Al$_2$O$_3$ at 573 K, 28.5 bar and a liquid flow rate of 0.02 mL/min with 2 g catalyst and 50 mL/min of H$_2$ flow. A fixed bed, down-flow reactor consisting of a half-inch stainless steel tube was used for all experiments as described in Chapter 2. The Pt-Re/C catalyst was mixed with equal volume of whole fused SiO$_2$ granules whereas Ce$_1$Zr$_1$O$_x$, Pd/ZrO$_2$ and Pt/ SiO$_2$-Al$_2$O$_3$ catalysts were mixed with crushed fused SiO$_2$ granules (Aldrich) in a 2:1 volumetric ratio to maintain bed height. The Pt-Re/C catalyst was reduced in situ at 723 K (ramp rate of 0.5 K min$^{-1}$) for 2 h, Ce$_1$Zr$_1$O$_x$ and Pd/ZrO$_2$ catalysts were reduced in-situ at 623 K (ramp rate of 0.5 K min$^{-1}$) for 2 h and Pt/SiO$_2$-Al$_2$O$_3$ catalyst was reduced in situ at 573 K (ramp rate of 0.5 K min$^{-1}$) for 2 h in flowing H$_2$ (200 cm$^3$(STP) min$^{-1}$). After the reduction was completed, the temperature and pressure were adjusted and the feed flow was started without flowing H$_2$ for Pt-Re/C and with flowing H$_2$ for the C-C coupling and hydrodeoxygenation reactions. The weight hourly space velocity (WHSV) was calculated for experiments using the mass flow rate of the liquid flow into the reactor and the mass of the catalyst used.

Experiments employing a double bed, single reactor configuration were performed in a fixed bed, down-flow reactor system consisting of a half-inch stainless steel tube. In contrast to the single bed experiments, two different catalysts were loaded in the same reactor, separated by whole fused SiO$_2$ granules. Pd/ZrO$_2$ catalyst (2 g) was placed on the quartz wool and fused SiO$_2$ granules were placed on top of this bed. Ce$_1$Zr$_1$O$_x$ catalyst (4 g) was then placed on the silica chips, so that the feed could pass through the ketonization catalyst first and the aldol condensation/hydrogenation catalyst second. Both catalysts were mixed with crushed fused SiO$_2$ granules (Aldrich) in a 1:1 volumetric ratio.

For all experiments, the rate of gas production was measured with a bubble flow
meter. An HP GC5890 gas chromatograph, equipped with a Haysep DB 100/120 column (Alltech) and thermal conductivity detector (TCD), was used to quantify CO and CO₂, and an Agilent GC6890, equipped with an Rtx column (Agilent) and a flame ionization detector (FID), was used to quantify gas-phase alkanes. Liquid phase analysis was performed with a Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID detector and a Shimadzu 2060 GC/MS with a NIST library of spectra. Liquid and gas analysis points were collected every 2-3 h, and steady state was usually achieved after 6 h time-on-stream.

5.2. Integration of Ketonization and Aldol Condensation Reactions

A liquid stream of mono-functional intermediates was obtained by processing an aqueous solution containing 60 wt% sorbitol over a 10 wt% Pt-Re/C catalyst at 503 K and 18 bar, operating at a weight hourly space velocity (WHSV) equal to 0.6 h⁻¹ over the course of one month, during which the catalyst bed remained stable. The carbon distribution among the gaseous phase, aqueous phase and organic phase (the latter denoted as inter-oil) is given in Table 5.1. The gas phase effluent contains about 39% of the carbon feed and consists of COₓ and light alkanes (C₁-C₆), and the aqueous phase (10% of the carbon feed) consists of higher oxygenates such as isosorbide. The carbon distribution in the inter-oil feed used for subsequent catalytic upgrading studies is shown in Table 5.1. (We note that the amount of C₄-C₆ alkanes in the inter-oil decreased to 1% from 8% due to evaporation during the time required to produce the inter-oil (e.g., 1 month) to the time at which the inter-oil was used as a feed for catalytic upgrading studies.) For the cascade system of two reactors, the organic liquid product of the ketonization reactor was collected over a period of time and then used as the feed for the aldol condensation/hydrogenation reactor, whereas the inter-oil feed was
supplied continuously to the dual-bed, single-reactor catalyst system. For both reactor systems, the effluent stream obtained from aldol condensation/hydrogenation step consisted of a mixture of ketones and alkanes that could not be readily separated in the GC and GC-MS. Accordingly, these streams were subjected to dehydration/hydrogenation reaction over a 2 wt% Pt/SiO$_2$-Al$_2$O$_3$ catalyst (denoted as Pt/SiAl) to obtain a mixture of linear and branched alkanes only, which are well separated in the GC.

Figure 5.1 shows reaction pathways involved in ketonization, aldol condensation/hydrogenation and dehydration/hydrogenation for representative C$_5$ species. Acids combine in ketonization reactions to form linear ketones, CO$_2$ and water, whereas ketones and alcohols combine in aldol condensation/hydrogenation reactions to form branched ketones and water.

![Reaction pathways](image)

**Figure 5.1** Reaction pathways for ketonization, aldol condensation/hydrogenation and dehydration/hydrogenation for representative C$_5$ species. Species II$_a$ and II$_b$ are formed by ring-opening through C-O bond cleavages denoted in the figure.

Under our reaction conditions secondary alcohols are equilibrated with corresponding ketones through metal (Pd) catalyzed dehydrogenation reaction. The condensation of alcohols are therefore initiated with the dehydrogenation reaction to form ketones. Similarly, primary alcohols can be condensed via the formation of aldehydes with the equilibrated
dehydrogenation reaction. When 2-ketones and/or secondary alcohols are combined, single methyl-branched ketones are obtained. When a 3-ketone/alcohol combines with a 2-ketone/alcohol, single ethyl branched ketones can be obtained.

Finally, when 3-ketones or tertiary alcohols undergo self-coupling, multiple branching in the product ketone takes place. Ring opening reactions of heterocyclics can also take place over Pd/ZrO$_2$ to form aldehydes or ketones, depending on the structure of the heterocyclic molecule and the location of C-C cleavage in the molecule. An aldehyde formed in this manner can couple with 2-ketones to form other linear ketones. In addition to coupling reactions, mono-functional species are also converted into alkanes over Pd/ZrO$_2$. As mentioned earlier, ketones are in equilibrium with the corresponding alcohols in our reaction conditions, and alkanes can be formed by α-scission over Pd sites and/or dehydration/hydrogenation of these alcohols over acid/metal sites. This latter pathway is important for Pd/ZrO$_2$ in view of the high concentration of acid sites for this catalyst,(4) leading to the formation of alkanes especially at low space velocities. The distributions of carbon in the effluent streams from various reactors involved in the overall conversion of sorbitol to hydrocarbons are shown in Figures 5.2A and 5.2B, starting from the conversion of the sorbitol solution over Pt-Re/C, followed by upgrading processes in the cascade system (Figure 5.2A) or the dual-bed catalyst system (Figure 5.2B). Table 5.2 summarizes the values for overall conversion of mono-functional species and the overall yield of C$_{7+}$ species, together with the selectivity values. In the cascade system, acids are completely converted to heavier linear ketones (C$_7$-C$_{11}$) in the ketonization reactor over Ce$_1$Zr$_1$O$_x$. Approximately 7% of the carbon leaves the ketonization reactor in the gaseous phase, and 20% and 40% of this gas stream consists of C$_1$-C$_6$ alkanes and CO$_x$ respectively, with the remainder being
present as mono-functional species. The liquid stream consists of heavy linear ketones and unreacted mono-functional species.

Table 5.1 Molar carbon distribution for the conversion of 60 wt% sorbitol solution over Pt-Re/C at 503 K and 18 bar with WHSV = 0.6 h⁻¹.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Carbon Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic (Inter-oil)</td>
<td>51</td>
</tr>
<tr>
<td>Gaseous</td>
<td>39</td>
</tr>
<tr>
<td>Aqueous</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species in the organic liquid (Inter-oil)</th>
<th>Carbon distribution in the organic liquid (Inter-oil) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>1</td>
</tr>
<tr>
<td>2-ketones</td>
<td>21</td>
</tr>
<tr>
<td>2-butanone</td>
<td>3</td>
</tr>
<tr>
<td>2-pentanone</td>
<td>7</td>
</tr>
<tr>
<td>2-hexanone</td>
<td>11</td>
</tr>
<tr>
<td>3-ketones</td>
<td>10</td>
</tr>
<tr>
<td>3-pentanone</td>
<td>3</td>
</tr>
<tr>
<td>3-hexanone</td>
<td>7</td>
</tr>
<tr>
<td>2°alcohols</td>
<td>15</td>
</tr>
<tr>
<td>2-butanol</td>
<td>3</td>
</tr>
<tr>
<td>2-pentanol</td>
<td>5</td>
</tr>
<tr>
<td>2-hexanol</td>
<td>7</td>
</tr>
<tr>
<td>3°alcohols</td>
<td>5</td>
</tr>
<tr>
<td>3-pentanol</td>
<td>2</td>
</tr>
<tr>
<td>3-hexanol</td>
<td>3</td>
</tr>
<tr>
<td>1°alcohols</td>
<td>1</td>
</tr>
<tr>
<td>1-butanol</td>
<td>1</td>
</tr>
<tr>
<td>Heterocyclics</td>
<td>30</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>3</td>
</tr>
<tr>
<td>2-Methyl-THF</td>
<td>7</td>
</tr>
<tr>
<td>Tetrahydropyran (THP)</td>
<td>2</td>
</tr>
<tr>
<td>2-Methyl-THP</td>
<td>3</td>
</tr>
<tr>
<td>2,5-DiMethyl-THF</td>
<td>9</td>
</tr>
<tr>
<td>2-Ethyl-THF</td>
<td>6</td>
</tr>
<tr>
<td>Carboxylic Acids</td>
<td>17</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>9</td>
</tr>
<tr>
<td>Pentanoic acid</td>
<td>5</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>3</td>
</tr>
</tbody>
</table>

This stream is then subjected to aldol condensation/hydrogenation over Pd/ZrO₂ in a separate reactor. The extent of alkane formation is more significant for this reactor, such that 19% of the carbon fed to the reactor leaves in the gas phase, 86% of this gas stream being
present as light alkanes. In addition, 11% of the inlet carbon exits in the liquid stream as C$_4$-C$_6$ alkanes.

![Diagram of carbon conversion process]

**Figure 5.2** Distribution of carbon for conversion of 60 wt% sorbitol solution over Pt-Re/C, ketonization of mono-functional intermediates over CeZrO$_x$ (WHSV = 0.24 h$^{-1}$) followed by aldol condensation/hydrogenation over 0.25 wt% Pd/ZrO$_2$ (WHSV = 0.48 h$^{-1}$) A) in a cascade system and B) in a dual-bed catalyst system.

The product C$_7^+$ species consist of both ketones and alkanes. The overall yield to C$_7^+$ species based on the inter-oil feed is 42%, with 71% conversion of the mono-functional species. The reported selectivities are based on the difference between the amount of mono-functional species in the feed and amount present in the liquid effluent of the aldol condensation reactor. It is calculated that 7% of the mono-functional species is lost to the gas phase, 55% is converted to C$_7^+$ species, and 38% is converted into C$_1$-C$_6$ alkanes. In the dual-
bed catalyst system, about 20% of the carbon feed leaves the reactor in the gas phase, only 14% of this gas stream being unconverted mono-functional intermediates. The remainder of the gas phase consists of C$_1$-C$_6$ alkanes (76%) and CO$_x$ (10%). In addition, 7% of the inlet carbon leaves the reactor as C$_4$-C$_6$ alkanes in the liquid stream. The rest of the liquid stream consists of C$_{7+}$ species and unconverted mono-functional species, corresponding to 42% and 31% of the inlet carbon, respectively. The overall yield for the dual-bed system is 42%, with 66% conversion of mono-functional species. Selectivity values and loss of mono-functional species to the gas phase are calculated the same way as in the cascade system, and these values are shown in Table 5.2. It is apparent from the data in Table 5.2 that the performance of the two reactor systems is essentially the same. The dual-bed, single reactor system is thus the preferred mode of catalytic upgrading, because the energy consumption as well as the reactor infrastructure associated with cooling and re-heating the products obtained from ketonization prior to the aldol condensation/hydrogenation step can be eliminated.

**Table 5.2** Comparison of dual-bed catalyst system and cascade system for conversion of mono-functional compounds.

<table>
<thead>
<tr>
<th></th>
<th>Dual-bed system</th>
<th>Cascade system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall conversion of mono-functional species (%)</td>
<td>66</td>
<td>71</td>
</tr>
<tr>
<td>Selectivity of C$_{7+}$ products (%)</td>
<td>61</td>
<td>55</td>
</tr>
<tr>
<td>Selectivity of light alkanes (%)</td>
<td>36</td>
<td>38</td>
</tr>
<tr>
<td>Loss of mono-functional species to gas phase (%)</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>Overall yield to C$_{7+}$ products (%)</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>Branched ketones/linear ketones</td>
<td>1.04</td>
<td>0.96</td>
</tr>
</tbody>
</table>

As mentioned earlier, both of the effluent streams from aldol condensation/hydrogenation were subjected to dehydration/hydrogenation reactions over Pt/SiAl. In this way, linear alkanes and branched alkanes could be separated from each other.
and the corresponding ketones could be quantified. The ratios of branched to linear ketones for the two reactor configurations are shown in Table 5.2, and both ratios are approximately equal to 1. The concentration of linear ketones formed by ketonization is known from the effluent of the ketonization reactor of the cascade system. If the rest of the C\textsubscript{7+} species in the final effluent were branched species formed by the condensation of ketones and alcohols, this ratio would be about 1.36. This comparison suggests that linear ketones are also formed during the aldol condensation step. For example, these linear ketones can be formed from the aldol condensation of 2-ketones with aldehydes generated by ring-opening reactions of heterocycles, as shown in Figure 5.1. Ring-opening reactions of heterocyclic species have, in fact, been reported in the literature.\(^7\) In addition, among the branched ketones or alkanes, only small amounts of single, ethyl-branched species are formed, showing that coupling of 2-ketones or alcohols are more favorable compared to coupling of 3-ketones/alcohols with 2-ketones/alcohols. Finally, the absence of species containing two branches indicates that coupling among 3-ketones/alcohols is not favorable. It is important to note that ketonization and aldol condensation reactions are unique routes to achieve C-C coupling, leading to reaction products that are valuable for diesel fuel production, as the extent of branching in the high molecular weight alkanes is minimized and controlled, in contrast to acid-catalyzed coupling processes such as oligomerization of olefins.\(^8\)

Dehydration/hydrogenation reactions are employed to convert the ketones obtained in the upgrading processes into fuel-grade alkanes. In this process, ketones are hydrogenated to corresponding alcohols, followed by dehydration on acid sites to form alkenes which are then hydrogenated to alkanes on metal sites. We have studied dehydration/hydrogenation reactions of simulated mixtures of mono-oxygenated species over Pt/SiAl at various
temperatures and pressures to minimize the extent of C-C cleavage reactions while maintaining complete conversion of mono-oxygenated species to alkanes. The optimal conditions for operation are 573 K and 28.5 bar. Table 5.3 shows the distribution of C$_7^+$ alkanes in the liquid phase obtained over the Pt/SiAl catalyst at these reaction conditions for both reactor configurations. It is interesting to note that 10% of C$_7^+$ alkanes are present as branched cyclic alkanes for both reactor configurations, resulting from cyclization reactions of olefins(9) produced from the dehydration of alcohols.

Table 5.3 Carbon distribution for C$_7^+$ alkanes obtained from dehydration/ hydrogenation over Pt/SiAl at 573 K, 28.5 bar, WHSV= 0.48 h$^{-1}$.

<table>
<thead>
<tr>
<th>Species</th>
<th>Dual-bed system</th>
<th>Cascade system</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_7$</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>C$_8$</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>C$_9$</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>C$_{11}$</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>C$_{12+}$</td>
<td>9</td>
<td>8</td>
</tr>
</tbody>
</table>

5.3. Conclusions

In summary, in this chapter we demonstrate that a dual-bed, single reactor catalyst system can be used to achieve effective C-C coupling processes to upgrade biomass-derived mono-functional species. In this dual-bed catalyst system, a Ce$_1$Zr$_1$O$_x$ catalyst is used to achieve ketonization of carboxylic acids, followed by a Pd/ZrO$_2$ catalyst to carry out aldol condensation/hydrogenation reactions. Importantly, this Pd/ZrO$_2$ catalyst operates effectively in the presence of CO$_2$ and water formed during up-stream ketonization reactions. This integration of two separate C-C coupling reactions in a single reactor is desirable for streamlining the overall
process and reducing capital and operating costs. More generally, this single-reactor upgrading strategy can be applied to other biomass-derived oils that contain carboxylic acids, ketones and alcohols. The major difference of this work compared to the work of Blommel et al. (10) is this integrated C-C coupling route to utilize both acids and ketones/alcohols in the biomass-derived mono-functional stream to increase the amount of fuel-grade components in the final effluent. Finally, this strategy for achieving C-C coupling, combined with a dehydration/hydrogenation step, produces a mixture of linear and singly branched alkanes that is desirable for diesel fuel applications.

5.4. References

Chapter 6: Reactive extraction of levulinate esters and conversion to γ-valerolactone for production of liquid fuels

As discussed in Chapter 1, a promising approach for the utilization of lignocellulosic biomass is the controlled reduction of the oxygen content of the biomass feedstock to produce platform chemicals that retain sufficient functionality for upgrading to a variety of end products. In this respect, levulinic acid (LA) has been identified as an attractive platform molecule from which fine chemicals (δ-aminolevulinic acid, diphenolic acid, etc.) and fuel additives (levulinate esters, methyltetrahydrofuran, etc.) can be produced. (1) A particularly promising derivative of LA is γ-valerolactone (GVL), (2) from which gasoline, jet fuel and Diesel fuel components can be produced. (3-6) Production of equimolar quantities of levulinic acid and formic acids can be achieved in good yield from lignocellulosic biomass (7, 8) and cellulose (5) through hydrolysis. Hydrolysis of cellulose has been demonstrated through multiple strategies. For example, treatments using dilute sulfuric acid, (5) concentrated hydrochloric acid, (9) solid acids (10) and ionic liquids, (11) all yield levulinic and formic acids as degradation products. To date, dilute sulfuric acid hydrolysis appears to offer the most promising balance of cost, yield, and scalability in the preparation of levulinic acid, although further development is needed in product recovery and sulfuric acid management. GVL can be obtained through reduction of levulinic acid over a metal catalyst, preferably consuming hydrogen generated in situ by decomposition of formic acid. (12-14) However, the production of GVL by catalytic reduction of LA is complicated by the need to separate LA from sulfuric acid as residual sulfur leads to low catalytic activity and deactivation with time-on-stream. (5, 15) Although promising strategies have been demonstrated for the production of GVL from levulinic and formic acids, (16, 17) these strategies are carried
out without sulfuric acid and its carryover must be addressed. Therefore, the motivation of the present work is to demonstrate improved sulfuric acid management in levulinic acid-centered biorefining. In the present state of the art, \( \text{H}_2\text{SO}_4 \) is recovered from LA in an energy-intensive process involving solvent extraction combined with distillation. In this chapter, we report an improved, synergistic biorefining strategy that does not require the use of external solvents or energy-intensive distillation steps to separate the levulinic and formic acids from \( \text{H}_2\text{SO}_4 \) and instead employs reactive extraction using butene to produce hydrophobic esters of levulinic and formic acids. Moreover, we show that these esters spontaneously separate from \( \text{H}_2\text{SO}_4 \) and can be converted to GVL over a dual-catalyst-bed system. As we have shown previously, GVL can be converted to butene and CO\(_2\) by catalytic decarboxylation over an acid catalyst,(3) thereby providing the source of butene required for the reactive extraction step.

