Catalytic Conversion of Carbohydrates

Osmundsen, Christian Mårup

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This thesis describes the work performed during my Ph.D. studies at the Technical University of Denmark, DTU. The project was performed at the department of physics, under the CASE (Catalysis for Sustainable Energy) initiative, which is funded by the Danish Ministry of Science, Technology and Innovation. The project was performed in close collaboration with Haldor Topsøe A/S. Furthermore, part of the work was carried out at the University of Wisconsin-Madison in the research group of Prof. James A. Dumesic.

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Christian Mårup Osmundsen
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Abstract

Modern civilization is dependent on oil to supply energy for power, heating and transportation and carbon for the production of the plethora of chemicals needed. Oil is however a limited resource and alternatives need to be identified before we freeze in the dark [1]. This thesis deals with the production of commodity chemicals from the most abundantly available renewable source of carbon, carbohydrates.

The production of alkyl lactates by the Lewis acid catalyzed conversion of hexoses is an interesting alternative to current fermentation based processes. A range of stannosilicates were investigated for this reaction; Sn-BEA, a zeolitic Lewis acid, displays a remarkably high activity for this reaction due to the presence of a uniquely strong acid site, a site which is not observed in other stannosilicates and is therefore likely related to the silicate structure. The tin site in Sn-BEA was studied using DFT calculations, which indicate that the strongest, and most stable, acid site is formed through the introduction of a silicon vacancy adjacent to the tin site.

Aromatics are an important class of compounds. In particular benzene, toluene and p-xylene finds use in a wide range of industries. The synthesis of these by the cycloaddition of ethylene to furanic compounds, followed by dehydrative aromatization, was demonstrated in good yields, using a strong Bronsted acidic catalyst, WO$_x$/ZrO$_2$. As both ethylene and furanics can be derived from carbohydrates by known processes, this constitutes a renewable route to aromatics.

The conversion of biomass by high temperature processes is a desirable prospect due to the high volumetric production rates which can be achieved, and the ability of these types of processes to convert a wide range of substrates. Current processes however typically have rather low selectivity towards any particular compound, which can be problematic for chemicals production. In the current work, a process for converting monosaccharides by high temperature thermoly-
sis was investigated. A wide range of substrates could be converted with a high selectivity towards C$_1$- to C$_3$-oxygenates through thermal retro-aldol condensations. One compound, glycolaldehyde, could be prepared in yields of over 60% by this method; as this compound can potentially be used as a starting point for producing a wide range of chemicals, such as ethylene glycol or acetic acid, this process could prove to be an efficient initial conversion step in the utilization of biomass for chemicals production.

The shift from an oil based chemical industry to one based on renewable resources is bound to happen sooner or later, however the environmental problems associated with the burning of fossil resources means that it is desirable to accelerate the process. To this end, processes for efficiently converting biomass to commodity chemicals are needed, and the above mentioned processes are a small step towards this goal.
Vores samfund er afhængig af fossile ressourcer, da vi fra dette får energi til at dække vores varme-, elektricitets- og transportbehov, samt det kulstof vi skal bruge til fremstilling af en lang række vigtige kemikalier. Olie er dog en begrænset ressource, og vi er derfor nødt til at finde alternative kilder til disse før vi ender med at fryse i mørket [1]. Denne afhandling omhandler metoder til at producere industrielle kemikalier fra den mest udbredte fornybare kulstofkilde, kulhydrater.

Omdannelse af kulhydrater til estre af mælkesyre, katalyseret af Lewis syrer, er et alternativ til de fermenteringsprocesser som benyttes nu. En række forskellige stannosilikater er blevet undersøgt som katalysator for denne reaktion; Sn-BEA, en Lewis sur zeolit, besidder en meget høj katalytisk aktivitet, hvilket sandsynligvis er pga. den usædvanligt høje syrestyrke som denne struktur sammenlignet med andre silikater. Indsættelsen af tin i zeolit BEA blev studeret ved hjælp af elektronstruktur (DFT) beregninger; disse indiker at den højeste syrestyrke, og den mest stabile indsættelse, opnås når tin er indsat ved siden af en siliciumvakance.