The process proposed herein relies on the extraction of levulinic and formic acids using alkenes (i.e., butene), in lieu of using alcohols, for the production of levulinate and formate esters, as first proposed by Manzer et al.(18) In particular, even though Ayoub(19) has demonstrated the reactive extraction of LA using alcohols, such as 1-pentanol, to form hydrophobic levulinate esters, this extraction requires an external source of alcohol and necessitates a distillation step for solvent recovery from the ester product. In contrast, the use of butene as an extracting solvent is particularly advantageous, because butene can be produced from GVL,(3) and butene separates spontaneously from the ester product upon decreasing the system pressure, eliminating both the use of externally produced extracting solvents and the need for distillative solvent recovery. The ester products can be used directly as fuel additives(18, 20) or to provide a platform for the production of specialty chemicals.(21) Importantly, we show in the present chapter that levulinate esters can be converted to GVL in good yield using a dual-
catalyst-bed in a single reactor system, while utilizing formate esters and unconverted formic acid (FA) as in situ sources of hydrogen. This dual-catalyst-bed system achieves almost quantitative yields of H₂ from FA and formate esters (over a Pd/C catalyst) as well as high rates of GVL production from LA and levulinate esters (over a Ru/C catalyst), whereas the simultaneous utilization of FA and formates to reduce LA and levulinates cannot be achieved using either of these catalysts alone.

6.1. Experimental

6.1.1. Reactive Extraction of Levulinate and Formate Esters with Butene

6.1.1.1. Preparation of Simulated Levulinic, Formic and Sulfuric Acid Solutions

Levulinic acid (LA) and formic acid (FA) solutions were concentrated under reduced pressure using a rotary evaporator. Water and FA were collected in the condensate-collecting flask (head) and this solution was used for further processing, while LA, sulfuric acid, residual FA and water remained in the evaporation flask (bottom). The final concentration in the bottom solution was determined by the conditions used for evaporation (temperature, pressure and time); however, for all cases 100% of sulfuric acid remained in the bottom solution.

6.1.1.2. Reactive Extraction Studies

Esterification reactions were carried out in a sealed 50 mL Hastelloy C-276 Parr reactor. The reactor was charged with a solution of LA, FA, sulfuric acid and water at the corresponding concentrations. 1-Butene (Airgas CP grade) was introduced into the reactor as a liquid using a high pressure syringe pump (Teldyne-Isco model 290D). The reactor was then heated to the reaction temperature under vigorous stirring. The final pressure in the reactor was determined by the vapor pressure of the butene at the reaction temperature. At the end of the reaction, excess butene was purged at room temperature. Initially, only one phase was obtained in the reactor.
Upon addition of water, 2 phases separated spontaneously. The top layer (organic) contained 100% of the esters produced (BL and BF), and a fraction of the unconverted LA and FA, 2-butanol and other minor impurities, such as butyl ether and octenes. The aqueous phase contained sulfuric acid and the remainder of the unconverted LA and FA and 2-butanol.

6.1.1.3. Feed Production for the Dual-Catalyst-Bed System

To prepare feed solutions of esters for subsequent catalytic production of GVL over Ru/C and Pd/C catalysts, reactive extraction with butene was carried out using a bottom solution of 6.3 M LA, 2.3 M FA and 1.6 M H$_2$SO$_4$ prepared in the rotary evaporator at 358 K and 400 mm Hg. The corresponding head solution consisted of 1.85 M FA in water. Typically 105 g of the bottom solution was transferred to a 350 mL stainless steel batch reactor (Parr Instruments) to carry out the esterification reaction with butene. After the reactor was sealed, 1-butene was added to achieve a molar ratio of butene:LA equal to 2:1 using a high pressure syringe pump (Teldyne-Isco model 290D). The reactor was then heated to 353 K and held at this temperature for 12 h under vigorous stirring. At the end of the reaction, the reactor was cooled and the excess butene was purged. At these conditions, LA and FA conversions were 60% and 49%, respectively, with yields to the esters of 59% and 47%. To separate the esters from the sulfuric acid, 50 mL of deionized water was added to the reaction products and two phases were obtained. The sulfuric acid was recovered almost quantitatively in the aqueous phase, whereas, the organic phase contained BL and BF, and a portion of the unconverted LA and FA.

6.1.1.4. Preparation of Lignocellulose (Poplar) Derived Feed

The sulfuric acid catalyzed hydrolysis of poplar for the production of levulinic and formic acids were carried out by our collaborators through Forest Products Laboratory under the supervision of Prof. Troy Runge. The hemicellulose portion in the wood chips was extracted
with dilute acid using a dual vessel pressurized reactor with heated liquor circulation, following a previously reported strategy. After washing, drying and grounding, the extracted wood meal was reacted with H₂SO₄ in a Hastelloy lined 20L PARR reactor at 190°C with 5.0 wt% H₂SO₄ for 50 minutes using a wood-to-liquor ratio of 1:10. The insoluble lignin and humins were separated and the collected solution was used to treat a second batch of extracted wood meal to increase the concentration of the levulinic and formic acid. The resulting solution was composed of 0.01, 20.2, 49.4, 0.08 and 7.01 g/L of hexoses, formic acid, levulinic acid, furfural and acid-soluble lignin, respectively. The yield of the levulinic acid from this process was approximately 60% of theoretical, considering the hybrid poplar chips hexose content was 44.9 wt%. Following this step, vacuum distillation was used by keeping the feed at a constant boil to concentrate levulinic acid and sulfuric acid to carry out the reactive extraction step. In addition to water, majority of formic acid was also evaporated. The concentration of levulinic, formic and sulfuric acids after evaporation were 3.96 M, 0.7 M and 3.08 M, respectively.

6.1.2. Conversion of Esters over Pd/C and Ru/C

6.1.2.1. Catalyst Preparation

Carbon-supported catalysts containing either 5 wt% Ru or 10 wt% Pd were purchased from Sigma-Aldrich. Both catalysts were reduced in situ under H₂ flow at 673 K (ramp rate of 0.5 K min⁻¹) for 2 h.

6.1.2.2. Reaction Kinetics Studies

A fixed bed, down-flow reactor consisting of a half-inch stainless steel tube was used for all experiments as described in Chapter 2. Experiments employing a dual-catalyst-bed, single reactor configuration were performed in a fixed bed, down-flow reactor system consisting of a half-inch stainless steel tube. In contrast to the single bed experiments, two different catalysts
were loaded in the same reactor, separated by fused SiO$_2$ granules and quartz wool. Ru/C (1.5 g) was placed on the quartz wool and more quartz wool and fused SiO$_2$ granules were placed on top of this bed. Pd/C (2 g) was then placed on the silica chips. Both catalysts were mixed with crushed fused SiO$_2$ granules (Aldrich) in a 1:1 volumetric ratio.

For all experiments, the gas flow rate was measured with a bubble flow meter. An HP GC5890 gas chromatograph, equipped with a Haysep DB 100/120 column (Alltech) and thermal conductivity detector (TCD), was used to quantify CO and CO$_2$, and an Agilent GC6890, equipped with an Rtx column (Agilent) and a flame ionization detector (FID), was used to quantify gas-phase alkanes. Organic liquid phase analysis was performed with a Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID detector and a Shimadzu 2060 GC/MS with a NIST library of spectra. Aqueous phase samples were analyzed by HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a RI 410 detector). Liquid and gas analysis points were collected regularly, and steady state was usually achieved after 6 h time-on-stream.

6.2. Overall Strategy

The strategy presented in this chapter, summarized in Figure 6.1, begins with the production of an aqueous solution containing equimolar concentrations (2 M) of LA and FA by hydrolysis of cellulose at 423 K using sulfuric acid (0.5 M). Some of the water and the FA co-product are then removed by an evaporation step to obtain a more concentrated solution of LA and sulfuric acid, containing residual amounts of water and FA, analogous to the initial stages of the Biofine Process. (7, 8) The FA product in water is retained for downstream hydrogen production (in the dual-catalyst-bed system mentioned above), and the concentrated LA product is contacted with butene, generating sec-butyl levulinate (BL) and sec-butyl formate (BF) esters as major and
minor products, respectively, using H$_2$SO$_4$ as a catalyst. We have demonstrated that high yields, 85%, of the levulinate ester can be attained at moderate temperatures (< 373 K) and short contact times (< 120 min). Excess butene can be recovered by vaporization, and the concentrated ester product is then contacted with water, during which the hydrophobic ester separates spontaneously from the aqueous phase, the latter of which retains 99% of the sulfuric acid to be recycled for use in biomass deconstruction. The BL and BF esters are subsequently processed in combination with the aqueous FA product stream (obtained from the evaporation step) using a dual-catalyst-bed in a single reactor to produce GVL in nearly quantitative yields with 2-butanol and CO$_2$ as co-products. The liquid effluent from this reactor, consisting of an aqueous solution of GVL and 2-butanol, can undergo decarboxylation and dehydration (of GVL and butanol, respectively) over a SiO$_2$/Al$_2$O$_3$ catalyst to obtain butene and CO$_2$.(3) Our experiments for the simultaneous conversion of GVL and a secondary alcohol over SiO$_2$/Al$_2$O$_3$ resulted in almost quantitative yields to the corresponding alkenes from both lactone and alcohol. A portion of the butene can be recycled for the reactive extraction step, and the remainder of the butene (with inert CO$_2$) can be upgraded by oligomerization to obtain high-molecular weight alkenes suitable for jet-fuel applications.(3) The details for the butene oligomerization step have been published previously,(3) where an 87% yield was reported for C$_{8+}$ alkenes from an equimolar mixture of butene and CO$_2$. 

6.3. Reactive Extraction of Levulinate and Formate Esters

Table 6.1 shows results for reactive extraction of levulinic and formic acids at various conditions. As shown in entry 1, esterification of the aqueous solution obtained directly from the cellulose deconstruction step described by Serrano-Ruiz et al.(5) (2 M LA and FA in 0.5 M H₂SO₄) does not take place at our reaction conditions, which are similar to those conditions suggested by Manzer et al.(18) Importantly, however, we have found that the formation of butyl esters can be achieved with high yields by employing a concentration step to remove at least a
portion of the water. The composition of the concentrated solutions at different temperatures and pressures are presented in Table 6.2. Increasing the concentration of LA and H$_2$SO$_4$ results in high yields of levulinates (>90%) at short contact times (2 h) (entry 2) and allows for quantitative recovery of the sulfuric acid upon contact with water. It is important to note that the concentration step can be accomplished with a single evaporation, and it is the only energy demanding separation in this process. Through the formation of hydrophobic butyl esters, the need for solvent extraction and distillation are eliminated, reducing the energy demand of levulinic acid recovery.

Table 6.1 Levulinic and formic acid conversions with sec-butyl levulinate and sec-butyl formate yields obtained for butene extraction experiments with different aqueous phase concentrations, temperatures and reaction times. Butene:LA molar ratio is equal to 5:1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$T$ (K)</th>
<th>Time (h)</th>
<th>FEED (M)</th>
<th>Conversion LA (%)</th>
<th>BL Yield (%)</th>
<th>LA org$^{[a]}$ (%)</th>
<th>LA aq$^{[a]}$ (%)</th>
<th>H$_2$O (g/g LA)</th>
<th>H$_2$SO$_4$ aq (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>403</td>
<td>16</td>
<td>2</td>
<td>0.5</td>
<td>40</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>353</td>
<td>2</td>
<td>8</td>
<td>0</td>
<td>2</td>
<td>4.5</td>
<td>91</td>
<td>85</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>333</td>
<td>4</td>
<td>8</td>
<td>0</td>
<td>2</td>
<td>4.5</td>
<td>86</td>
<td>78</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>403</td>
<td>2</td>
<td>8</td>
<td>0</td>
<td>2</td>
<td>4.5</td>
<td>85</td>
<td>73</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>373</td>
<td>2</td>
<td>8</td>
<td>0</td>
<td>2</td>
<td>4.5</td>
<td>91</td>
<td>82</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>353</td>
<td>2</td>
<td>4</td>
<td>0</td>
<td>1</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>353</td>
<td>2</td>
<td>6.4</td>
<td>0</td>
<td>1.6</td>
<td>16.5</td>
<td>55</td>
<td>48</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>353</td>
<td>2</td>
<td>6.3</td>
<td>2.3</td>
<td>1.6</td>
<td>11.3</td>
<td>84(48)$^{[c]}$</td>
<td>78(43)$^{[c]}$</td>
<td>5(28)$^{[c]}$</td>
</tr>
<tr>
<td>9$^{[b]}$</td>
<td>353</td>
<td>12</td>
<td>6.3</td>
<td>2.3</td>
<td>1.6</td>
<td>11.3</td>
<td>60(49)$^{[c]}$</td>
<td>59(47)$^{[c]}$</td>
<td>20(27)$^{[c]}$</td>
</tr>
</tbody>
</table>

[a] The percentages are calculated based on LA in the initial feed. Partition coefficient (M$_{org}$/M$_{aq}$ =1) [b] Butene:LA molar ratio is equal to 2:1 [c] Refer to FA/BF

Increasing the temperature leads to a decrease in the yields (entries 3-6), an increase in the production of degradation products, and a reduction in the amount of H$_2$SO$_4$ recovered. The amount of FA present in the LA solution is determined by the extent of evaporative concentration step (see Table 6.2). The presence of FA decreases the concentration of water and increases the yield of BL from 48% (entry 7) to 78% (entry 8), with 43% yield of BF from FA.
Table 6.2 Distribution of levulinic and formic acids and water in the head and bottom solutions obtained by evaporation using a rotary evaporator with changing $T$ (K), $P$ (mm Hg) and time (h). Starting solution: 25 mL of 2M LA, 2M FA, 0.5 M H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$T$ (K)</th>
<th>$P$ (mm Hg)</th>
<th>Time (h)</th>
<th>LA (%) Head</th>
<th>Bottom</th>
<th>FA (%) Head</th>
<th>Bottom</th>
<th>Water (%) Head</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>368</td>
<td>400</td>
<td>3</td>
<td>0.4</td>
<td>99.6</td>
<td>70.6</td>
<td>29.4</td>
<td>94.9</td>
<td>5.1</td>
</tr>
<tr>
<td>2</td>
<td>358</td>
<td>400</td>
<td>3</td>
<td>0.2</td>
<td>99.8</td>
<td>54.8</td>
<td>45.2</td>
<td>91.3</td>
<td>8.7</td>
</tr>
<tr>
<td>3</td>
<td>353</td>
<td>400</td>
<td>6</td>
<td>0.8</td>
<td>99.2</td>
<td>79.9</td>
<td>20.1</td>
<td>93.2</td>
<td>6.8</td>
</tr>
<tr>
<td>4</td>
<td>403</td>
<td>760</td>
<td>6</td>
<td>0.1</td>
<td>99.9</td>
<td>42.8</td>
<td>57.2</td>
<td>87.4</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Upon contact with water after the esterification step, the aqueous phase contains the H$_2$SO$_4$ and a portion of the unconverted LA and FA, and this aqueous solution can be recycled to the cellulose deconstruction reactor, in which the LA and FA species are essentially inert. A The organic phase after the esterification step and contacting with water contains the BF and BL esters and the rest of unconverted LA and FA (see Table 6.1). The amounts of the sulfuric acid, LA and FA in the aqueous and organic phases depended on the amount of water added, as shown in Figure 6.2. For instance, as shown in entry 7, at 55% conversion of LA, when 6 g of water per g of LA is added, only 11% of the unconverted acid is retained in the organic phase, whereas 89% remains in the aqueous phase. At a similar LA conversion (60%), in entry 9, when only 1 g of water per gram of LA is added, 50% of the unconverted LA is partitioned into the organic phase and the remainder (50%) remains in the aqueous phase. At these conditions the organic stream contains 80% of the LA initially present in the aqueous feed solution with sulfuric acid, 60% being in the form of the ester product and 20% being the unconverted LA, while 99% of the SA is recovered (1.6 M) in the aqueous phase with the remainder of the unconverted LA (20%).
Figure 6.2 Percentages of unconverted LA (squares) and FA (triangles) present in the aqueous phase versus the amount of water added to extract the esters (g of water per gram of initial g LA).

6.4. Conversion of Butyl Formate and Butyl Levulinate to H₂ and GVL

Table 6.3 shows that it is possible to convert BL to GVL and butanol over a Ru/C catalyst (entry 1). While this conversion has been proposed in a patent by the Shell Oil Company,(24) we demonstrate here that the rate of GVL production can be increased significantly by co-feeding water along with the ester (entry 2). We suggest that the presence of water leads to hydrolysis of the ester and thereby enables the reduction to proceed through an LA intermediate, leading to a higher overall rate for GVL production. However, an important deficiency of the Ru/C catalyst is that it does not achieve effective conversion of LA and BL in the presence of FA and BF. For example, it can be seen from entries 3 and 4 in Table 6.3 that BF inhibits the production of GVL from BL over Ru/C. Moreover, the Ru/C catalyst leads to the undesirable dehydration of FA to
produce CO and H\textsubscript{2}O, as well as the desirable dehydrogenation pathway to yield CO\textsubscript{2} and H\textsubscript{2} (25) thereby decreasing the hydrogen production rate from BF. In addition, the Ru/C catalyst leads to methanation of CO (26) (formed by dehydration of formic acid), which consumes additional H\textsubscript{2} (required for LA reduction).

Table 6.3 Butyl levulinate and butyl formate conversions with GVL and CO\textsubscript{2} yields and production rates for various feed compositions over 10 wt% Pd/C, 5 wt% Ru/C or the dual-catalyst-bed system. P= 35 bar, T=423K for entries 3 and 4 and T=443 K for the other entries.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Feed</th>
<th>Catalyst</th>
<th>WHSV (h\textsuperscript{-1})</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
<th>Gas phase conversion (%)\textsuperscript{[f]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{[a]}</td>
<td>2M BL</td>
<td>Ru/C</td>
<td>5.5\textsuperscript{[b]}</td>
<td>21 / -</td>
<td>19 / -</td>
<td>0.5</td>
</tr>
<tr>
<td>2\textsuperscript{[a]}</td>
<td>2M BL &amp; 6M H2O</td>
<td>Ru/C</td>
<td>5.5\textsuperscript{[b]}</td>
<td>78 / -</td>
<td>76 / -</td>
<td>0.9</td>
</tr>
<tr>
<td>3\textsuperscript{[a]}</td>
<td>1M BL &amp; 6M H2O</td>
<td>Ru/C</td>
<td>0.9\textsuperscript{[b]}</td>
<td>91 / -</td>
<td>89 / -</td>
<td>1.5</td>
</tr>
<tr>
<td>4\textsuperscript{[a]}</td>
<td>1M BL &amp; 1M BF &amp; 6M H2O</td>
<td>Ru/C</td>
<td>1.3\textsuperscript{[b]}</td>
<td>24 / 45</td>
<td>22 / 22</td>
<td>0.7</td>
</tr>
<tr>
<td>5\textsuperscript{[a]}</td>
<td>2M BF</td>
<td>Pd/C</td>
<td>0.5\textsuperscript{[b]}</td>
<td>- / -</td>
<td>- / -</td>
<td>-</td>
</tr>
<tr>
<td>6\textsuperscript{[a]}</td>
<td>2M BF &amp; 6M H2O</td>
<td>Pd/C</td>
<td>0.5\textsuperscript{[b]}</td>
<td>- / 43</td>
<td>- / 41</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Extraction product\textsuperscript{[d]}</td>
<td>Pd/C</td>
<td>1.5\textsuperscript{[e]}</td>
<td>51 / 98 (including FA)</td>
<td>4 / 95</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>(Table 6.1, entry 9)</td>
<td>Pd/C+Ru/C</td>
<td>0.9\textsuperscript{[e]}</td>
<td>96/98 (including LA &amp; FA)</td>
<td>95 / 92</td>
<td>12</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} 1-butanol is the solvent \textsuperscript{[b]} WHSV is calculated using the weight of only the esters in the feed \textsuperscript{[c]} Organic stream: 4.43 M BL and 1.55 M BF (no additional solvent), aqueous stream: 1.96 M FA \textsuperscript{[d]} Organic stream: 3.40 M BL, 1.23 M LA and 0.96 M BF, 0.67 M FA (no additional solvent), aqueous stream: 1.83 M FA \textsuperscript{[e]} WHSV is calculated using total weight of feed and catalyst. (Aq. stream volume/org. stream volume= 1.5) For entry 8, wt. of Pd/C / wt. of Ru/C =1.3 \textsuperscript{[f]} Light alkanes produced from the total butanol present (solvent + obtained from conversion of butyl esters).

The limitations of the Ru/C catalyst for the combined conversion of levulinic and formic esters can be alleviated by using an upstream bed of Pd/C, which favors the desirable dehydrogenation of FA to H\textsubscript{2} and CO\textsubscript{2} compared to dehydration reactions leading to H\textsubscript{2}O and CO. In particular, it has been reported that nearly quantitative yields of CO\textsubscript{2} and H\textsubscript{2} can be obtained from FA over Pd/C at temperatures from 360 to 470 K. (27) As seen in entries 5 and 6, we have observed that water is necessary to achieve high rates of BF conversion over Pd/C, suggesting that this conversion takes place through the intermediate formation of FA. In the
presence of water, CO$_2$ is obtained with almost 100% selectivity, confirming a negligible rate of dehydration compared to the dehydrogenation of FA. The positive effect of water on the conversion of levulinic and formic esters is particularly advantageous, since it allows co-feeding over the dual-catalyst-bed system of the aqueous solution of FA, obtained from the evaporation step prior to reactive extraction, along with the organic ester stream. Entry 7 of Table 6.3 shows that a Pd/C catalyst alone is not effective to convert a feed mixture that contains BL and BF in the organic stream and FA in the aqueous stream. Specifically, while 50% of BL is converted to LA over Pd/C, further reduction to GVL takes place at a very slow rate (0.002 mmol min$^{-1}$ g$^{-1}$). In contrast, it has been demonstrated that nearly quantitative yields of GVL can be obtained from the reduction of LA over Ru/C(6, 18, 28, 29) at higher activities compared to Pd/C, Pt/C, Rh/C, Re/C and Ni/C.(28) Thus, given the comparable reaction conditions for decomposition of formate esters over Pd/C and for hydrogenation of levulinate esters over Ru/C, along with the lack of CO$_2$ methanation over Ru/C,(26) it is synergistic to combine the catalytic properties of Pd/C and Ru/C in a dual-catalyst-bed reactor to achieve in situ hydrogen generation alongside GVL production. To study this hypothesis, a dual-catalyst-bed of Pd/C followed by Ru/C was used to convert the organic solution of levulinate and formate products obtained by reactive extraction with butene (see Table 6.1, entry 9), along with the aqueous solution of FA obtained in the evaporation step prior to reactive extraction. Table 6.4 shows the composition of the feed used for the dual-catalyst-bed obtained from the reactive extraction in Table 6.1, entry 9. Entry 8 in Table 6.3 shows that BF and FA are converted to CO$_2$ and H$_2$ over Pd/C (92% yield), and the conversion of BL and LA to GVL over Ru/C is excellent (95% yield).
Table 6.4 Molar concentrations and corresponding distributions of various species in the organic phase obtained from reactive extraction using butene at 353 K, for 12 h with butene:LA equal to 2:1.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (M)</th>
<th>Molar distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sec-butyl levulinate</td>
<td>3.7</td>
<td>39</td>
</tr>
<tr>
<td>Sec-butyl formate</td>
<td>0.9</td>
<td>9</td>
</tr>
<tr>
<td>Levulinic acid</td>
<td>1.5</td>
<td>16</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.9</td>
<td>10</td>
</tr>
<tr>
<td>Butene</td>
<td>0.9</td>
<td>10</td>
</tr>
<tr>
<td>2-butanol</td>
<td>1.4</td>
<td>14</td>
</tr>
<tr>
<td>Others(^{[a]})</td>
<td>0.2</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Others include octene, butyl ether, octyl levulinate

In the effluent from this dual-catalyst-bed reactor, a small amount of sulfuric acid was detected (0.01 M); however, the catalytic process is stable versus time-on-stream with this feed stream, as demonstrated in Figure 6.3, where the GVL production rate remains constant at 0.05 mmol min\(^{-1}\)g\(^{-1}\) after 400 hours on stream, corresponding to 94% conversion of LA and BL.

![Figure 6.3](image.png) 

**Figure 6.3** Rates of production of GVL (squares) and CO\(_2\) (triangles) versus time-on-stream over the dual-catalyst-bed reactor system (2 g 10 wt% Pd/C followed by 1.5 g 5 wt% Ru/C) co-feeding the organic stream prepared from the butene extraction step and the aqueous stream obtained from the evaporation step prior to extraction. \(T\approx 443\) K, \(P=35\) bar.
Following these experiments, the performance of the dual-bed system was investigated by processing a feed derived from lignocellulose (poplar). Poplar derived aqueous mixture consisting of levulinic, formic and sulfuric acids was first concentrated to reach the concentrations required for carrying out the reactive extraction step as described in earlier sections. The components and corresponding molarities obtained in the organic mixture following the reactive extraction step is given in Table 6.5.

Table 6.5 Molar concentrations of various species in the organic phase obtained from reactive extraction of poplar-derived feed using butene at 353 K, for 12 h with butene:LA equal to 2:1.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sec-butyl levulinate</td>
<td>3.46</td>
</tr>
<tr>
<td>Sec-butyl formate</td>
<td>0.15</td>
</tr>
<tr>
<td>Levulinic acid</td>
<td>0.12</td>
</tr>
<tr>
<td>Butyl ether</td>
<td>0.84</td>
</tr>
<tr>
<td>Butene</td>
<td>0.65</td>
</tr>
<tr>
<td>2-butanol</td>
<td>1.42</td>
</tr>
<tr>
<td>Others[a]</td>
<td>0.1</td>
</tr>
</tbody>
</table>

[a] Others include octene, octyl levulinate

This poplar-derived feed was then reacted over the dual-catalyst-bed reactor to test the stability of the system. As shown in Figure 6.4, the experiment was first started with a simulated feed mixture (reactants with same concentrations as the poplar-derived feed, Table 6.5), for which the dual-bed reactor was stable. After 90 h of operation (first dashed line), the organic feed was switched to the poplar-derived feed for another 105 h, after which (second dashed line) the feed was switched back to the simulated feed mixture. As it can be seen in Figure 6.4, the dual-catalyst-bed system remained stable with the biomass-derived feed, even though GVL production rate was reduced by 25%.
Figure 6.4 Rates of production of GVL (squares) and CO₂ (diamonds) versus time-on-stream over the dual-catalyst-bed reactor system (2 g 10 wt% Pd/C followed by 1.5 g 5 wt% Ru/C) co-feeding the organic stream prepared from the butene extraction step and the aqueous stream obtained from the evaporation step prior to extraction. \( T=443 \) K, \( P=35 \) bar. The experiment is started with a simulated feed mixture, the feed is switched to poplar-derived feed at the first dashed line and switched back to the simulated feed at the second dashed line.

6.5. Technoeconomic Evaluation of the Overall Strategy

6.5.1. Material Balance for Butene Formation Starting From Cellulose

For proper evaluation of the proposed process and to carry out a technoeconomic analysis in collaboration with Prof. Maravelias and Murat Sen, we developed a process model and carried out a detailed material balance for the results described in Table 6.3, Entry 8, starting from lignocellulose. The first step of the biomass-to-biofuels conversion involves the solubilization and removal of hemicellulose fraction of biomass using a dilute acid pretreatment. Solubilized hemicellulose is burned in the turbogenerator unit. Pretreated biomass, containing insoluble
cellulose and lignin, is then deconstructed at 373 K and 16 bar according to an experimentally obtained biomass-to-water ratio and sulfuric acid concentration. In a batch reactor, cellulose is hydrolyzed to produce an equal molar mixture of levulinic and formic acids with 60% conversion (5), whereas remaining cellulose is converted to humins due to undesired polymerization reactions. Insoluble materials, mainly lignin and humins, are separated from the liquid mixture using a pressure filter system assuming that 96% cake washing efficiency is possible in two wash cycles with a wash water to feed mass ratio of 0.58 as described in the NREL report (30). Wet biomass residue mixed with hemicellulose is sent to a boiler/turbogenerator unit to produce heat and generate electricity. In the filtration step, 1.7% of LA, FA and sulfuric acid is lost with the wet residue. For steps involving catalytic reactions (esterification, GVL production and butene production), experimental results for conversions and yields were used. For the reactive extraction (esterification) step, the results given in Table 6.1, entry 9 were used, and for GVL production, selectivities given in Table 6.3, entry 8 were used (note that experiment shown in Table 6.3, entry 8 was carried out using the product of the experiment given in Table 6.1, entry 9). The material balance with the flow chart is given in Figure 6.5. The amount of cellulose feed is chosen to give 100 moles of levulinic and formic acids, each with a 60% yield. Accordingly, 40% of the cellulose is converted to humins, which are solid polymer side-products that can be separated from the solution. Stream 1 consists of levulinic and formic acids converted from cellulose together with sulfuric acid (not shown on the flow chart) as well as the unconverted acids and 2-butanol present in the aqueous sulfuric acid recycle stream (stream 4) recovered from the reactive extraction step. Stream 1 goes into a single evaporation step, in which about 52% of the formic acid and 20% of the 2-butanol are evaporated together with water and separated as stream 2 from the residual liquid (stream 3) that
contains all of the levulinic acid and the remainder of the formic acid and 2-butanol. Stream 3 is used as the feed for the esterification step together with butene (streams 11 and 12). Stream 5 represents the organic layer collected following the esterification reaction and contains butyl esters, part of the unconverted acids, 2-butanol and butyl ether produced from butene and some unidentified side products. Unidentified products are quantified by subtracting the overall carbon balance at each step from 100%. For esterification, GVL production and butene production steps, this number ranges between 1-2%. It is important to note that the product distribution in Stream 5 is slightly different from the distribution given in Table 6.4, since this organic feed was obtained by mixing the organic layers from more than one batch of esterification experiments. Stream 4 represents the aqueous stream obtained after washing the organic stream with water to remove sulfuric acid quantitatively and contains part of the unconverted levulinic and formic acids and 2-butanol as well. This stream is recycled back to the cellulose deconstruction step, in which levulinic and formic acids as well as 2-butanol behave as inert species. The molar quantity of butene used in the esterification step is twice that of levulinic acid fed and comes partly from the recycle stream (stream 11) and partly from a pure butene stream (stream 12) to keep this 2:1 ratio. When the esterification reaction is complete, all of the excess butene can be recovered upon release of system pressure with no impurities. This excess butene in stream 12 can be reused for the esterification step to maintain the butene: levulinic acid ratio as 2, thus eliminating any need for fresh butene. Stream 5 and stream 2 are co-fed to the dual-catalyst-bed system, consisting of Pd/C followed by Ru/C. Over these catalysts, formic acid and butyl formate are converted nearly quantitatively to CO₂ and H₂. The hydrogen generated matches the stoichiometric amount required for in situ reduction of levulinic acid and butyl levulinate to produce GVL. GVL is obtained with 99% yield over the dual-catalyst-bed. Stream 6 consists of
the gas phase products: CO₂, methane, butane and hydrogen. Methane is produced over Ru by methanation of CO (obtained from formic acid decomposition). Butane is the deep hydrogenation product. This stream is not recycled back to esterification step, but the hydrogen can be recycled back to the dual-bed reactor system for GVL production. In that case, either hydrogen can be isolated from the rest of these species (in which case the butane, methane and CO₂ stream can be utilized for generating heat) or a purge stream has to be used to avoid accumulation of the gas phase products. Stream 7(liquid phase) consists of GVL, 2-butanol, butyl ether and some unidentified side products. This stream is reacted over the SiO₂/Al₂O₃ catalyst with nearly quantitative yields to butene in the gas phase. Unidentified side products are collected in the liquid phase in stream 8. Part of stream 9 is recycled back to the esterification step (stream 11), whereas the remainder is collected as the butene product (stream 10). It is important to note that when GVL is converted to butene, equimolar CO₂ is generated as well, all of which will pass to down-stream oligomerization process (stream 10), as the necessary amount of butene is liquefied (with temperature decrease to room temperature) for the recycle stream (stream 11). When the unconverted LA and FA are recycled to the cellulose deconstruction step, 98% GVL and 88% butene yields can be obtained taking into account all the losses in the process, which include unidentified side products and butane (deep hydrogenation product). In terms of a mass basis, 18.3 kg of butene can be obtained from 100 kg of cellulose and this number corresponds to 88% of the theoretical maximum when 60% yield towards levulinic and formic acids is taken as the basis.
Figure 6.5 Material balance in term of moles for the conversion of cellulose to butene. Amount of cellulose is set to have 100 moles of levulinic and formic acids each as a basis assuming 60% yield towards the acids. The streams with solid diamonds are recycle streams. All the values are in moles. LA, FA, BL, BF, BuOH and BE stand for levulinic acid, formic acid, sec-butyl levulinate, sec-butyl formate, 2-butanol and butyl ether, respectively. Side products are cumulative and calculated based on the carbon that could not be accounted for at each step and ranges from 1-2% of the inlet carbon.

After developing the process model, the process streams that need heating and cooling were identified and integrated by allowing heat exchange between streams to reduce the total utility consumption. According to heat integration results, cooling water needs to be purchased additionally. The heating for the thermal fluid is provided in a power cycle that involves a boiler/turbogenerator system to produce heat and generate electricity. In the power cycle, biomass residues, mainly hemicellulose, lignin and humins, are burnt in a fired heater. Hot
Combustion gases provide the energy required for thermal fluid heating. Remaining energy of hot combustion gases is used to produce 83,600 kg/hr of superheated steam in a boiler/superheater system. Then, superheated steam at 783 K and 86 bar is expanded to generate electricity in a turbine. Wet vapor outlet (having vapor fraction of 0.957) at 369 K and 1 bar is subcooled down to condense the remaining vapor. Condensation is required to save energy when the fluid is pressurized again to 86 bar for steam regeneration. The cooling requirement is 152.2 MW for this operation. The net power generation from the biomass residue (having 235 MW of energy content) is 57.2 MW, while 25.5 MW of energy is spent to heat the thermal fluid. The overall efficiency (the ratio of net power generation plus thermal fluid heating to biomass energy content) is found to be 35%. Excess electricity generated in the power cycle is assumed to be sold to the grid.

### 6.5.2. Cost Calculations

Techno-economic analysis was performed to assess the esterification strategy for a 2,000 dry tons of corn stover processing per day. The capital and operating cost distributions for the esterification strategy are given in Figure 6.6. The major constituent of the capital costs is the cost of the boiler/turbogenerator unit, which requires a $95 million investment (45% of the total equipment cost). Dilute acid pretreatment takes 17% of the total equipment cost, whereas the capital investment for the cellulose deconstruction section is estimated to be $19.6 million, which is 9% of the total equipment cost. The contributions of other processing sections to the capital investment are found to be less than 5%. The total project investment is projected to be $487 million including the other direct (e.g., instrumentation, insulation) and indirect (e.g., engineering, contingency) costs.

Total operating cost is found to be $90.7 million annually. Feedstock cost makes up the
major part (64%) of the total operating cost, when the corn stover is purchased at $83/ton (31). The total cost of other raw materials (i.e. sulfuric acid, makeup water, boiler chemicals, wastewater chemicals) is approximately $11.3 million per year, which is 13% of the total operating cost. Fixed operating costs including operating labor, maintenance, insurance and plant overhead add $9.9 million more to the annual operating cost. Electricity requirement of the process, which is actually provided by the electricity generated in the power cycle, would constitute 4% of the total operating cost. Since heating requirement for the entire process is recovered by the heat integration of process streams as well as thermal fluid heating in the fired heater, only cooling water needs to be paid for, which comprises 2% of the total operating cost. We assumed that 10% of the catalyst is refurbished in every 6 months at a cost equivalent to 20% of its original value, which requires $3.2 million annually (catalyst cost is estimated at $920/kg). Waste disposal cost accounts for only 2% of the operating costs.

![Figure 6.6](image)

**Figure 6.6** Distribution of (A) capital and (B) operating costs for the overall strategy for processing 2,000 dry tons of corn stover processing per day.
After capital and operating costs were determined, the MSP (minimum selling price) of butene oligomers was calculated in terms of $ per gallons of gasoline equivalents (GGE) to compare it with the MSP of ethanol reported by Kazi et al. (31). Return on investment (ROI) is a function of the discount rate (6.74%) and the equipment life span (20 years), represents the contribution of the capital expenditures to the MSP. Income tax is calculated based on the difference between the net profit (total revenues minus total costs) and the depreciation of the unit equipments by assuming that the income tax rate is 35% and process and power generation plants depreciate in 7 and 20 years, respectively. An additional revenue is obtained by selling the excess electricity to the grid at a price of 5.4¢/kW.hour. Finally, the MSP of butene oligomers is determined at the break-even point, where total costs and total revenues are equal. For the basic design, the MSP of the butene oligomers is found to be $8.01/GGE as shown in Figure 6.7.

As described earlier, xylose recovered from corn stover through the solubilization of hemicellulose by dilute acid pretreatment is burned to produce heat and generate electricity. As an alternative, xylose can be sold as an end product or can be converted to more valuable chemicals, such as furfural. The selling price of xylose was determined assuming that butene oligomers could be sold at the price reported by Kazi et al. (31) for ethanol, which is $5.13/GGE. The revenue from excess electricity decreases by 63¢/GGE since less amount of biomass residue is sent to the power generation unit. The effluent from the hemicellulose hydrolysis step needs to be neutralized by using lime before xylose can be sold or converted to other chemicals, hence lime cost adds 10¢ to the operating costs for this case.
Figure 6.7 Costs and revenues for (a) corn stover feedstock with xylose burning (b) corn stover feedstock with xylose utilization (c) loblolly pine feedstock with xylose burning.

Accordingly, xylose needs to be sold at 31¢ per kg, which corresponds to a MSP of $5.13/GGE as shown in Figure 6.7. If the actual market value of xylose gets higher than 31¢/kg, selling or conversion of xylose into more valuable chemicals becomes a more reasonable approach, otherwise xylose can be burned for power generation. Another variation in the strategy is using loblolly pine as feedstock as opposed to corn stover, since loblolly pine has a higher C₆ sugar content (55 wt%). Annual feedstock cost is found to be $27.4 million assuming that the loblolly pine feedstock can be purchased at a price of $57 per dry ton (32). In comparison with the case of corn stover, unit operating cost decreases by $2.40/GGE due to higher C₆ sugar content and lower feedstock price. On the other hand, the revenue obtained from excess
electricity decreases by 34¢/GGE, since less biomass residue is processed in the power
generation plant. In addition, the dilute acid pretreatment step to remove hemicellulose can be
eliminated, since, xylan content of loblolly pine feedstock is very low (~6 wt%), which provides
significant savings in the capital cost. For this case, total capital investment is estimated to be
$358 million and this reflects to the MSP as a decrease of 76¢/GGE in the ROI. For loblolly pine
feedstock processing, the MSP of the butene oligomers is found to be $5.01/GGE.