Omdannelse af biomasse ved hjælp af højtemperaturprocesser er en tiltalende ide, da der kan opnås høje volumetriske produktionshastigheder, og fordi et bredt spektrum af substrater kan omdannes. Nuærende processer har dog typisk lav selektivitet, hvilket kan være problematisk hvis de skal anvendes til kemikalieproduktion. I denne afhandling bescribes en proces til omdannelse af monosakkarider
Resumé (in danish)

ved hjælp af højtemperatur thermolyse. En række forskellige substrater kan om-
dannes med høj selektivitet til C₁- til C₃-oxygenater gennem retro-aldol kon-
densationer. Én forbindelse, glycolaldehyd, kan fremstilles med et udbytte på
over 60% ved denne metode; da dette kemikalie potentielt set kan bruges som
udgangsstof til fremstilling af en række forskellige kemikalier, f.eks. ethylen-
lykol eller eddikesyre, kan denne proces vise sig at være et effektivt indledende
omdannelsesstrin i udnyttelsen af biomasse til kemikalieproduktion.

Før eller senere vil der ske et skifte fra en kemisk industri baseret på olie til en
industri baseret på fornybare ressourcer. De miljømæssige problemer forbundet
med afbrænding af olie gør dog, at det er ønskværdigt at accelerere denne proces.
For at opnå dette er det nødvendigt at identificere processer der effektivt kan
omdanne biomasse til industrielle kemikalier; de ovenfor nævnte processer er et
lille skridt mod dette mål.
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The apex of the Washington Monument is capped by a 2.8kg aluminum block, making it, at the time of construction, the largest single block of aluminum ever cast. Aluminum was considered a precious metal commanding a price comparable to silver; this despite the fact that aluminum is the most abundant metal in the Earth’s crust [2]. This was due to the stability of aluminum oxide, which meant that a costly reduction of AlCl$_3$ with metallic sodium was the dominant production method. Two years later, the electrolytic reduction of aluminum oxide by the Hall-Héroult process was discovered, and quickly commercialized, causing the price of aluminum to plummet: From over 500$/kg to the current price of less than 3$/kg [2]. In only a couple of years, aluminum went from a rare and precious metal, to one available in abundance, because of a technological breakthrough.

One of the great challenges today is the production of cheap, abundant energy. This is currently done through the combustion of fossil resources, such as coal, oil, and natural gas, however this is not a sustainable approach: The rate with which oil is consumed is many orders of magnitude greater than the rate with which it is created. Although the ratio between proven reserves and current consumption has been increasing steadily over the last many decades [3], the day will come, in a not to distant future, when oil will no longer be available at a sufficiently low price. The available reserves of coal and natural gas will last longer [3], but these too will be expended. In addition to the problem of renewability, the release of vast quantities of CO$_2$ from the combustion of fossil resources have raised atmospheric concentration of CO$_2$ to a level surpassing anything observed
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over the last 600,000 years, causing problems related to climate change and ocean acidification [4]. Although the exact scale of the problem, and the best solutions to it, has yet to be determined, postponing action will only increase the cost of mitigation [5], and thus solutions need to be implemented now. One solution is to dramatically scale back the energy consumption of modern society, a solution which is unlikely to be popular among the billions of people who will have to accept a decreased standard of living. A much more sensible solution is finding ways to continue our way of life in a more sustainable manner.

Several annually renewable energy sources exist: Geothermal energy from Earth’s core, kinetic energy from wind and waves, potential energy from lakes, and chemical energy from biomass. Ultimately all of these, with the exception of geothermal energy, can be traced back to the influx of electromagnetic energy from the sun. The rate of energy input from the sun is approx. 120,000 TW, dwarfing the current human consumption of 15 TW [6]. It is thus not a question of whether the energy is available, but rather if we are able to efficiently harness it. Two systems exist for capturing the energy of sunlight directly: Photovoltaics and photosynthesis. A direct comparison between the two for electricity generation comes out heavily in favor of photovoltaics; while commercial solar cells can achieve conversion efficiencies close to 20%, the efficiency with which photosynthesis converts sunlight to chemical energy is typically less than 1% [6]. Although photovoltaics will need to be coupled with electrolyzers to store energy, e.g. in the form of hydrogen, the efficiency remains an order of magnitude higher than for biological systems. Thus for on-grid energy generation the use of biomass over alternative sources seems injudicious.