6.6. Conclusions

In summary, we have described an integrated biorefining strategy for the production of
butyl esters and GVL starting from cellulose and utilizing reactive extraction of levulinic and
formic acids with butene. This strategy simplifies the recovery and recycle of sulfuric acid for
cellulose deconstruction and enables downstream catalytic processing in the absence of sulfur.
The mixture of levulinic and formic esters, along with residual levulinic and formic acids, can be
converted to an aqueous solution of GVL and 2-butanol in a single step over a dual-catalyst-bed
consisting of Pd/C followed by Ru/C, in which H₂ generated from FA and its ester over Pd/C is
used for the reduction of LA and its ester to GVL over Ru/C. This dual-catalyst-bed system
operates over a wide range of organic acid and ester concentrations, making it adaptable to
various extraction conditions. In addition, it was demonstrated that the reactive extraction and
dual-catalyst-bed system works effectively for the conversion of a lignocellulose (poplar)
derived feed. Furthermore, the biorefining strategy described here eliminates the need for
extraction/distillation to recover sulfuric acid and purify levulinic acid, thus potentially
advancing the cost effective production of alkenes from renewable lignocellulosic resources.
Finally, with minor alterations to this strategy, levulinic acid, levulinates or GVL can be obtained
as alternative end-products. In the case of GVL production, increased processing cost due to
product isolation may be justified in value added applications, such as the production of α-methylene-γ-valerolactone,(28) caprolactone(33) or adipic acid.(33) Finally, a detailed technoeconomic analysis showed that the main cost drivers of the esterification strategy are heating requirement for the evaporation unit and cost of reactive extraction unit due to its high loading of butene. The use of loblolly pine feedstock leads to significant improvements in the MSP of butene oligomers corresponding to $5.01/GGE, which is 12¢/GGE better than that of reported by Kazi et al. (31). When starting from corn stover, which has significant amounts of hemicellulose, xylose can be recovered as an end product to be sold at a price of 31¢/kg, in order to obtain an MSP for butene oligomers at $5.13/GGE (31).

6.7. References


Chapter 7: Conversion of Hemicellulose to Furfural and Levulinic Acid Using Biphasic Reactors with Alkylphenol Solvents

The conversion of lignocellulosic biomass to fuels and chemicals requires the effective utilization of the \( \text{C}_5 \) and \( \text{C}_6 \) sugars present in hemicellulose and cellulose, respectively. Two classes of processing strategies have been explored in this respect, in which the hemicellulose and cellulose fractions are either processed together or are separated and processed separately. While simultaneous processing, such as in gasification or pyrolysis, offers the potential for simplicity of operation, the fractionation of hemicellulose and cellulose allows the processing of each fraction to be tailored to take advantage of the different chemical and physical properties of these fractions, and provides increased flexibility of operation. For example, the different affinities for biological organisms to ferment \( \text{C}_5 \) and \( \text{C}_6 \) sugars could be accommodated by using chemical methods to process the \( \text{C}_5 \) sugars in hemicellulose, while employing recent advances in biological conversions to convert the \( \text{C}_6 \) sugars in cellulose to fuels and/or chemicals.\(^{(1, 2)}\) Alternatively, it may be desirable to employ chemical processing steps to convert the \( \text{C}_5 \) sugars to fuels and/or chemicals, while taking advantage of the physical properties of cellulose for pulp and paper applications. We show in the present chapter that the hemicellulose fraction of lignocellulosic biomass can be converted to furfural and levulinic acid using biphasic reactors with alkylphenol solvents that selectively partition furanic compounds from acidic aqueous solutions. These furfural and levulinic acid products are valuable compounds for a variety of chemical applications,\(^{(3, 4)}\) and they serve as precursors for the synthesis of liquid transportation fuels.\(^{(5-7)}\)
The conversion of cellulose to chemicals and liquid fuels has been demonstrated through the formation of several platform molecules, such as glucose, 5-hydroxymethylfurfural, and levulinic acid (LA), utilizing chemical routes;[6-9] however, fewer studies address the conversion of hemicellulose to chemicals and fuels.[10, 11] Previous studies for the production of furfural (FuAL) from C5 sugars (i.e., xylose) suffer from the low concentrations of FuAL in the product stream due to low xylose concentrations (1-2 wt%) obtained from hemicellulose degradation.[10, 11] In addition, even though the production of LA from furfuryl alcohol (FuOH) has been reported with good yields over ion-exchange resin catalysts (e.g., Amberlyst).[12, 13] the regeneration of these catalysts following deactivation by deposition of solid humins during reaction is problematic. In addition, while zeolite catalysts (i.e. ZSM-5) can be used to replace resin catalysts and can be regenerated with a calcination treatment following deactivation,[13] these catalysts result in significantly lower LA yields, especially when increased LA concentrations are desired in the product stream.

Considering the aforementioned challenges for processing hemicellulose, we present a new biorefining strategy for converting the hemicellulose portion of lignocellulosic biomass to FuAL and LA utilizing biphasic systems that consist of an extractive organic layer and an aqueous layer that contains a mineral acid to catalyze the dehydration of xylose to furfural, and the hydrolysis of furfuryl alcohol to levulinic acid. These biphasic systems achieve high concentration of FuAL and LA, enabling the recovery of both products at the top of distillation columns, and eliminating issues related to deactivation and regeneration of solid acid catalysts. Three new organic solvents, 2-sec-butylphenol (SBP), 4-n-hexylphenol (NHP) and 4-propyl guaiacol (PG) are used as extracting agents for the production of FuAL and LA in these biphasic systems. The use of these solvents is particularly advantageous since they (i) have high partition
coefficients for extraction of FuAL, FuOH and LA, (ii) do not extract significant amounts of mineral acids from aqueous solutions, (iii) have higher boiling points compared to that of the final product, and (iv) could potentially be synthesized directly from biomass (i.e., lignin), such that these solvents would not have to be transported to the site of the biomass conversion steps.

7.1. Experimental

7.1.1. Hemicellulose Deconstruction

A mixture consisting of approximately 5.3 wt% solid corn stover from the Great Lakes Bioenergy Research Center (GLBRC; 5% moisture) and 0.1 M or 0.25 M aqueous HCl solution saturated with NaCl was added to a 450 mL Parr reactor. The reactor was purged 3 times with helium, heated to 373 K in approximately 20 min, and held at 373 K for an additional 5 h (0.1 M HCl) or 2 h (0.25 M HCl). The reactor was cooled using in-line water cooling. The contents of the reactor were filtered (0.2 μm membrane; Corning), and the aqueous phase was analyzed by HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a RI 410 detector). This treatment resulted in more than 90% of the hemicellulose being solubilized to xylose (~89%) and FuAL (~5%), with less than 13% of the cellulose being solubilized to glucose. For 2 cycles of corn stover deconstruction, a second bolus of 5 wt% corn stover was added to the 450 mL Parr reactor after cooling, and the steps listed above were carried out again. With two cycles of corn stover deconstruction, more than 90% of the hemicellulose can be solubilized to xylose (~88%) and FuAL (~10%), doubling the concentration of xylose (2.1 wt%).

7.1.2. Dehydration of Xylose to Furfural

Dehydration of xylose in aqueous solutions to obtain furfural was carried out using HCl as catalyst. An organic extracting solvent, 2-sec-Butylphenol (SBP), was used to extract furfural
continuously to separate it from xylose and the mineral acid and to inhibit further degradation. SBP (98%) and xylose (≥99%) were purchased from Alfa Aesar and Sigma-Aldrich, respectively and used directly. It should be noted that SBP has a health hazard rating of 3 and should be handled with utmost care. SBP is a petroleum derivative and was purchased at the time of experiments for about 56$ per kg. However, we foresee that these alkylphenol compounds can be derived from lignin to implement an efficient biorefining strategy. The experiments with simulated aqueous solutions were carried out in 10 mL glass reactors kept at constant temperature in a pre-heated oil bath using magnetic stirring. The experiments were carried out at 443 K. In a typical experiment, aqueous xylose solution with the desired sugar composition and 0.25 M HCl concentration was prepared and then saturated with NaCl. The aqueous xylose solution and SBP were added into the glass reactor to reach the desired mass ratio (aqueous layer (g) / SBP (g)). To end the reactions, the glass reactors were taken out from the oil bath and cooled in an ethylene glycol bath kept at freezing temperature with dry ice. The two phases were then separated and analyzed to quantify furfural and xylose using GC (Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID) and HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a UV detector) for organic and aqueous phase analyses, respectively.

The xylose dehydration experiments using the feed from the hemicellulose deconstruction (corn stover) discussed previously were carried out in 10 mL glass reactors described above or by adding the aqueous solution to a 450 mL Parr reactor followed by addition of SBP in a 6.67:1 aqueous to organic mass ratio. The reactor heating mantle was pre-heated for 6 min, and then placed on the reactor. The temperature reached 443 K in approximately 15 min.
The reactor was held at 433 K for the time specified, and then cooled using in-line water cooling, and weighed. The contents were filtered (Whatman Grade 1 filters) and the aqueous phase was analyzed by HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a RI 410 detector) and the organic layer was analyzed by GC (Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID). All the yields reported in Table 7.1 are based on GC and HPLC analyses and are not isolated yields.

Samples from SBP layers after contacting with aqueous phase containing HCl and NaCl were sent to Galbraith Laboratories for Cl⁻ analysis. Through ion chromatography, only negligible amounts (i.e., 13 ppm) of Cl⁻ ions were detected. In addition, no chlorinated organic compounds were detected within our detection limits.

7.1.3. Furfuryl Alcohol Conversion to Levulinic Acid

Conversion of furfuryl alcohol to levulinic acid was carried out in a biphasic reactor system consisting of an aqueous layer containing the acid catalyst, such as 1M H₂SO₄ or ZSM-5, and an organic layer consisting of furfuryl alcohol in 2-sec-butylphenol (SBP), 4-n-hexyl phenol (NHP), or 4-propyl guaiacol (PG). SBP (98%), NHP (98%) and PG (≥99%) were purchased from Alfa Aesar, TCI America (219 $/25 g) and Sigma-Aldrich (174 $/kg), respectively and used directly. Furfuryl alcohol (98%) was purchased from Sigma-Aldrich and used without purification. The health hazard rates of PG and NHP are 3 and 2, respectively and both should be handled with utmost care. The toxicity of these alkylphenol solvents (i.e., SBP, NHP and PG) are in the range of many organic solvents used and handled safely in the chemical industry, such as aromatics, halogenated hydrocarbons and ethers. It should be noted that very low volatilities (vapor pressures being lower than 0.03 mmHg at room temperature) of these alkylphenol
solvents facilitate their handling compared to some common solvents, such as, 1,2-dichloroethane and diethyl ether. In addition, since the final products in this process are obtained as top products in distillation (purification) steps, the minimal carryover of these alkylphenol solvents can be ensured in accordance with safety regulations. Similar to SBP, we foresee that these petroleum-derived phenolic species can be produced from lignin in near future. Single-phase experiments (ethanol and water) using 1 wt% furfuryl alcohol feeds with solid acid catalysts (Amberlyst-15 (Sigma-Aldrich) and ZSM-5) were carried out in 10 mL glass reactors using 4 g of solution and 0.1 g of catalyst. ZSM-5 (Engelhard/BASF) was calcined at 673 K for 3h under flowing air prior to reactions. Initial experiments for biphasic conversion of furfuryl alcohol (Table 7.2) were carried out at 398 K with 1 wt% furfuryl alcohol feeds in SBP and 1 M H₂SO₄ aqueous phase in 10 mL glass reactors kept at constant temperature in a pre-heated oil bath using magnetic stirring. In a typical experiment, aqueous solution and organic solution were added into the glass reactor to reach the desired volume ratio (organic (mL) / aqueous (mL)). To end the reactions, the glass reactors were taken out from the oil bath and cooled in an ethylene glycol bath kept at freezing temperature with dry ice. The two phases were then separated and analyzed to quantify levulinic acid and furfuryl alcohol using GC (Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID) and HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a UV detector) for organic and aqueous phase analyses, respectively.

Additional experiments for conversion of furfuryl alcohol (Table 7.3) were carried out in a 50 mL Parr reactor in a semi-batch mode. The monophasic aqueous experiments were carried out using ZSM-5 as the catalyst. ZSM-5 (Engelhard/BASF) was calcined at 673 K for 3h under
flowing air prior to reactions. The reactors were first loaded with water and ZSM-5 and heated to reaction temperature (398 K), and the aqueous furfuryl alcohol feed solutions were then slowly pumped into the reactor using an HPLC pump (Lab Alliance series 1) to reach the weight hourly space velocity (WHSV) given in Table 7.3. For biphasic reactions, the reactor was loaded with aqueous sulfuric acid solution and heated to the reaction temperature (398 K). When the reaction temperature was reached, furfuryl alcohol feed solutions in the organic solvents were pumped into the reactor using an HPLC pump (Lab Alliance series 1) to reach the weight hourly space velocity (WHSV) and volume ratio of organic to aqueous layer given in Table 7.3. In some cases, part of the organic solvent was also loaded in the reactor with the aqueous sulfuric acid solution prior to heating and feeding of furfuryl alcohol solutions. At the end of the reactions, the two phases were separated and analyzed to quantify levulinic acid and furfuryl alcohol using GC (Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID) and HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a UV detector) for organic and aqueous phase analyses, respectively. All the yields reported in Table 7.2 and Table 7.3 are based on GC and HPLC analyses and are not isolated yields.

7.2. Overall Strategy

For the first step of this biorefining strategy (Figure 7.1), solid biomass (i.e. corn stover) is subjected to mild pretreatment in a dilute-acid, aqueous solution to solubilize the hemicellulose as xylose. After filtering the solution from the solid cellulose and lignin, an organic solvent (i.e., SBP) is added to the aqueous solution and these liquids are heated in a biphasic reactor to achieve dehydration of xylose to FuAL, which is a valuable chemical intermediate. (3) FuAL can be distilled from SBP and sold as a chemical or as depicted in Figure
7.1, converted to LA by first hydrogenating FuAL to FuOH over a metal-based catalyst (e.g., copper)(14, 15) and then reacting the FuOH with water in a biphasic reactor to form LA. Similar to FuAL, the LA product can be distilled from the organic solvent and sold as a chemical.

7.3. Biphasic Production of Furfural

Xylose dehydration to FuAL has been demonstrated with high yields (~90%) in several previous studies using mineral acids and salts in biphasic systems with organic solvents, such as methyl isobutyl ketone (MIBK), 2-butanol and tetrahydrofuran (THF). (9, 11, 16) An important factor in choosing extractive solvents in biphasic systems is the partitioning of furfural between two phases. The partition coefficient, R, is defined as the ratio of the furfural concentration in the organic phase to its concentration in the aqueous phase. Higher values of R correspond to more efficient extraction of furfural to the organic layer, which in turn generally corresponds to higher furfural selectivities. The value of R can be altered by using different extractive solvents or saturating the aqueous layer with an inorganic salt, which is referred to as the salting-out effect. (17) This effect of salt can be explained as the alteration of the intermolecular forces between the organic and aqueous solutions, in which the mutual solubility of the two phases is decreased. The presence of inorganic salts is also useful to achieve biphasic systems with organic solvents that are miscible with water without the presence of salts. However, the low (~20) partition coefficients for extraction of FuAL in the previous systems that consisted of an aqueous layer saturated with salt and organic layer consisting of MIBK, 2-butanol or THF required the use of large amounts of the organic solvent relative to the aqueous xylose solution, resulting in lower concentrations of FuAL in the organic phase compared to the starting concentration of xylose in the aqueous phase. This problem is exacerbated by the low concentrations of xylose
(e.g., 1-2 wt%) typically obtained in aqueous solutions from dilute acid treatment of real biomass feedstocks (e.g. corn stover). Thus, it is important to identify new methods to produce higher concentrations of FuAL in the organic phase of biphasic reactor systems to improve the efficiency of downstream processing options, such as distillation or further upgrading reactions.

Figure 7.1 Schematic representation of the conversion of hemicellulose to furfural (FuAL) involving the biphasic dehydration of xylose to furfural using an organic solvent, followed by the production of levulinic acid (LA) by reduction of furfural to furfuryl alcohol (FuOH) over a metal catalyst and further reaction of furfuryl alcohol with water in a biphasic reactor to form LA.
A new extracting solvent, SBP, has been identified in our group for the effective extraction of LA from acidic aqueous solutions (18). We have now expanded this idea and now show for the first time that SBP is also effective for extracting FuAL from acid aqueous solutions, with an exceptionally high partition coefficient (measured at mass ratio of organic to aqueous layer being 2) of ~50 in the absence of salt in the aqueous phase and increasing to >90, when the aqueous phase is saturated with NaCl. This high partition coefficient of FuAL in the water-SBP system allows for high yields of FuAL in the organic phase, even when small amounts of the SBP solvent are used in the biphasic reactor (i.e., when the mass ratio of the aqueous solution to SBP is increased). Therefore, higher concentrations of FuAL can be obtained in a single stage compared to the starting xylose concentration. As shown in Table 7.1, entry 1, a 1.5 wt% xylose feed in an aqueous solution containing 0.1 M HCl and saturated with NaCl, with small amounts of SBP (xylose solution:SBP mass ratio = 6.67), results in high yields of FuAL (78%), with 90% of FuAL partitioning to SBP. The final organic phase contains 4.1 wt% FuAL in SBP. Another advantage of using SBP as the organic solvent is that it extracts only negligible amounts (13 ppm, detected via ion chromatography in Galbraith Laboratories) of Cl− ions residing in the aqueous phase originating both from HCl and NaCl. In addition, no chlorinated organic compounds were detected within our detection limits.

To produce an aqueous solution of xylose from the hemicellulose fraction of a real biomass feedstock, corn stover was treated for 5 h at 363 K in an aqueous solution containing 0.1 M HCl and saturated with NaCl. This treatment resulted in more than 90% of the hemicellulose being solubilized to xylose (~89%) and FuAL (~5%), with less than 13% of the cellulose being solubilized to glucose. This corn stover feed (1.1 wt% xylose) resulted in a maximum yield of ~70% for production of FuAL (Table 7.1, entry 2), with again ~90% of FuAL partitioning to
SBP, using our biphasic reactor system. The small decrease in yield compared to the simulated feed could be due to inhibiting effects of some by products obtained in the hemicellulose deconstruction step, but, the overall yield from this biomass derived feed can be increased to ~75% by increasing the HCl concentration to 0.25 M (entry 2).

**Table 7.1** Results of xylose dehydration experiments carried out at 443 K in a biphasic reactor system, using SBP as the extracting solvent in a 6.67:1 aqueous:organic mass ratio, with aqueous solutions containing 0.1 M or 0.25 M HCl and saturated with NaCl. For all experiments, approximately 90% of total furfural is partitioned to SBP phase.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Xylose (wt%)</th>
<th>HCl Concentration (M)</th>
<th>Time (min)</th>
<th>Xylose conversion (%) (± 2)</th>
<th>Furfural Selectivity (%) (± 2)</th>
<th>Furfural Yield (%) (± 2)</th>
<th>Final furfural in SBP (wt%) (± 0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[a]</td>
<td>1.5</td>
<td>0.1</td>
<td>15</td>
<td>92</td>
<td>83</td>
<td>76</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>98</td>
<td>80</td>
<td>78</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>30</td>
<td>100</td>
<td>71</td>
<td>71</td>
<td>3.7</td>
</tr>
<tr>
<td>2[a]</td>
<td>1.1 (from corn stover)</td>
<td>0.1</td>
<td>15</td>
<td>77</td>
<td>88</td>
<td>69</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>95</td>
<td>74</td>
<td>70</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td>40</td>
<td>98</td>
<td>39</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>92</td>
<td>91</td>
<td>75</td>
<td>3.2</td>
</tr>
<tr>
<td>3[a]</td>
<td>5</td>
<td>0.1</td>
<td>10</td>
<td>61</td>
<td>84</td>
<td>51</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td>92</td>
<td>77</td>
<td>71</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>99</td>
<td>68</td>
<td>67</td>
<td>11.4</td>
</tr>
<tr>
<td>4[a]</td>
<td>2.1 (2 cycles from corn stover)</td>
<td>0.25</td>
<td>12.5</td>
<td>93</td>
<td>75</td>
<td>70</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td>95</td>
<td>75</td>
<td>71</td>
<td>5.3</td>
</tr>
<tr>
<td>5[b]</td>
<td>2.1 (2 cycles from corn stover)</td>
<td>0.25</td>
<td>1.5</td>
<td>92</td>
<td>71</td>
<td>66</td>
<td>5.3</td>
</tr>
</tbody>
</table>

[a]Experiments were carried out in 10 mL glass reactors heated in oil bath. [b]Experiments were carried out in a 450 mL PARR reactor, and reaction times given are after the reactor reaches 443 K.

It should be noted that, increasing the HCl concentration for corn stover deconstruction step, results in the same xylose yields by decreasing the total reaction time to 2h. It is shown in entry 3, with a simulated 5 wt% xylose feed that the overall furfural yield (~71%) and partitioning in SBP stays similar if the xylose concentration is increased. The xylose concentration in the aqueous phase can be increased by adding corn stover to the HCl solution in
progressive stages. With two cycles of corn stover deconstruction, more than 90% of the hemicellulose can be solubilized to xylose (~88%) and FuAL (~10%), doubling the concentration of xylose (2.1 wt%). Using this feed for biphasic dehydration (entry 4), a maximum FuAL yield of ~71% is obtained with ~90% of FuAL partitioning to SBP, resulting in a 5.3 wt% FuAL in SBP. Finally, as demonstrated in entry 5, scaling up the biphasic reaction from a 10 mL glass reactor to a 450 mL Parr reactor, results in a similar overall yield to FuAL (66%).

As shown in Figure 7.1, FuAL can be distilled out of SBP following the biphasic xylose dehydration step. ASPEN PLUS modeling software was used to conduct simulations of the distillation column for this separation using the feed composition obtained as the product of the xylose (corn stover derived) dehydration experiment shown in Table 7.1, entry 4. The feed consists of 5.3 wt% furfural, 0.0001 wt% acetic acid and 0.3 wt% levulinic acid in SBP with some heavier by-products. Since these by-products are undetermined but known to be heavier than SBP, we assumed that the remainder of the feed stream was composed of SBP. With a basis of obtaining 100 kmol/hr furfural product and with the feed entering at 443 K (temperature of the biphasic dehydration) at 1 atm, we calculated that 99.7% mass purity of furfural can be obtained at the top of a distillation column that consists of 12 stages (the feed stream enters at the 6th stage). All of acetic acid is recovered in the top product, whereas all of the levulinic acid is recovered at the bottom with SBP.

**7.4. Biphasic Production of Levulinic Acid**

Following the distillation of FuAL out of SBP, it can be sold as a chemical, or it can be hydrogenated with almost quantitative yields over a metal catalyst (e.g., copper) in the vapor phase to form FuOH, an important chemical in polymer industry. (14, 15) Importantly, this FuOH
intermediate can be used in another biphasic reactor system to produce LA, another attractive platform molecule from which fine chemicals (δ-aminolevulinic acid, diphenolic acid, etc.) and fuel additives (levulinate esters, MTHF, etc.) can be produced.\(^\text{(19)}\)

The conversion of FuOH in alcohol solvents to produce levulinate esters has been reported in the literature with high yields;\(^\text{(13)}\) however, when LA is the desired product, the conversion of FuOH to LA in aqueous acidic solutions is plagued by polymerization reactions that lead to low selectivities at even modest concentrations (e.g., 1 wt\%) when compared to production of levulinate esters. For instance, as shown in Figure 7.2, an ethyl levulinate yield of 85\% was achieved starting with 1 wt\% FuOH in ethanol using Amberlyst-15 as the acid catalyst, as opposed to a lower yield of 55\% for production of LA in water at 398 K with equal amount of catalyst and reaction time. The same trend is also seen for ZSM-5 in Figure 7.2. There was a 64\% yield to ethyl levulinate in alcohol compared to 15\% yield to LA (Table 7.2, entry 1) in water at the same reaction conditions. This is because the rates of undesirable reactions in acidic aqueous solutions increase more rapidly with reactant concentration than the rates of desirable reactions, such that the selectivity for desirable reactions becomes lower at higher reactant concentrations. The strategy employed in this paper is to utilize biphasic reactors to achieve a low concentration of reactive species in acidic aqueous solutions to increase LA yields by minimizing undesirable polymerization reactions, and yet to achieve a high concentration of the final product to facilitate product separation and purification. In this processing approach, the purpose of the organic solvent is to selectively extract highly reactive species from the acidic aqueous solution in which the desirable reactions take place at low concentrations of reactive species.
Figure 7.2 Ethyl levulinate and ethanol yields achieved from 1 wt\% furfuryl alcohol in ethanol and water, respectively over Amberlyst 15 and ZSM-5 at 398 K.

To apply this concept, a biphasic reactor with SBP was employed to form LA, as seen in Figure 7.1, in a manner analogous to the case of xylose dehydration to FuAL. In the case of FuOH conversion to LA, the organic extracting solvent partitions the reactant out of the reactive aqueous phase, whereas in the case of xylose dehydration to FuAL, the product is partitioned out of the reactive aqueous phase. Due to high partition coefficient (7.5) of FuOH in the SBP-water system, the FuOH reactant mostly remains in the organic phase, decreasing the FuOH concentration in the acidic aqueous medium and, thus, decreasing the rates of degradation reactions accordingly. When the reaction is carried out in a biphasic reactor, mineral acids can be used instead of solid acid catalysts, and these mineral acids can be recovered and recycled, (18, 20) eliminating any issues of deactivation and regeneration of possible solid acid catalysts. It should be noted that another important function of the extracting solvent for production of LA is to extract majority of LA to the organic layer to ensure its separation from the mineral acid in the
aqueous layer. It can be seen in Table 7.2 that up to ~72% yield of LA can be obtained using a biphasic system containing aqueous 1 M H₂SO₄ solution and SBP (entry 3 and 4), while only 32% yield of LA is obtained in a single aqueous phase medium with 1 M H₂SO₄ and 1 wt% FuOH feed (Table 7.2, entry 2).

**Table 7.2** Yields to levulinic acid starting from furfuryl alcohol solutions in 2-sec-butylphenol (SBP) in a biphasic reactor system with water or in a monophasic system with water at 398 K. All reactions were carried out in a batch reactor system. LA and SA correspond to levulinic acid and 1 M sulfuric acid, respectively. Furfuryl alcohol conversion is complete for all experiments.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Furfuryl alcohol (wt%)</th>
<th>Organic Solvent</th>
<th>org / aq (mL/mL)</th>
<th>catalyst</th>
<th>t (h)</th>
<th>Yield to LA (%)</th>
<th>%LA in org</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>ZSM-5</td>
<td>1</td>
<td>15±1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>SA</td>
<td>1</td>
<td>32±1</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>SBP</td>
<td>1</td>
<td>SA</td>
<td>1</td>
<td>68±4</td>
<td>67±5</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>SBP</td>
<td>1</td>
<td>SA</td>
<td>3</td>
<td>72±4</td>
<td>67±5</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>SBP</td>
<td>2</td>
<td>SA</td>
<td>1</td>
<td>66±4</td>
<td>81±5</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>SBP</td>
<td>4</td>
<td>SA</td>
<td>1</td>
<td>60±4</td>
<td>89±5</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>SBP</td>
<td>1</td>
<td>SA</td>
<td>1</td>
<td>31±2</td>
<td>66±2</td>
</tr>
</tbody>
</table>

Approximately 68% of LA can be retained in the SBP layer when the volume ratio of organic to aqueous layer is 1 (entry 3). However, by decreasing the amount of aqueous layer to obtain a ratio of 2 (entry 5), a higher amount of LA (~81%) can be recovered in the organic layer, while still reaching approximately 66% total yield. A further decrease in the aqueous amount (entry 6), results in retention of most of the LA in the organic layer (~89%); however, the overall yield of LA is decreased to ~60%.

While use of the SBP solvent leads to a significant increase in the yield of LA compared to monophasic reaction in water, it can be seen in Table 7.2, entry 7 that increasing the concentration of FuOH from 1 to 10 wt% in SBP leads to a decrease in the LA yield (~31%). An additional strategy to insure that the concentrations of the reactant and the intermediates always
remain low versus time is to employ semi-batch operation, similar to Lang et al. (13) (see Supporting Information), in which the FuOH solution in SBP is slowly fed to the reactor that includes a heated solution of 1 M H$_2$SO$_4$ solution. This semi-batch operation resulted in LA yields of around 65% starting with 10-20 wt% FuOH solutions (Table 7.3 entries 3-6), and more than 70% of the total LA is partitioned into the organic layer. In contrast to these high yields obtained using SBP and semi-batch operation, the yields of LA are still low (Table 7.3, entries 1-2) in a semi-batch mode with a single aqueous phase using ZSM-5, these yields being ~45% and ~35% starting with feeds containing 10 and 20 wt% FuOH concentrations, respectively. Thus, the high partition coefficient of FuOH in the SBP-water system allows for high yields of LA even at high feed concentrations that cannot be processed in monophasic water systems. From this point, the solution of LA in SBP can be processed further as presented in our earlier work to form GVL over a Ru-Sn catalyst (18).

Since the boiling point of LA (519 K) is higher than that of SBP (500 K), LA cannot be removed from the SBP solvent at the top of a distillation column. For this reason, two possible alkylphenol solvents with higher boiling points were studied. One alkylphenol solvent is 4-n-hexyl phenol (NHP; boiling point 560 K), which as seen in Table 7.3 (entry 7), resulted in good yields of LA (~70%) with a 10 wt% FuOH feed and 1:1 volume ratio of the organic solvent to the acidic aqueous solution. Compared to SBP, the partitioning of LA to NHP is lower, with 60% of LA being in the organic layer; however, this lower partitioning can be overcome by decreasing the relative amount of the acidic aqueous layer and increasing the starting FuOH concentration. As shown in entry 8, ~68% of LA can be recovered in the organic layer with a 20% FuOH feed and half the volume of aqueous layer; however, the overall yield to LA decreases to ~52%.
Another possible alkylphenol solvent for biphasic reactor operation is 4-propyl guaiacol (PG), which has a boiling point of 562 K. Importantly, this compound has been reported to be isolated from lignin degradation.\(^{(21)}\) It can be seen in Table 7.3 that good overall yields of LA (\(~69\%)\) can be obtained with 1:1 organic to aqueous volume ratio. However, the partitioning of LA in the PG solvent is relatively low (36\% being in PG), but, as shown in entry 10, by decreasing the acidic aqueous volume relative to that of PG, good yields can be maintained (\(~69\%)\) with significant amounts (58\%) of the LA being partitioned in the PG solvent. As shown in entries 11-12, higher concentrations of FuOH result in lower overall yields, yet, the yields of LA in these biphasic reactor systems are still considerably higher than those obtained in monophasic aqueous phase systems with ZSM-5.

**Table 7.3** Yields to levulinic acid starting from furfuryl alcohol solutions in 2-sec-butylphenol (SBP), 4-n-hexylphenol (NHP) or 4-propyl guaiacol (PG) in a biphasic reactor system with water or in a monophasic system with water at 398 K. All reactions were carried out in a semi-batch reactor system. LA and SA correspond to levulinic acid and 1 M sulfuric acid, respectively. Furfuryl alcohol conversion is complete for all experiments.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Furfuryl alcohol (wt%)</th>
<th>Organic Solvent</th>
<th>org / aq (mL/mL)</th>
<th>catalyst</th>
<th>WHSV (h(^{-1}))</th>
<th>Yield to LA (%)</th>
<th>%LA in org wt. %</th>
<th>LA in sol wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 (20)(^{[a]})</td>
<td>-</td>
<td>-</td>
<td>ZSM-5</td>
<td>0.24</td>
<td>45±1</td>
<td>-</td>
<td>5.7</td>
</tr>
<tr>
<td>2</td>
<td>20 (40)(^{[a]})</td>
<td>-</td>
<td>-</td>
<td>ZSM-5</td>
<td>0.48</td>
<td>35±1</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>10(^{[b]})</td>
<td>SBP</td>
<td>1</td>
<td>SA</td>
<td>0.08</td>
<td>65±2</td>
<td>72±1</td>
<td>5.1±0.2</td>
</tr>
<tr>
<td>4</td>
<td>10(20)(^{[a]})</td>
<td>SBP</td>
<td>1</td>
<td>SA</td>
<td>0.08</td>
<td>67±2</td>
<td>72±1</td>
<td>5.2±0.2</td>
</tr>
<tr>
<td>5</td>
<td>20(^{[b]})</td>
<td>SBP</td>
<td>1</td>
<td>SA</td>
<td>0.16</td>
<td>65±2</td>
<td>67±1</td>
<td>10.2±0.2</td>
</tr>
<tr>
<td>6</td>
<td>10(^{[b]})</td>
<td>SBP</td>
<td>2</td>
<td>SA</td>
<td>0.16</td>
<td>62±2</td>
<td>83±1</td>
<td>5.7±0.2</td>
</tr>
<tr>
<td>7</td>
<td>10(^{[b]})</td>
<td>NHP</td>
<td>1</td>
<td>SA</td>
<td>0.08</td>
<td>70±2</td>
<td>60±2</td>
<td>4.7±0.2</td>
</tr>
<tr>
<td>8</td>
<td>20(40)(^{[a]})</td>
<td>NHP</td>
<td>2</td>
<td>SA</td>
<td>0.32</td>
<td>52±3</td>
<td>68±2</td>
<td>8.3±0.4</td>
</tr>
<tr>
<td>9</td>
<td>10(^{[b]})</td>
<td>PG</td>
<td>1</td>
<td>SA</td>
<td>0.08</td>
<td>69±3</td>
<td>36±2</td>
<td>2.8±0.4</td>
</tr>
<tr>
<td>10</td>
<td>10(^{[b]})</td>
<td>PG</td>
<td>2</td>
<td>SA</td>
<td>0.16</td>
<td>69±3</td>
<td>58±2</td>
<td>4.6±0.4</td>
</tr>
<tr>
<td>11</td>
<td>20(40)(^{[a]})</td>
<td>PG</td>
<td>2</td>
<td>SA</td>
<td>0.32</td>
<td>59±3</td>
<td>61±2</td>
<td>8.8±0.6</td>
</tr>
<tr>
<td>12</td>
<td>30(60)(^{[a]})</td>
<td>PG</td>
<td>2</td>
<td>SA</td>
<td>0.48</td>
<td>55±3</td>
<td>60±2</td>
<td>13.0±0.6</td>
</tr>
</tbody>
</table>

\(^{[a]}\)Experiments carried out by starting with solvent and catalyst and feeding a concentration of furfuryl alcohol (shown in parenthesis) to reach a final furfuryl alcohol concentration (value not in parenthesis). \(^{[b]}\)Experiments carried out by starting with aqueous SA solutions and feeding the given concentration of furfuryl alcohol.
Figure 7.3 summarizes the comparison between the three solvents in a biphasic semi-batch system in terms of the levulinic acid yields achieved and the resulting levulinic acid concentration (wt%) in the organic solvent.

**Figure 7.3** Levulinic acid yield and levulinic acid concentration achieved (wt%) in the organic phase for the biphasic hydrolysis of furfuryl alcohol with feed concentrations between 10-20 wt% using 2-sec-butylphenol (SBP), n-hexylphenol (NHP) and 4-propyl guaiacol (PG) in a semi-batch reactor system at 398 K.

### 7.5. Liquid Phase Hydrogenation of Furfural

If furfuryl alcohol or levulinic acid is the desired end product, it would be more energy efficient to eliminate the furfural distillation step and hydrogenate the furfural to furfuryl alcohol in the liquid phase in the alkylphenol solvent instead of in the gas phase. As in the gas phase, Cu-based catalysts, such as Cu/SiO$_2$ is selective for the production of FuOH from FuAL in the
SBP solvent (see Table 7.4) and minimal quantities of the deep hydrogenation products, such as tetrahydrofurfuryl alcohol and methyl tetrahydrofuran, are formed. However, leaching of Cu in liquid phase reactions is a well-known problem and results in irreversible deactivation (22). The same problem occurs, in terms of Cu leaching and inability of regeneration of the catalyst, for the Cu-ZnO-Al₂O₃ catalyst. On the other hand, precious metals, such as Pd, Pt and Ru monometallics, that are less prone to leaching can be used for the hydrogenation of furfural; however, these catalysts result in low selectivities (<60%) due to the formation of deep hydrogenation products. In addition, these metals result in the hydrogenation of the C=O bonds in SBP solvent forming butyl-cyclohexanone (18), which is undesirable since it increases the solvent refurbishing costs. Our strategy for solving this problem is to modify the selectivity of Ru, Pt and Pd based catalysts (that are less prone to leaching) by adding Sn, with the aim of hydrogenating the C=O group in furfural without hydrogenating the C=C bonds in 2-sec-butylphenol and furfural/furfuryl alcohol. Thus, Sn was added to 5 wt% Ru/C in a 1:3 Ru:Sn molar ratio, to 5 wt% Pt/C in a 3:1 Pt:Sn molar ratio, and to 5 wt% Pd/C in a 3:1 Pd:Sn molar ratio. Table 7.4 compares the results for conversion of FuAL and selectivity and yield for FuOH for these bimetallic catalysts and the previously mentioned copper based catalysts. As seen in Table 7.4, the selectivity for production of FuOH over the RuSn/C catalyst (66%) and PdSn/SiO₂ catalyst (47%) was still low, with methyl tetrahydrofuran being the major by-product. However, the PtSn/C catalyst resulted in high furfuryl alcohol selectivity (98%) even at complete conversion as suggested in earlier work (23), and with a furfuryl alcohol production rate that was an order of magnitude higher compared to the other bimetallic catalysts.
Table 7.4 Furfural conversion, furfuryl alcohol selectivity/yield and production rate over different catalysts. T = 373 K, P= 34 bars in H₂, Feed = 5 wt. % furfural in SBP.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Furfural Conversion (%)</th>
<th>Furfuryl alcohol selectivity (%)</th>
<th>Furfuryl alcohol yield (%)</th>
<th>Furfuryl alcohol Production Rate (mmol min⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Cu/SiO₂</td>
<td>98</td>
<td>94</td>
<td>92</td>
<td>0.06</td>
</tr>
<tr>
<td>Cu-ZnO-Al₂O₃</td>
<td>97</td>
<td>90</td>
<td>87</td>
<td>0.03</td>
</tr>
<tr>
<td>5% RuSn(1:3)/C</td>
<td>93</td>
<td>66</td>
<td>61</td>
<td>0.01</td>
</tr>
<tr>
<td>5% PtSn(3:1)/SiO₂</td>
<td>99</td>
<td>98</td>
<td>97</td>
<td>0.18</td>
</tr>
<tr>
<td>5% PdSn(3:1)/SiO₂</td>
<td>85</td>
<td>47</td>
<td>40</td>
<td>-</td>
</tr>
</tbody>
</table>

Importantly, SBP solvent stayed completely inert. Moreover, even though the PtSn catalyst deactivated with time-on-stream, it could be regenerated completely through a calcination step in air, as shown in Figure 7.4, without changing the rate of deactivation significantly. These results showed that coking was the main reason for deactivation, and activity could be restored with calcination treatment under air flow at 623 K.

Figure 7.4 Rate of furfuryl alcohol production (mmol/min/g cat) over 5 wt% PtSn/C in a 3:1 Pt:Sn molar ratio T = 373 K, P= 34 bars in H₂, Feed = 5 wt. % furfural in SBP, H₂ flow of 30 cm³/min. WHSV= 21.5 h⁻¹. Blue lines represent a calcination treatment with 50 cm³/min of air at 623 K for 3h.
7.6. Conclusions

The biorefining strategy outlined in this chapter offers the production of FuAL and LA from the hemicellulose portion of lignocellulosic biomass utilizing biphasic systems with new solvent systems. In the case for xylose dehydration, the presence of an extractive organic solvent ensures the continuous removal of the highly reactive product (FuAL) from the acidic aqueous medium to prevent further degradation. In the case of FuOH hydrolysis, the biphasic system avoids high concentrations of the highly reactive reactants and/or intermediates in the acidic aqueous medium to prevent oligomerization reactions of FuOH that result in the formation of solid humins. In both of these reaction systems, the organic solvent extracts the majority of the furfural and LA products, enabling the separation of these valuable products from the mineral acid in the aqueous layer. Use of solvents such as SBP, NHP and PG allows for the production of FuAL and LA at higher concentrations compared to monophasic reactions in water, leading to more efficient separation of these products at the top of distillation columns. In addition, these three new solvents may possibly be produced from lignin, leading to new research directions for the creation of sustainable biorefineries that utilize effectively the hemicellulose, cellulose, and lignin fractions of lignocellulosic biomass. Finally, if FuOH or LA is desired as the end product, furfural hydrogenation can be carried out in the alkylphenol solvent over a PtSn/SiO$_2$ bimetallic catalyst for the selective formation of furfuryl alcohol, while the alkylphenol solvent stays unconverted.