Energy is however not the only important asset extracted from fossil resources: The carbon content is equally vital as this allows for the production of fuels and chemicals. Crude oil derived liquid transportation fuels are an extremely well suited energy carrier: They posses very high volumetric and gravimetric energy density, are easily transportable and transferable, and can be stored efficiently. Alternative energy carriers currently being developed, such as batteries or hydrogen (fuel-cells), are inferior on several of these criteria; at least at the moment [7]. Production of transportation fuels compatible with the current infrastructure from biomass would obviate these concerns. Equally important is the production of chemicals, for which there does not appear to be any alternative feedstocks other than biomass. The carbon content of biomass may be a more important resource than the energy content.
1.1 The best use of biomass

The total production of biomass on Earth is more than 170 billion tonnes per year [8, 9], far surpassing the 4.4 billion tonnes of oil currently consumed [3]. Such a comparison is however very misleading: Although only 3.5% of the formed biomass is currently being utilized by humans, the vast majority of the remaining is not available for industrial use; either because it is an intricate part of the local ecosystem, or because it resides in areas where collection is unpractical. Thus, to identify the actual amount of available biomass, one must solely consider the part which is available in a sustainable manner.

Taking the US as an example, the current utilization of biomass for non-food purposes is approx. 190 million tonnes each year. In comparison, the current consumption of oil is close to 1 billion tonnes (see Figure 1.1), and a significant increase in the amount of utilized biomass is therefore required. Any projection of the potential amount of biomass available is of course highly speculative, however in a report by the US Department of Energy [10], it was estimated that the US could increase the amount of harvested biomass to 1.2 billion tonnes within 50 years without significantly impacting food production\(^1\). As both the energy and carbon density of biomass is significantly lower than oil, even such a dramatic increase in the biomass production would, assuming similar conversion efficiencies, only be able to substitute half of the current oil need. As biomass production is likely not going to be able to equal even current oil consumption, it is necessary to consider the best use of the available biomass.

The “best” use is of course an ill-defined term, which is highly dependent on local conditions, such as societal needs and available resources, however some general considerations can be inferred. Despite the fact that the amount of crude oil used for fuels production far outweigh the amount used for chemicals, the revenues derived from the two industries are roughly equal as the value-addition is much greater for the latter [12]. The success of the petrochemical industry is however reliant on the association with fuels production: Due to the sizable capital costs associated with oil extraction and treatment, the high volume of fuels produced is needed to achieve the economy of scale required for a financially viable business. Such an association is not necessarily required for production of chemicals from biomass as the cost of the feedstock scales more linearly. Furthermore, while crude oil is geographically concentrated, biomass is relatively homogeneously dispersed over the entire globe and many, smaller processing plants are therefore

\(^{1}\)This number should not be considered an upper limit: The study was tasked with identifying 1 billion tonnes, and thus simply looked at the most easily available resources.
required to avoid excessive transportation of the feedstock [13]. Thus, the production of low volume, but high value, products is a much more viable option from biomass.

Another consideration is the chemical characteristics of the feedstock. A convenient parameter for comparing different feedstocks is the hydrogen to carbon ratio adjusted for heteroatoms, the so-called effective H/C ratio, which is calculated from the following equation (for a molecule containing only H, C, and O):

\[
\text{H/C}_{\text{eff}} = \frac{n(H) - 2 \cdot n(O)}{n(C)}
\]  

In Figure 1.2, a number of fossil and biomass resources are arranged according to their H/C\text{eff}. Crude oil consists mainly of hydrocarbons with a very low degree of functionalization and thus has a H/C\text{eff} of approx. 2, which is in the same range as most common transportation fuels. Indeed, the conversion of crude oil to fuels consists of a distillation, to obtain the desired physical parameters, followed by desulphurization and denitrogenation steps for environmental reasons. The changes in the chemical characteristics of the feedstock is rather limited, which makes for a highly efficient process, thus the amount of waste generated is more than an order of magnitude lower than the amount of product formed [14]. The biomass equivalent to crude oil would be triglycerides, which can similarly be converted into a transportation fuel, bio-diesel, through a relatively simple transesterification reaction [15]. Although triglycerides can account for more than
Figure 1.2: A range of fossil and biomass derived resources, intermediates and target chemicals arranged vertically according to their H/C\textsubscript{eff}. Horizontally they are arranged qualitatively according to their degree of processing, with target chemicals (highly processed) in the center, and resources (no processing) along the sides. B = Benzene, T = Toluene, X = Xylenes, EG = Ethylene glycol, PG = Propylene glycol, PE = Polyethylene, PP = Polypropylene, GVL = γ-Valerolactone [11].