7.7. References

Chapter 8: Conversion of Hemicellulose to Furfural Using Solid Acid Catalysts in γ-Valerolactone, A Biomass-Derived Solvent

As discussed in the previous chapter, among the products that can be obtained from the hemicellulose portion of biomass, the production of furfural is a particularly promising option since furfural can replace crude-oil-based organics for the production of resins, lubricants, adhesives and plastics. Furfural can also be used to produce other valuable chemicals, such as furfuryl alcohol, tetrahydrofurfuryl alcohol, furanoic acid, and tetrahydrofuran \( (1, 2) \). However, current methods for production of furfural from hemicellulose suffer from drawbacks that do not comply with the principles of green and sustainable biorefining. In particular, current production methods use mineral acids to catalyze the dehydration of xylose, which are difficult to recover from the reaction mixture. Furthermore, the use of homogeneous mineral acids is corrosive and poses environmental and health risks. On the other hand, the use of solid acids in aqueous environments is problematic in view of catalyst degradation and/or leaching of catalyst components into aqueous solution at elevated temperatures (e.g., 430 K). Importantly, current yields of furfural are low (e.g., <60%) in the aqueous phase.\( (3) \) As presented in literature and our previous work (Chapter 7), the yields of furfural and its separation from the mineral acid can be improved by using biphasic systems; however, achieving effective mixing between the two phases is still a considerable challenge for scaling up biphasic processes. In addition, the other concerns related to the presence of mineral acids remain for the biphasic systems. Therefore, in this chapter, we investigate an alternative strategy for the conversion of hemicellulose to furfural.

All of the aforementioned difficulties associated with the conversion of xylose to furfural can be alleviated using γ-valerolactone (GVL) as a solvent in a monophasic system and using
solid acid catalysts. Importantly, GVL is a green solvent that can be produced from lignocellulose (4), and Horvath has been a strong proponent for the use of GVL as a solvent in biomass processing (5). Using GVL as the solvent decreases the furfural degradation rates and increases xylose conversion rates. In addition, furfural, having a higher volatility than GVL, could be obtained as a top product in a distillation step and if desired GVL could be synthesized as the end-product of the process, eliminating any product purification steps. Furthermore, the use of a monophasic reaction system eliminates the need for a liquid-liquid separation step, the loss of the product in the aqueous phase, and reduces mixing requirements. Moreover, by minimizing the concentration of water present in the reactor, it is possible to use solid catalysts for the conversion of xylose (and xylose oligomers) to furfural, with minimal degradation of the catalyst and without leaching of acid sites into solution, as opposed to the case of using solid acid catalysts in aqueous solutions at elevated temperatures.

8.1. Experimental

8.1.1. Catalyst Synthesis

Dehydration of xylose to furfural was carried out using GVL as the solvent with a homogenous mineral acid (0.02 M H$_2$SO$_4$) and with solid acid catalysts, including sulfonic acid functionalized catalysts (Amberlyst 70, Nafion SAC-13, sulfonated carbon and propylsulfonic acid functionalized SBA-15), zeolites (H-ZSM-5, H-Mordenite and H-Beta) and sulfated inorganic metal oxides (sulfated zirconia). Amberlyst 70 (The Dow Chemical Company) was washed, dried and crushed before use. Nafion SAC-13 was purchased from Sigma-Aldrich and used directly. Propylsulfonic acid functionalized SBA-15 (S-SBA-15), sulfonated carbon (S-Carbon) and Sn-SBA-15 catalysts were synthesized following Zhao et al. (6), Takagaki et al. (7)
and Shah et al. (8), respectively as also described in Chapter 2. Sulfated zirconia catalyst (MEI) was calcined at 723 K for 6 h prior to reactions. ZSM-5, mordenite and beta zeolites were purchased from Zeolyst and used after a calcination treatment at 723 K for 6 h.

8.1.2. FTIR Spectroscopy Studies of Pyridine Adsorption

FTIR analysis was carried out using a Thermo Nicolet 6700 spectrophotometer equipped with a pyroelectric detector (DTGS type) using a resolution of 4 cm$^{-1}$. Self-supported pellets of calcined H-mordenite, Sn-SBA-15 and $\gamma$-alumina were placed in an IR cell equipped with CaF$_2$ windows and dried under air flow at 573 K for 2 h.

![FTIR spectra for pyridine adsorption over calcined (a) $\gamma$-alumina, (b) H-mordenite and (c) Sn-SBA-15.](image)

Figure 8.1 FTIR spectra for pyridine adsorption over calcined (a) $\gamma$-alumina, (b) H-mordenite and (c) Sn-SBA-15.

The pellets were then contacted with helium saturated with pyridine at room temperature for 30 min. Finally, the cell was flushed with helium at 373 K for 1 h to remove hydrogen-
bonded pyridine. The spectra for both catalysts are shown in Figure 8.1. Pyridine reacts with Brønsted and Lewis acid sites, forming PyH\(^+\) and PyL species with IR bands at 1545 and 1450 cm\(^{-1}\), respectively, over H-mordenite, whereas there are only Lewis sites present for \(\gamma\)-alumina and Sn-SBA-15 forming PyL species with IR band at 1450 cm\(^{-1}\).

8.1.3. Hemicellulose Deconstruction with Hot Water Treatment and Concentration of Pre-hydrolysis Liquor

Wood chips (poplar) were treated in hot water to obtain an aqueous solution of C\(_5\) and C\(_6\) sugars/oligomers, referred to as pre-hydrolysis liquor (PHL). The hot water treatment was carried out using a methodology similar to that presented by Li et al. (9) In one batch, 5 g of wood chips were mixed with 20 g of water in a 50 mL Parr reactor. The reactor was purged 3 times with helium, pre-heated to 353 K in approximately 20 min, then heated to 443 K in one hour, and subsequently kept at 443 K for an additional hour. The reactor was cooled, the contents of the reactor were filtered (0.2 \(\mu\)m membrane; Corning), and the aqueous phase (PHL) was analyzed by HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column and a RI 410 detector). This treatment resulted in about 50\% of the xylose content of woodchips being solubilized in the form of oligomers, xylose and furfural (FuAL), with less than 2\% of the C\(_6\) sugars being solubilized to glucose and oligomers. The C\(_5\) sugar content of the PHL was determined by hydrolysis using 4 wt% sulfuric acid (1:20 mass ratio of PHL solution:sulfuric acid solution) at 393 K for 1 h (9). The C\(_6\) sugar content of the PHL was determined by quantifying the levulinic acid produced from hydrolysis using 0.1 M HCl at 443 K for 3 h. At these conditions, as determined from mixtures of glucose and cellobiose, the yield of levulinic acid at complete conversion is equal to 55\%. The yield of levulinic acid was then used to
calculate the C\textsubscript{6} sugar content of the PHL feed. PHL was concentrated in an oil bath kept at 368 K by removing approximately 90\% of the water. Some of the acetic acid and furfural (~40\% each) were also removed in the evaporation step. The product distribution in the concentrated PHL solution after addition of GVL is shown in Table 8.1.

**Table 8.1** Composition of monomeric and oligomeric sugars, acetic acid, furfural and 5-hydroxymethylfurfural (HMF) in the dehydration reactor (mixture of evaporated PHL and GVL).

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylose</td>
<td></td>
</tr>
<tr>
<td>monomeric</td>
<td>1.43</td>
</tr>
<tr>
<td>oligomeric</td>
<td>0.49</td>
</tr>
<tr>
<td>Glucose</td>
<td></td>
</tr>
<tr>
<td>monomeric</td>
<td>0.06</td>
</tr>
<tr>
<td>oligomeric</td>
<td>0.23</td>
</tr>
<tr>
<td>Arabinose</td>
<td></td>
</tr>
<tr>
<td>monomeric</td>
<td>0.02</td>
</tr>
<tr>
<td>oligomeric</td>
<td>-</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.22</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.03</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.09</td>
</tr>
<tr>
<td>HMF</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**8.1.4. Reaction Studies**

Xylose (≥99\%) and γ-valerolactone (GVL) (≥98\%) were purchased from Sigma-Aldrich and used without further purification. Experiments using xylose or hemicellulose extract (PHL) were carried out in 10 mL glass reactors kept at constant temperature (448 K) in a pre-heated oil bath with magnetic stirring. In a typical experiment starting from xylose, the required amounts of xylose, water and GVL were mixed in the reactor. The ratio of the mass of xylose to the catalyst amount was kept at 6.4, 1.6, 1.6, 1.6, 0.5, 0.5, 0.5 and 10.7 for Amberlyst 70, Nafion SAC-13, sulfonated SBA-15, sulfonated carbon, sulfated zirconia, H-ZSM-5, H-mordenite, H-Beta and sulfuric acid, respectively. To end the reactions, the glass reactors were taken out of the oil
bath and cooled in air followed by an ice bath. The liquid was analyzed to quantify fufural and xylose using GC (Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID) as well as HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-87H column, RI 410 detector (xylose) and a UV detector (furfural)).

The experiments starting with glucose, fructose, fufural, formaldehyde, glucose/xylose, fufural/xylose and formaldehyde/methanol were carried out and analyzed in a similar manner. For results presented in Figure 8.3, Figure 8.6 and Table 8.3, the xylose to catalyst mass ratio was kept at 0.5. In Figure 8.4A, for experiments with 2 wt% xylose in GVL (10 wt% water), the xylose to catalyst mass ratio was kept at 0.5 for H-mordenite and 6.4 for Amberlyst 70, whereas in Figure 8.4B, this ratio was 0.5 for H-mordenite and 1.6 for Amberlyst 70. For experiments starting with fufural, all the above ratios were halved as the catalyst amounts were kept the same and 1 wt% fufural was used as opposed to 2 wt% xylose. For experiments presented in Figure 8.5 (feed: 2 wt% xylose, 1 wt% fufural), the xylose to catalyst and fufural to catalyst mass ratios were kept the same as in Figure 8.4. Starting from 0.5 wt% glucose or fructose feeds, the catalyst amount was kept the same as xylose experiments, such that the reactant to catalyst mass ratio decreased to 0.1. The ratio of the mass of glucose/fructose to the catalyst amount was kept at 1.7, 0.1, 0.1, 0.1, and 0.4 for Amberlyst 70, H-ZSM-5, H-mordenite, H-Beta and γ-alumina, respectively. The xylose dehydration experiments using the PHL feed from wood chips (poplar) were carried out in 10 mL glass reactors described above. Prior to the experiments, PHL was concentrated by evaporating 90% of the water in an oil bath at 368 K. The required amounts of the evaporated PHL and GVL were added to the reactor to attain 10 wt% water, and mixed with H-mordenite. After the reaction was completed, the reactor was cooled and the liquid was
analyzed following the methodology described above. All yields reported are based on GC and HPLC analyses and are not isolated yields. For the recycle experiments, H-mordenite was collected after each use and washed with deionized water several times at room temperature and dried at 373 K prior to reuse.

8.2. Xylose Dehydration and Effect of Water

Figure 8.2 shows the yields of furfural that were achieved using GVL as a solvent in absence of water at complete conversion of xylose over a range of solid acid catalysts with Brønsted and/or Lewis acidity. Lewis acid catalysts containing no Brønsted acidity (see Figure 8.1 for FTIR measurements for pyridine adsorption), γ-Al₂O₃ and Sn-SBA-15, resulted in the lowest yields of furfural corresponding to 5% and 40%, respectively. On the other hand, high yields of furfural can be achieved in GVL over a wide range of acid catalysts (>70%) containing Brønsted acidity, such as sulfonic acid functionalized catalysts (Amberlyst 70, Nafion SAC-13, sulfonated carbon and propylsulfonic acid functionalized SBA-15), zeolites (H-ZSM-5, H-mordenite and H-beta), sulfated inorganic metal oxides (sulfated zirconia), and a homogenous mineral acid (0.02 M H₂SO₄). These results suggest that the presence of Brønsted sites is particularly important for the selective conversion of xylose to furfural, as suggested earlier by Weingarten et al. (10). The yields obtained over these catalysts are comparable to the yields of furfural obtained over sulfonic acid functionalized materials (i.e., 75% yield over sulfonic acid functionalized MCM-41) using dimethyl sulfoxide (DMSO) as a solvent (11). However, the use of GVL as a biomass-derived green solvent is a substantial improvement over using petroleum derived solvents. The use of zeolitic materials is of particular interest because of their low cost, potential for regeneration with a calcination treatment following deactivation upon deposition of
carbonaceous deposits (e.g., humins) and because these catalysts become highly selective for furfural production in the GVL solvent.

![Figure 8.2](image)

**Figure 8.2** The maximum furfural yield achieved with different acid catalysts at 448 K, with a feed of 2 wt. % xylose in GVL. S-Zirconia, S-Carbon and S-SBA-15 refer to sulfated zirconia, sulfonated carbon and propylsulfonic acid functionalized SBA-15, respectively.

For example, the yield of furfural achieved using H-mordenite as a catalyst in GVL is approximately equal to 80%, in contrast to the low yields of furfural reported in the literature using faujasite and mordenite in aqueous solution, i.e., values of only 40% and 30%, respectively (12) or yields of 50-65% reported using silicoaluminophosphates (SAPO-5 and SAPO-11) in water. (13) Accordingly, H-mordenite was chosen in this work as the solid acid catalyst for more detailed studies.

Since, xylose is obtained in aqueous solutions through various hemicellulose solubilization strategies, it is anticipated that water will be present in xylose feed streams from biomass resources. Therefore, xylose dehydration over H-mordenite was studied with changing water concentrations in the GVL solvent. As demonstrated in Figure 8.3, as the water
concentration is increased, the rate of furfural production decreases, and this effect of water is particularly significant at water concentrations higher than 10 wt%.

Figure 8.3 The furfural yield achieved with time for different water concentrations in the feed (0 (●), 5 (■), 10 (▲), 15 (★) and 20 wt% (●)) of 2 wt% xylose in GVL at 448 K over H-mordenite.

In order to determine how water affects the furfural formation reaction and whether H-mordenite has a role, we performed reactions to monitor the formation and degradation of furfural in pure water solvent as well as the GVL solvent (containing 10 wt% water) over H-mordenite in comparison with another common Brønsted acid catalyst utilized for sugar dehydration reactions, i.e., Amberlyst 70. In Figure 8.4A, furfural yields and xylose conversions achieved with time starting from 2 wt% xylose in GVL solvent over H-mordenite and Amberlyst 70 are shown. In addition, in the same figure, the results of a separate set of experiments, in which changing furfural concentration was measured with time starting from a 1 wt% furfural feed in GVL over both catalysts are shown. Figure 8.4B, demonstrates the results obtained from the same experiments when the solvent was switched to pure water. For both catalysts, the
The furfural yield that can be achieved is significantly lower when pure water is used as the solvent. In addition to the inhibiting effect of water on the acid sites of the solid catalyst, the presence of water has been reported to accelerate furfural degradation reactions, thereby decreasing the furfural yield (14). Furfural can undergo undesirable degradation reactions, such as fragmentation, resinification and condensation. Several smaller molecules, such as formic acid, formaldehyde, acetaldehyde and lactic acid can be produced from furfural fragmentation (15). Particularly, water is known to react with furfural to form formic acid, yielding a C₄ compound that reacts to form polymeric by-products (14). In resinification reactions, furfural reacts with another furfural molecule. Condensation reactions can take place between furfural and pentose molecules or intermediates. Products of both condensation and resinification reactions lead to the formation of solid humin products (1). The degradation of furfural in the experiments starting from 1 wt% furfural feed in Figure 8.4, in the absence of xylose and xylose intermediates, is the combination of fragmentation and resinification reactions only. Quantitatively, the rate of furfural degradation in pure water (0.90 mol furfural (mol H⁺)⁻¹ s⁻¹) is approximately 2 times faster than in the GVL solvent containing 10 wt% water (0.47 mol furfural (mol H⁺)⁻¹ s⁻¹) over H-mordenite, while over Amberlyst 70 the rates are similar in both solvents (1.90 mol furfural (mol H⁺)⁻¹ s⁻¹ in water and 1.95 mol furfural (mol H⁺)⁻¹ s⁻¹ in GVL solvent).
Figure 8.4 A) Furfural yield achieved over H-mordenite (●) and Amberlyst 70 (□) starting from 2wt% xylose feed and the furfural concentration (µmol/mL) over H-mordenite (△) and Amberlyst 70 (×) starting from 1wt% furfural feed in GVL solvent containing 10 wt% water with time. Solid and dashed lines show the xylose conversion over H-mordenite and Amberlyst 70, respectively. B) Furfural yield achieved over H-mordenite (●) and Amberlyst 70 (□) starting from 2wt% xylose feed and the furfural concentration (µmol/mL) over H-mordenite (△) and Amberlyst 70 (×) starting from 1wt% furfural feed in water with time. All reactions are carried out at 448 K. Solid and dashed lines show the xylose conversion over H-mordenite and Amberlyst 70, respectively.
The reactant/catalyst ratios were adjusted, for the experiments in Figure 8.4 such that the initial rates ($\mu$mol mL$^{-1}$ min$^{-1}$) for degradation of furfural and the initial yields for production of furfural from xylose over both catalysts would be similar in both solvent systems. Even though the furfural degradation rates as shown in Figure 8.4 are similar, the yield for production of furfural from xylose is decreased more significantly over Amberlyst 70 compared to H-mordenite at higher xylose conversions, especially in the water solvent. This behavior suggests that furfural degradation, as it is being formed from xylose, may not be proceeding only by fragmentation or resinification reactions, but it can also take place by condensation reactions between furfural and reaction intermediates from xylose.

The importance of furfural condensation reactions was further investigated by conducting experiments in which xylose (2 wt%) and furfural (1 wt%) were both introduced into the feed solutions over both catalysts in GVL solvent (containing 10 wt% water) (Figure 8.5A), as well as in pure water (Figure 8.5B). The dashed lines in Figure 8.5A and B are for reference and represent the maximum furfural concentration that would be achieved (over H-mordenite, 80% yield in GVL solvent and 46% in water) according to the results demonstrated in Figure 8.4A and B, if the furfural in the feed remained inert. As can be seen in Figure 8.5A for the GVL solvent, the theoretical maximum furfural concentration was nearly reached by both catalysts. Over H-mordenite, the furfural concentration increased to 211 $\mu$mol/mL maximum, compared to the theoretical maximum of 222 $\mu$mol/mL; and, the furfural concentration reached 196 $\mu$mol/mL over Amberlyst 70, compared to the theoretical maximum of 207 $\mu$mol/mL. However, as seen in Figure 8.5B for the pure water solvent, the effect of furfural degradation was significant in water, especially for the Amberlyst 70 catalyst.
Figure 8.5 A) Xylose conversion achieved over H-mordenite (◆) and Amberlyst 70 (■) and furfural concentration over H-mordenite (◇) and Amberlyst 70 (□) starting from 2wt% xylose and 1 wt% furfural feed in GVL solvent containing 10 wt% water with time. B) Xylose conversion achieved over H-mordenite (◆) and Amberlyst 70 (■) and furfural concentration over H-mordenite (◇) and Amberlyst 70 (□) starting from 2wt% xylose and 1 wt% furfural feed in water with time. All reactions are carried out at 448 K.

The difference in the extent of furfural degradation over H-mordenite and Amberlyst 70 in the presence of xylose and water, despite the fact that the extent of furfural degradation
(combined fragmentation and resinification, see Figure 8.4B) was similar for both catalysts in water, suggests that furfural condensation with reaction intermediates from xylose becomes more pronounced in the presence of water over Amberlyst 70. In terms of the effect of water, the results of the present study would suggest that the intermediates formed from xylose are more reactive in the presence of water and therefore more prone to coupling reactions with furfural. Importantly, H-mordenite results in higher furfural yields compared to Amberlyst 70 in both solvents, and this inhibition of furfural degradation reactions in the presence of xylose could be due to the shape selectivity provided by H-mordenite. For example, it has been suggested in earlier reports that the limited pore size of H-mordenite could inhibit the formation of bulky high molecular weight products (8), which in the present case result from condensation reactions between furfural and pentose intermediates.

Despite the negative effects of water documented above, the presence of a limited amount of water in GVL (e.g., 10 wt%) is desirable, because water increases the solubility of xylose and facilitates the separation of furfural from GVL by distillation. ASPEN PLUS modeling software was used to conduct simulations of the distillation column for the separation of furfural from the water-GVL system with various concentrations of furfural and water feed. Simulations were run using NRTL as well as NRTL-Redlich-Kwong (NRTL-RK) equations of state. All three compounds were present in the ASPEN database. The separation of furfural at low concentrations (~1-2 wt%) from GVL is energy intensive in the absence of water, requiring high reflux ratios and number of stages, as demonstrated in Table 8.2. In contrast, the distillation step becomes manageable at levels of furfural equal to 1 wt% in the presence of 10 wt% water, this case being similar to the case of having 10 wt% furfural in GVL without water. This behavior appears to be related to strong interactions between furfural and water, as evidenced by the
formation of a minimum boiling (positive) azeotrope (1). In view of the facilitated separation of furfural from GVL in the presence of water, and because we achieve high yields of furfural at high rates in the presence of 10 wt% water in GVL, we chose this solvent mixture for further studies.

**Table 8.2** Results of the distillation simulations (using NRTL) with changing furfural and water concentrations in GVL. In all cases, 99.9 % furfural is recovered in the top stream with 95% mass purity.

<table>
<thead>
<tr>
<th>Weight Fraction (wt%)</th>
<th>Mass Recovery (%)</th>
<th>Number of Stages</th>
<th>Feed Location</th>
<th>Reflux Ratio</th>
<th>Boilup Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>GVL</td>
<td>Water</td>
<td>GVL (bottom)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>99</td>
<td>0</td>
<td>99.95</td>
<td>49</td>
<td>6</td>
</tr>
<tr>
<td>1[a]</td>
<td>99</td>
<td>0</td>
<td>99.95</td>
<td>65</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
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<td>37</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
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<td>99.72</td>
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<td>6</td>
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<td>10</td>
<td>90</td>
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<td>5</td>
<td>85</td>
<td>10</td>
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<td>12</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>10</td>
<td>99.34</td>
<td>12</td>
<td>6</td>
</tr>
</tbody>
</table>

[a] NRTL-RK

The stability of the H-mordenite under reaction conditions was investigated by employing this catalyst in a series of xylose dehydration reactions in GVL solvent containing 10 wt% H₂O. Prior to each cycle, the H-mordenite catalyst was washed with deionized water and dried at 373 K. The furfural yield versus holding time is shown in Figure 8.6 for the fresh catalyst and for the catalyst after the 1st, 2nd, and 3rd recycle. Importantly, the catalytic activities of the recycled catalysts were similar to that of the fresh catalyst, and the maximum yield of furfural achieved was ~80% even after the third recycle. In addition, unlike sulfonated solid acid
catalysts, zeolite catalysts (i.e., H-mordenite) can be subjected to calcination treatments at elevated temperatures (e.g., 700 K) to remove carbonaceous deposits that may form on the catalyst during prolonged use.

**Figure 8.6** Furfural yield reached with time over fresh (◇) and recycled (1st recycle (▲), 2nd recycle (□) and 3rd recycle (●)) H-mordenite at 448 K, with a feed of 2 wt. % xylose and 10 wt. % H₂O in GVL.

### 8.3. Processing of Pre-hydrolysis Liquor

The strategy presented here for the conversion of xylose to furfural using solid acid catalysts and GVL as a solvent can be implemented in various biorefining scenarios. The implementation of a biorefinery based on the catalytic conversion of both hemicellulose (for the production of furfural) and cellulose (for the production of GVL and fuels) to transportation fuels and chemicals is a long-term goal that requires a significant capital investment (16). We anticipate that a more near-term strategy is to implement the ideas we have presented here at a pulp and paper facility, such that the hemicellulose fraction of the wood feedstock would be converted to furfural, and the cellulose fraction would be used to produce dissolving pulp. We choose
dissolving pulp for this implementation, because this type of pulp requires nearly complete removal of hemicellulose from the cellulose fibers, leading to an aqueous stream (i.e., a pre-hydrolysis liquor, PHL) that contains high concentrations of soluble sugars and sugar-oligomers (e.g., as high as 5 wt%) (17). In addition, an existing pulp and paper facility would already have capital equipment in place to handle and pretreat solid biomass feedstocks, and it would have a turbo-generator in place for combustion to produce heat and power (18).

The conversion of a PHL stream from a dissolving pulp operation by current approaches (e.g., production of ethanol) faces important challenges. Firstly, the PHL stream contains a mixture of C₅ and C₆ sugars (e.g., xylose and glucose, respectively), although the C₅ sugars are typically predominant. Secondly, the sugars in PHL are present as monomers and oligomers. Importantly, however, these attributes of a PHL stream are not limitations for the approach of the present paper. As shown in Table 8.3 (entries 2-3), glucose is converted over H-mordenite to valuable products in the presence of water in the solvent GVL under similar reaction conditions as employed for the conversion of xylose to furfural. Interestingly, the main product of glucose conversion is furfural, followed by the formation of levulinic acid (with equimolar amounts of formic acid) and 5-hydroxymethylfurfural (HMF). Thus, as reported in entries 4-6 in Table 8.3, high yields of furfural can be achieved by the combined conversion of xylose and glucose over the zeolite catalyst. It should be noted that the yield of furfural from glucose has been estimated based on experiments carried out with pure glucose. The production of furfural from glucose has been reported to take place with low yields (~5%) through the intermediate formation of pentoses in aqueous solutions under hydrothermal conditions (19) or over acid catalysts (20). Importantly, the yields of furfural from glucose that we have achieved (e.g., 30%) are the highest yields reported to date; therefore this reaction is investigated further in the following section.
Table 8.3 Results of xylose and glucose dehydration experiments carried out at 448 K in a monophasic reactor system, containing 2 wt.% xylose or 0.5 wt.% glucose or both. All the entries contain 10 wt.% H₂O in GVL with H-mordenite. Entries 7 and 8 show the results starting with the concentrated PHL feed (90% of the water is evaporated) in GVL.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Feed</th>
<th>t (min)</th>
<th>Conversion (%)</th>
<th>Xylose products (molar yields based on xylose)</th>
<th>Glucose products (molar yields based on glucose)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Xylose</td>
<td>Glucose</td>
</tr>
<tr>
<td>1</td>
<td>xylose</td>
<td>120</td>
<td>100</td>
<td>81</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>glucose</td>
<td>120</td>
<td>-</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>glucose</td>
<td>280</td>
<td>-</td>
<td>93</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>xylose/glucose</td>
<td>120</td>
<td>99</td>
<td>67</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>xylose/glucose</td>
<td>180</td>
<td>100</td>
<td>87</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>xylose/glucose</td>
<td>300</td>
<td>100</td>
<td>91</td>
<td>78</td>
</tr>
<tr>
<td>7</td>
<td>PHL</td>
<td>90</td>
<td>98</td>
<td>98</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>PHL</td>
<td>120</td>
<td>100</td>
<td>99</td>
<td>74</td>
</tr>
<tr>
<td>9</td>
<td>PHL</td>
<td>420</td>
<td>100</td>
<td>100</td>
<td>64</td>
</tr>
</tbody>
</table>

Following our experiments involving the conversion of various sugars over H-mordenite in GVL solvent, we studied the catalytic conversion of a PHL stream derived from poplar wood chips. Approximately 90% of the water in the PHL stream was first evaporated, and GVL was added to achieve 10 wt% H₂O in the GVL solvent. Entries 7-9 in Table 8.3 show the yields obtained for production of furfural, LA/FA and HMF in GVL. The yield of furfural from xylose and oligomers of xylose in the PHL-derived feed was 75%, only slightly lower than the value of 80% obtained from xylose. Thus, the presence of sugar oligomers along with sugar monomers is not a problem for our approach using H-mordenite in GVL, because this solid acid catalyst achieves hydrolysis of sugar oligomers to produce monomers under the conditions employed for the conversion of xylose to furfural. The high vapor pressures of furfural and formic acid then allow these species to be separated from the mixture of levulinic acid (produced from glucose) in the GVL solvent, and the levulinic acid can then be reduced to GVL over a supported metal.
catalyst (21). The overall conversion of the C₅ and C₆ sugars in the PHL using GVL as the solvent thus leads to the production of furfural and formic acid (that are volatile) along with the production of additional GVL solvent as shown in Figure 8.7. Another variation of our processing approach is to convert furfural to GVL through the intermediate formation of furfuryl alcohol and levulinic acid in the GVL solution. In this way, GVL can be obtained as an end-product from both C₅ and C₆ sugars, and the need for product separation steps can be eliminated.

**Figure 8.7** Schematic representation of monophasic solid acid catalyzed process to convert C₅ and C₆ sugars in PHL to furfural and levulinic acid.

As mentioned earlier, for this conversion strategy, most of the water is removed before the conversion step over H-mordenite, and this water is recycled back to the hemicellulose deconstruction step. The heat requirement for this step can be reduced by taking advantage of the high temperature (443 K) and elevated pressure (7.5 bar) of the hot water treatment employed in hemicellulose deconstruction. For example, a substantial amount of the steam/water can be
recovered in a flash tank after the hemicellulose extraction is completed (18). The remaining stream can be concentrated with an evaporation step with an efficient heat integration strategy in the biorefinery or as an alternative using reverse osmosis to decrease the heating and steam requirements (18).

### 8.4. Reaction Scheme for Furfural Production

The results of this study show high yields for production of furfural from conversion of xylose and glucose over H-mordenite in GVL solvent (e.g., 80% and 30%, respectively). Figure 8.8 shows the reaction network that we propose to explain the product distribution that we have observed over a wide range of conditions for the conversions of xylose and glucose in the GVL solvent. The conversion of xylose is straightforward, and involves three sequential dehydration steps. As proposed in earlier reports, the conversion of glucose to furfural is initiated by the tautomerization of glucose to form a ketose, followed by the formation of a pentose through a retro-aldol reaction, yielding formaldehyde as the by-product (19, 22). The pentose intermediate then undergoes dehydration to form furfural. We have detected the formation of formaldehyde by liquid chromatography in low concentrations starting from glucose, while higher concentrations of formaldehyde are produced at higher rates when fructose (an example of a ketose) is converted over H-mordenite. We have observed in our studies of both glucose and fructose conversion in GVL that the concentration of formaldehyde initially increases and then decreases with increasing reaction times. Further experiments were thus carried out to probe the predominant reaction pathways over H-mordenite, starting from formaldehyde (2 wt% formaldehyde, 10 wt% water in GVL). It was observed that formaldehyde undergoes self-disproportionation reactions (23), resulting in the formation of equal molar amounts of formic
acid and methanol. However, further experiments starting from mixtures of formaldehyde with methanol (2 wt% each) showed that methanol can be consumed through its direct coupling with formaldehyde to form 1-methoxy-methanol, as identified by GC-MS. Further etherification of 1-methoxy-methanol with methanol results in the formation of dimethoxymethane, as shown in Figure 8.8. In addition to these reactions, formaldehyde can undergo decarbonylation at high temperatures and acidic conditions to form H₂ and CO (23) and polymerization reactions (24). Finally, methyl formate was formed in small amounts as a result of the esterification of formic acid with methanol.

In accordance with our observation that formaldehyde is formed at higher rates from fructose compared to glucose, we have observed that the rate of furfural production from fructose is significantly higher (by a factor of ~10) than from glucose. These findings support the proposition that glucose first undergoes an isomerization step to form a ketose prior to the retro-aldol reaction that yields formaldehyde and the pentose precursor to furfural. We note that the ketose formed from glucose (e.g., fructose) may undergo further tautomerization steps prior to the retro-aldol reaction (19). It has been suggested that the formation of furfural may take place through the intermediate formation of HMF (19); however, experiments starting from HMF over H-mordenite showed that this conversion does not take place under our reaction conditions. We have investigated the conversion of glucose and fructose to furfural over various acid catalysts in GVL and in pure water solvent to understand the effects of catalyst and solvent on the formation of furfural from glucose. It can be seen in Table 8.4 by comparing entries 1-6 that the yield for production of furfural is minimal over Amberlyst 70 (containing sulfonic acid groups) and mineral acids (i.e. H₂SO₄ and HCl), whereas the furfural yield is significant over zeolites.
This behavior could be due to the presence of Lewis acid sites on zeolite catalysts, which can be attributed to non-framework aluminum species (as shown through IR spectroscopy for H-mordenite, see Figure 8.1) that can promote both isomerization and retro-aldol reactions (25). To investigate the importance of these Lewis acid sites, the conversion of glucose in GVL solvent was studied over γ-alumina (Table 8.4, entry 7). The formation of furfural did not take place over this catalyst, even though the presence of Lewis sites were confirmed through IR spectroscopy (Figure 8.1), and isomerization of glucose to fructose (with ~25% yield) was observed to take
place. This result shows that the presence of Lewis acid sites to achieve isomerization of glucose is not sufficient for the production of furfural.

To further probe the pathway for production of furfural from glucose, we studied glucose conversion over a physical mixture of $\gamma$-alumina and Amberlyst 70, to investigate whether the combination of Lewis and Brønsted acid sites is responsible for the increased yields of furfural over zeolites. As seen in entry 8 in Table 8.4, this combination of Lewis and Brønsted acid sites did not enhance the yields of furfural, and furfural yields were similar to that obtained over Amberlyst 70 alone. In agreement with this conclusion, the yield of furfural from fructose over Amberlyst 70 (Entry 10) was similar to the yield from glucose, but significantly lower compared to H-mordenite (Entry 9). These findings show that zeolites exclusively promote the formation of furfural from C$_6$ sugars. Among the zeolites, the extent of furfural formation over H-ZSM-5 is lower compared to that on H-mordenite and H-beta, suggesting that the smaller pore sizes of H-ZSM-5 may limit the diffusion of glucose into the pores or the diffusion of furfural out of the pores, as proposed for the case of glucose dehydration to form HMF over the Y zeolite (26, 27).

As seen in Table 8.4, the rate of furfural formation as well as the yield of furfural from glucose (entry 11) and fructose (entries 12 and 13) decrease when water is used as the solvent compared to the use of GVL with 10 wt% water as the solvent. This decrease in the furfural yield from glucose in water can be attributed to inhibition of isomerization and/or retro-aldol reaction rates and/or to an increase in rates of furfural degradation reactions in the presence of water. In this respect, it has been reported using results from computational studies that water has little effect on retro-aldol reactions of glucose and fructose (28).
In contrast, the rates of isomerization reactions have been reported to be faster in aprotic solvents, such as dimethyl sulfoxide, due to the higher abundance of the acyclic form of sugars in aprotic solvents (29). However, the conversion of fructose in water over H-mordenite (entry 12) as well as Amberlyst 70 (entry 13) shows a low yield of furfural, indicating that the low yield from glucose in water is not related to the rate of isomerization between these two sugars either.
Based on the above results, we suggest that the low yields of furfural from conversion of fructose and glucose in water over both H-mordenite and Amberlyst 70 can be related to increased rates of degradation reactions of furfural, especially condensation reactions between furfural and sugar intermediates, as shown for the case of furfural production from xylose. Moreover, the high yields for production of furfural over H-mordenite in the GVL solvent can be related to the microporous nature of the zeolite that inhibits bi-molecular reactions leading to furfural degradation, as shown in the case of xylose dehydration over zeolites compared to other Brønsted acid catalysts.

8.5. Conclusions

We have presented a processing strategy for the hemicellulose portion of biomass, that is especially applicable in a pulp and paper facility, in which xylose and its oligomers are converted to furfural with high yields (~80%) over H-mordenite in a GVL solvent containing 10 wt% water. It was also demonstrated that the presence of GVL significantly reduces the rates of furfural degradation reactions, due to the inhibition of condensation reactions between furfural and pentose intermediates. H-mordenite was found to be especially effective for suppression of these degradation reactions, which can be attributed to the shape selectivity provided. Finally, it was determined that a considerable yield of furfural (e.g., 30%) can be produced from glucose in the GVL solvent over zeolites. This formation of furfural from C₆ sugars is greatly suppressed in the presence of water and over common dehydration catalysts (i.e., mineral acids and ion exchange resins), which explains why this conversion was not found to be significant in earlier reports.
8.6. References

Chapter 9: Conclusions and Recommendations

9.1. Summary of Conclusions

As our dependence on limited supply of petroleum raise concerns in its environmental, political and economic consequences, utilization of biomass as an alternative resource has become of increasing importance. Biomass, being the only renewable resource of carbon, has the potential for establishing a sustainable platform for the production of energy as well as chemicals. Similar to development of petroleum based technologies, field of catalysis will undoubtedly play a vital role in the development of biomass based technologies. However, the research being conducted in the past couple of years revealed a new set of challenges to be tackled in catalysis research for efficient utilization of biomass. Biomass, being an overfunctionalized starting material, requires selective oxygen removal reactions (i.e., hydrogenation, dehydration, hydrogenolysis etc.) to obtain platform molecules (e.g., alcohols, acids, ketones, furanic species etc.) selectively with diverse and limited functionalities, on which biorefining strategies can be established. In addition, presence of an aqueous/condensed phase environment and competing coke forming side reactions in most of the biomass conversion reactions present challenges for utilization of conventional catalysts. Even though the catalysis research conducted in petroleum refining provides a tremendous background for catalysis research in biomass conversion, there are still many opportunities for scientific and technological advancement to create efficient biorefining strategies.

The conversion of lignocellulosic biomass to fuels and chemicals requires the effective utilization of both hemicellulose and cellulose, consisting primarily of C₅ and C₆ sugars, respectively. Two classes of processing strategies have been explored in this respect, in which
the hemicellulose and cellulose fractions are either processed together, or they are separated and processed separately. While the simultaneous processing of all carbohydrates, such as in gasification or pyrolysis, offers the potential for simplicity of operation, the fractionation of hemicellulose and cellulose allows the processing of each fraction to be tailored to take advantage of the different chemical and physical properties of these fractions, as well as, increased flexibility of operation. For example, it may be desirable in specific applications to employ chemical processing steps to convert the C$_5$ sugars in hemicellulose to fuels and/or chemicals, while taking advantage of the physical properties of cellulose for pulp and paper applications. Alternatively, the preference of biological organisms for fermentation of C$_6$ sugars versus C$_5$ sugars can be accommodated by using chemical methods to process the C$_5$ sugars in hemicellulose, while employing recent advances in biological conversions to convert the C$_6$ sugars in cellulose to fuels and chemicals. As another option, chemical methods can be employed to process hemicellulose and cellulose after fractionation of biomass, taking into account the different reactivities of C$_5$ versus C$_6$ sugars.

In this thesis, several aqueous phase catalytic strategies for the conversion of both cellulose and hemicellulose (and corresponding sugar derivatives, i.e., glucose and xylose) are presented. The first strategy focuses on the conversion of cellulose derived carbohydrates (glucose and sorbitol) to high molecular weight alkanes suitable for gasoline and diesel fuel applications. This strategy is initiated with the controlled partial deoxygenation of carbohydrates into mixtures of monofunctional organic species, such as carboxylic acids, ketones, alcohol and heterocycles over PtRe/C. It has been demonstrated that these mixtures can be upgraded by consecutive C-C coupling reaction steps, i.e., ketonization and aldol condensation, to form high
molecular weight ketones that can be converted to alkanes suitable for gasoline and diesel fuel. In this thesis, we focused on the aldol condensation step in terms of elucidating the reaction network and kinetics. Studies of aldol condensation/hydrogenation reactions of 2-hexanone were carried out over Pd/CeZrOₓ and CeZrOₓ catalysts at temperatures between 573 and 673 K, and pressures of 5 to 26 bar. Characterization by XRD, TPR and NH₃/CO₂-TPD showed that Pd/CeZrOₓ catalyst consists of a partially reducible solid solution of cerium and zirconium oxides, and possesses both acidic and basic functionalities. Reaction kinetics studies show that in addition to the expected C₁₂ condensation product (7-methyl-5-undecaone), the CeZrOₓ-based catalysts produce C₁₈ and C₉ secondary species, along with light alkanes (<C₇). Low loadings of Pd (e.g., 0.25 wt. %) lead to optimal activity and selectivity for the production of C₁₂ species. The high activation energy of C₉ formation (140 kJ/mol) compared to the formation of C₁₂ and C₁₈ species (15 and 28 kJ/mol, respectively) indicate that these species may be formed as a result of the decomposition of heavier condensation products. The self-coupling of 2-hexanone was found to be positive order in both 2-hexanone and hydrogen. The addition of primary alcohols and carboxylic acids as well as water and CO₂ to the feed was found to reversibly inhibit the self-coupling activity of 2-hexanone. This inhibition is strongest in the presence of CO₂, and temperature programmed surface reaction studies indicate that CO₂ is removed from the surface by conversion to CO in the presence of reduced ceria species. Following this study, ceria-zirconia mixed oxides with different compositions including pure ceria and pure zirconia were prepared and characterized using temperature-programmed desorption of CO₂ and NH₃, X-ray diffraction, and BET surface area measurements. Bi-functional catalysts for C–C coupling of ketones by aldol condensation/hydrogenation were prepared by depositing palladium on these ceria zirconia mixed oxides, and these catalysts were studied for the conversion of 2-hexanone.
The Pd/ZrO$_2$ catalyst showed the best resistance to inhibition by CO$_2$, an important factor in catalyst performance because of the presence of CO$_2$ in biomass-derived feed streams. Furthermore, this catalyst displayed high activity for aldol condensation, as well as good resistance to inhibition by water. These properties make Pd/ZrO$_2$ a desirable catalyst for integration in a single reactor of aldol condensation/hydrogenation reactions with ketonization processes, the latter of which convert carboxylic acids to ketones plus CO$_2$ and H$_2$O. The feasibility of this integration was studied with the mixture of a carboxylic acid (butanoic acid) and a ketone (2-hexanone) in a double bed system, and the integrated process showed high activity as well as selectivity to C–C coupling products. Using the aforementioned approach, an aqueous feed containing 60 wt% sorbitol was converted to a liquid stream of alkanes, 53% of which consisted of C7+ alkanes with minimal branching, desirable for diesel fuel using only three catalytic reactors operated in a cascade mode. In the first reactor mono-functional intermediates are produced by catalytic conversion of sorbitol over PtRe/C catalyst. The second reactor achieves C–C coupling of monofunctional intermediates using a dual-bed catalyst system, where the upstream catalyst bed (Ce$_1$Zr$_1$O$_x$) is employed to carry out ketonization of carboxylic acids, and the downstream catalyst bed (Pd/ZrO$_2$) is used to achieve aldol condensation/hydrogenation of alcohols and ketones. The high molecular weight ketones produced by C–C coupling reactions in the dual bed catalyst system are subsequently converted to alkanes by hydrodeoxygenation (i.e., dehydration/hydrogenation) over a Pt/SiO$_2$–Al$_2$O$_3$ catalyst.

Following this work, catalytic conversion of cellulose was explored through another valuable platform molecule, levulinic acid (LA). A particularly promising derivative of LA is $\gamma$-
valerolactone (GVL),\(^1\) from which gasoline, jet fuel and diesel fuel components can be produced as also shown in our group previously.\(^{2-5}\) While the production of equimolar quantities of levulinic and formic acids can be achieved in good yields from lignocellulosic biomass\(^6,\,\)\(^7\) or cellulose\(^4\) using aqueous solutions of sulfuric acid, the production of GVL by catalytic reduction of LA is complicated by the need to separate LA from sulfuric acid, because the presence of sulfur leads to low catalytic activity and deactivation with time-on-stream.\(^{4,\,8}\) In this thesis, we demonstrated an integrated biorefining strategy for GVL production from cellulose via the formation of levulinate (sec-butyl levulinate) and formate (sec-butyl formate) esters for improved management of sulfuric acid. The esters are obtained from the corresponding acids by a reactive extraction step using butene. Indeed, butene is preferred for the esterification since it can be produced from GVL in down-stream processing \(^2\), and it is readily separated from the ester products by decreasing the system pressure, eliminating the need for any external solvent or distillation step. We demonstrated that esterification of the aqueous solution obtained directly from the cellulose deconstruction step described by Serrano-Ruiz et al.\(^5\) \((2\,\text{M LA and FA in 0.5 M H}_2\text{SO}_4)\) does not take place at our reaction conditions; however, the formation of butyl esters can be achieved with high yields by employing a concentration step to remove at least a portion of the water. Following that, we showed that GVL together with 2-butanol could be obtained from levulinate and formate esters over a dual-catalyst-bed consisting of Pd/C followed by Ru/C in a single reactor, eliminating the energy consumption as well as the reactor infrastructure associated with cooling and re-heating between two reaction steps. In the dual-catalyst-bed system, over Pd/C, almost quantitative yields of H\(_2\) from FA and formate esters could be achieved and over Ru/C, high rates of GVL production from LA and levulinate esters could be reached using the in situ generated H\(_2\), whereas the simultaneous utilization of FA and
formates to reduce LA and levulinates cannot be achieved using either of these catalysts alone. We also demonstrated that the rate of H$_2$ and GVL production could be increased significantly by co-feeding water along with the esters. We suggested that the presence of water lead to hydrolysis of the ester and thereby enabled the reduction to proceed through the LA and FA intermediates, leading to a higher overall rate for GVL production.

The conversion of cellulose to chemicals and liquid fuels has been demonstrated through the formation of several platform molecules, such as glucose, 5-hydroxymethylfurfural, and levulinic acid (LA), utilizing chemical routes$^{[6-9]}$ as some examples are shown in this thesis as well; however, fewer studies address the conversion of hemicellulose to chemicals and fuels.$^{[10, 11]}$ Therefore, in thesis two strategies for the conversion of hemicellulose to valuable chemicals (i.e., furfural, levulinic acid) and fuels were developed and investigated. In the first strategy, furfural and levulinic acid are produced from the hemicellulose portion of lignocellulosic biomass, utilizing biphasic reactor systems that consist of an alkylphenol solvent and an aqueous mineral acid solution to catalyze xylose dehydration to form furfural and to catalyze furfuryl alcohol hydrolysis to levulinic acid. In the case of xylose dehydration, the alkylphenol solvent is used to extract furfural to prevent further acid catalyzed degradation reactions. Even though biphasic reactors have been used several times in earlier studies, we show here for the first time that an alkylphenol solvent (i.e., 2-sec-butylphenol) has an exceptionally high partition coefficient for extraction of furfural (~90) when salt (NaCl) was added into the aqueous phase, allowing concentrated streams of furfural (~4 wt%) to be obtained with good yields (~78%) starting with more dilute aqueous solutions of xylose (1-2 wt%) obtained from deconstruction of hemicellulose in corn stover. In addition, the high boiling point of the alkylphenol solvent enables the recovery of furfural as the top product of distillation. We also show for the first time
that biphasic reactors with alkylphenol solvents can be used for the production of levulinic acid from furfuryl alcohol, where the purpose of the alkylphenol solvent is to selectively extract the highly reactive reactant (furfuryl alcohol) from the acidic aqueous solution in which desirable reactions take place at low concentrations. The best selectivities reported in the literature for furfuryl alcohol hydrolysis in monophasic aqueous solution are obtained using catalysts consisting of sulfonic acid moieties anchored on organic scaffolds (e.g., Amberlyst), leading to difficulties with regeneration of these catalysts following deactivation by deposition of solid humins during reaction. When these catalysts are replaced with zeolites, which can be regenerated upon deactivation, low yields to levulinic acid are obtained, especially when higher concentrations of levulinic acid are desired. Use of a biphasic reactor with alkylphenol solvents, such as 2-sec-butylphenol, 4-n-hexylphenol, 4-propyl guaiacol, leads to an increase in the overall yield of levulinic acid (~70%) compared to monophasic aqueous systems with zeolite catalysts. The biphasic reactor also allows concentrated streams of levulinic acid (5-10 wt%) to be produced. Similar to furfural, levulinic acid can be recovered as the top product of distillation.

In the second strategy, we demonstrate an alternative to the biphasic systems, in which we utilize solid acid catalysts (i.e., H-mordenite) for the production of furfural with high yields (80%) in a monophasic system using a lignocellulose-derived green solvent, $\gamma$-valerolactone, with presence of minimal amount of water. Importantly, we demonstrate that the furfural degradation reactions, especially the condensation reactions between furfural and sugar intermediates, can be decreased significantly when water amount is minimized in the reaction. These condensation reactions can be inhibited further with the use of zeolites (i.e., H-mordenite), resulting in high furfural yields. We also demonstrate that this strategy can be applied in a pulp and paper facility for the conversion of the hemicellulose waste stream (i.e., pre-hydrolysis
liquor, PHL), in which xylose and its oligomers are converted to furfural with high yields (75%), while trace amounts of glucose and oligomers are converted to valuable products such as furfural, 5-hydroxymethylfurfural and levulinic acid. Finally, it was determined that furfural production from glucose becomes significant (~30% yield) over zeolites when water amount is minimized and proceeds through tautomerization and retro-aldol reaction steps.

9.2. Future Directions

9.2.1. Mechanistic and Catalyst Characterization Studies for Furfural Production from Xylose and Glucose

In Chapter 8, we have shown that high furfural yields (80%) can be obtained in GVL solvent with minimal water over H-mordenite. In addition, we also showed that furfural stays stable in the GVL solvent as opposed to in water over both H-mordenite, and a common Brønsted acid catalyst, Amberlyst 70. Furthermore, it was shown that furfural degradation through condensation reactions between furfural and pentose intermediates could be the leading source of low furfural yields in water, which becomes more prominent over Amberlyst 70 compared to H-mordenite. However, it is not clear how water accelerates these furfural degradation reactions, including fragmentation and condensation. Therefore, the furfural degradation mechanism needs to be investigated by more elaborative techniques, such as isotopic tracing combined with liquid chromatography-mass spectrometry (LC-MS) and in situ vibrational spectroscopy techniques. For instance, O\textsuperscript{18} labeled water can be used to trace the intermediates and products that are formed with water acting as a reactant for the conversion of furfural and xylose. In addition, C\textsuperscript{13} labeled xylose can be reacted to probe how the ring opening and closing steps proceed for the production of furfural. In these experiments, LC-MS is
essential for determining molecular weights and fragmentation patterns for the reaction intermediates and products, such that the labeled atoms and their positions in the molecules can be identified. One dimensional and two dimensional NMR can also be used as an additional technique for the identification of the intermediates, following the isolation of the intermediates via liquid chromatography. In situ FTIR (Fourier Transform Infrared Spectroscopy) reaction analysis (ReactIR) can also be used to monitor the reaction intermediates formed from the conversion of xylose in water compared to the GVL solvent. As shown in Figure 9.1, reactions can be performed in a specially-designed Hastelloy autoclave equipped with an in situ attenuated-total-reflection infrared (ATR IR) probe. The ATR IR spectrometer used is configured with a silver halide fiber optic cable connected to a probe equipped with a diamond ATR crystal. Thus, the instrument provides real-time, in situ IR spectra of the reaction mixture.

![Figure 9.1 Schematic of the set-up for the FTIR reaction analysis (ReactIR) system.](image)

In addition to the conversion of xylose to furfural, we determined in Chapter 8 that furfural can also be obtained from glucose and this conversion becomes substantial (highest
yields reported to date) over zeolites (i.e., H-mordenite and H-beta) when the water amount is minimized. It has been proposed in literature that glucose first undergoes tautomerization reactions, followed by a retro-aldol reaction step, in which formaldehyde is produced as observed experimentally. However, the actual reaction mechanism has not been confirmed and could be investigated by the experimental techniques discussed earlier for xylose conversion. For instance, using C\textsubscript{13} labeled glucose molecules (for C’s at different positions) through LC-MS analysis of the reaction intermediates and products, how formaldehyde is cleaved from the open-chain sugar molecule can be determined. In addition, the ReactIR measurements similarly can give idea on how are the intermediates changed between water and GVL solvent, and why higher furfural yields are achieved in the absence of water.

9.2.2. Conversion of Furfural to Levulinic Acid – An Integrated Biorefining Strategy

As discussed earlier, levulinic acid is an important platform chemical upon which biorefining strategies can be established. In terms of processing the C\textsubscript{6} portion of lignocellulose, levulinic acid can be obtained from the decomposition of 5-hydroxymethylfurfural (HMF) or direct hydrolysis of cellulose (6, 7, 9) using mineral acid catalysts. Levulinic acid can also be obtained from the hemicellulose portion of biomass. As demonstrated in Chapters 7 and 8, furfural can be synthesized through dehydration of pentoses, obtained from deconstruction of hemicellulose. In a subsequent step, furfural can be hydrogenated over a metal catalyst to form furfuryl alcohol, which can then undergo hydrolysis over an acid catalyst to form levulinic acid. Levulinic acid being a common intermediate from cellulose as well as hemicellulose offers an integrated biorefining strategy.
Figure 9.2 shows a schematic representation of the roadmap for the conversion of lignocellulosic biomass to fuels and chemicals based on levulinic acid as a platform molecule. Solid biomass is first subjected to mild pre-treatment in aqueous solution containing dilute acid to solubilize the hemicellulose as xylose, followed by heating this aqueous stream to achieve dehydration of xylose to furfural, the latter species being a valuable chemical intermediate. The remaining biomass is then subjected to further treatment in aqueous solution containing a more concentrated acid at higher temperature to solubilize the cellulose as levulinic and formic acids, passing through glucose as an intermediate. The levulinic acid can then be extracted from the acidic aqueous phase for use as a chemical intermediate, and the formic acid can be used as a source of H₂ for downstream biorefining operations. Alternatively, levulinic acid can be converted to levulinate esters by reaction with alcohols for use as blending components in transportation fuels. Furthermore, if desired, the furfural produced from hemicellulose can be converted to levulinic acid or levulinate esters, passing through the intermediate production of furfuryl alcohol, which is also a valuable chemical intermediate. The levulinic acid produced from the C₅ and/or C₆ sugars of biomass can be reduced to GVL, the latter serving both as a chemical intermediate for polymers and solvents, as well as serving as a blending agent for transportation fuels. The energy density of GVL for use as a transportation fuel can be increased by reduction to methyltetrahydrofuran (MTHF) or by decarboxylation to form butene, followed by butene oligomerization to gasoline (branched C₈ species) or jet fuel (branched C₈-C₁₆ species) (2). Finally, the remaining lignin fraction of biomass can be used for heat and power generation, or it can undergo catalytic conversion to aromatic components for use as chemicals or as fuel components. This roadmap becomes especially attractive if gasoline or jet fuel is the desired product through the intermediate formation of GVL and GVL is used as a solvent for the
production of furfural (as shown in Chapter 8) as well as levulinic acid (as demonstrated in our group recently). Levulinic acid can be hydrogenated to GVL in the GVL solvent (10), and if furfural can be converted to levulinic acid or esters in the GVL solvent, any kind of energy intensive separation steps (i.e., distillation) can be avoided. Therefore, it is highly important to develop conversion strategies for furfural to furfuryl alcohol and levulinic acid in liquid phase, utilizing heterogenous catalysts.

We have shown in Chapter 7 that PtSn/SiO₂ catalyst could selectively convert furfural to furfuryl alcohol in the presence of a solvent in the liquid phase. However, this catalyst still has some disadvantages. Firstly, it consists of an expensive precious metal (Pt). In addition, even though it can be regenerated, PtSn/SiO₂ deactivates very rapidly due to coke formation, which is not ideal from an industrial application point of view. Therefore, development and synthesis of new catalytic materials is desired for this reaction. In order to avoid leaching of non-precious Cu and coking problems present for Cu as well as non leaching bimetallics, such as PtSn. This could be realized by creating a controlled environment around the active metal center (e.g., changing the steric or electronic environment). For instance, a recent work demonstrated that overcoating of supported metal nanoparticles with alumina through atomic layer deposition (ALD) deactivation by coking and sintering could be greatly reduced for oxidative dehydrogenation of ethane (11). The conversion of furfuryl alcohol in alcohol solvents to produce levulinate esters has been reported in the literature with high yields.(12) However, the formation and the conversion of levulinate esters to GVL necessitates the presence of an external alcohol solvent. Therefore, the ideal case is to convert furfural to levulinic acid in water. However, carrying out the conversion in water becomes very problematic. First of all, similar to the xylose dehydration
case, coke forming reactions become more pronounced in water compared to alcohol solvents. For instance, the yield for production of ethyl levulinate is 85% starting with 1 wt% furfuryl alcohol in ethanol using Amberlyst-15 as the acid catalyst, as opposed to a lower yield of 55% for production of levulinic acid in water at 398 K for the same amount of catalyst and reaction time.(13)

Figure 9.2 Roadmap for conversion of lignocellulosic biomass (green) to chemicals (orange) and fuels (yellow), passing through the intermediate formation of C5 and C6 sugars (blue).

Secondly, removal of coke by calcination is not an option for most of the active solid acid catalysts, such as ion exchange resins (i.e., Amberlyst 15), since the structure of these catalysts are destroyed at high temperatures. Finally, the leaching of the acid sites is a common problem for most solid acids in aqueous environments at high temperatures. Zeolites can be used to replace resin catalysts, and these materials do not suffer from leaching and they can be
regenerated with a calcination treatment following deactivation. However, these zeolite catalysts result in significantly lower yields of levulinic acid (e.g., 15% over ZSM-5 compared to 55% over Amberlyst-15) in the presence of water, especially when increased levulinic acid concentrations are desired in the product stream. As a result, the reaction conditions are needed to be improved or novel solid acid catalysts are needed to be developed in order to effectively carry out this conversion. One option in terms of modifying reaction conditions is to decrease the water amount and carry out the reaction in a GVL rich solution, which was shown to be effective for the xylose dehydration reaction in Chapter 8. In addition, this conversion can be carried out in a semi-batch system, which was shown in Chapter 7 to be effective in obtaining a product in high yields and concentrations when the reactant (furfuryl alcohol) is prone to polymerization reactions. A further improvement in levulinic acid yields can be obtained by creating a controlled environment around the active acid site (e.g., changing the steric or electronic environment by incorporating non-polar/polar surface moieties or modifying pore size) as mentioned above for the case of furfural hydrogenation. In this case, the pore structures of the zeolites can be modified to increase the diffusion limitations, such that furfuryl alcohol concentration on the acid sites can be minimized at any time. This way, the extent of the furfuryl alcohol polymerization reactions can be reduced more prominently compared to the furfuryl alcohol hydrolysis that lead to levulinic acid. This modification can be carried out by the deposition of a thin layer of oxides through atomic layer deposition (ALD) within the pores of microporous zeolitic materials. Since ALD employs a sequence of self limiting reactions between a gas phase precursor and the surface, the deposition can be carried out on complex geometries, such as in zeolites, to the extent (monolayer count) desired.
9.2.3. Technoeconomic Analysis for Hemicellulose Processing Strategies

During the past years we have conducted techno-economic analyses of our catalytic strategies to convert cellulose to biofuels in collaboration with Professor Maravelias. We have found the results of these analyses to be invaluable in assessing the factors that control the economics of our approach, providing directions for future research to debottleneck our process. In all these analyses, hemicellulose portion is either burned for heat and power generation or xylose is sold as an end product. However, techno-economic analyses for the processing strategies for hemicellulose for the production of valuable chemicals or fuels will be invaluable in assessing the merits of an overall biorefining strategy, in which in addition to cellulose, hemicellulose is also utilized for the production of high value chemicals (e.g., furfural) or fuels. In fact, these analyses will help decide whether the hemicellulose portion should be utilized for chemicals or fuels, and even where these hemicellulose conversion strategies are suited better, in a pulp and paper facility or a combined chemical conversion strategy.

9.3. References