60% of the dry-mass of certain fruits and seeds [16], they only constitute a minor fraction of the total available biomass. The most abundant type of biomass, lignocellulose, consists of approx. 40% cellulose, a linear polymer of glucose, 30% hemicellulose, a highly branched polymer of primarily xylose, glucose and mannose, but also a wide range of other pentose and hexose sugars, and 25% lignin, a complex three-dimensional polymer consisting of a range of aromatic subunits, with the remainder being accounted for by fats, salts and other minor constituents; the exact distribution can however vary significantly between different sources [17, 18]. Thus the majority of the available biomass is in the form of carbohydrates; these are highly oxygenated molecules, and significant modification is therefore required to convert them into fuels compatible with combustion engines, i.e. increase the H/C\textsubscript{eff} to the range of hydrocarbons by the addition of H\textsubscript{2} or the expulsion of CO\textsubscript{2}, CO or C (in order of decreasing efficiency). Current industrial processes for achieving this change, such as fermentation to ethanol, have questionable energy balances and environmental benefits [19, 20], and although several promising processes have been demonstrated in lab scale [21–25], the low energy density of carbohydrates, coupled with the extensive chemical modifications required, means that the production of chemicals which are solely desired for their energy content is a difficult proposition.
Commodity chemicals on the other hand, comprise chemicals which span a much wider range of H/C\textsubscript{eff}; from polyethylene (H/C\textsubscript{eff} = 2) to phthalic acid (H/C\textsubscript{eff} = -0.25). Chemicals in the lower end of this range are extensively functionalized, and the selective introduction of this functionality in crude oil is challenging and must therefore typically be done in a number of discrete reaction steps, leading to lower yields and significantly more waste [14]. For instance, the introduction of oxygen functionality by oxidation reactions, leads to loss of substrate carbon due to over oxidation. For chemicals production it would seem that carbohydrates may be a more suitable feedstock, as many important large scale chemicals can be made with minimal need for changes in the average oxidation state of the carbon backbone, instead relying primarily on fragmentation or rearrangement reactions. Although all chemicals and fuels will at some point need to be made from sources other than crude oil, for the first steps away from oil, highly oxygenated chemicals are likely the target with the lowest barrier for entry.

1.2 The current work

For the above mentioned reasons this work has focused on a number of processes for producing commodity scale chemicals from carbohydrates. The aim has been to investigate processes which utilize the inherent chemistry of carbohydrates, rely on heterogeneous catalysis, and which maximize the retention of substrate atoms in product molecules, with the ultimate aim of developing sustainable routes to chemicals from biomass-derived substrates. Chapter 3 details an investigation of Lewis acidic silicates as catalysts for the conversion of carbohydrates to alkyl lactates. In Chapter 4, the production of aromatics through cycloaddition reactions is described. Finally, Chapter 5 deals with selective high temperature thermolysis as a method for producing chemicals from carbohydrates.
A Sustainable Chemical Industry

The modern petrochemical refinery is one of the great scientific accomplishments of the 20th century. Starting from crude oil, a complicated mixture of hydrocarbons, this construction is able to remove unwanted impurities, such as sulfur, nitrogen, and metals, and then convert the oil into fuels with well defined physical properties and pure streams of a diverse range of chemicals. All of this is done through a range of highly optimized and integrated processes, so that the overall process only generates very small amounts of waste [26]. It is through the development of the petrochemical refinery that modern society has unlocked the potential of oil as an abundant and inexpensive source of concentrated energy and carbon, and thus it has been instrumental in allowing for the industrialization of large parts of the world.

As a replacement for the petrochemical refinery, the concept of a biorefinery is often suggested [27]. This construction would, analogously to the petrochemical refinery, accept a wide range of biomass resources and convert them into desired chemicals. To which extent such a concept makes sense, or more precisely how closely the analogy holds, is still unclear, however several problems still remain to be solved before an industry based on biomass can become a reality.
2.1 Designing a chemical industry

While fuels do not have a well defined chemical composition, but rather consists of hundreds of different compounds which add up to the desired overall properties, the chemical industry has a much more strict focus on purity. This is a challenging goal, as the feedstock is a complicated mixture of a plethora of different compounds. To overcome this, the chemical industry is organized around a few key intermediates (shown in Figure 2.1), from which the majority of chemicals are produced [28]. These compounds can be derived from crude oil relatively easily, at low cost, in high volume, and in sufficient purity. The demonstration of processes for the production of these platform chemicals from biomass would in principle be a major step towards replacing oil, however this is an inefficient strategy as it fails to utilize the inherent chemistry of the substrate: Excessive removal of oxygen from the substrate will invariably lower the overall efficiency of the process (with one possible exception being the production of methanol by gasification, as this will allow for the utilization of biomass resources, which cannot be efficiently converted by other methods). Thus focus has instead been on finding alternate chemicals which can more easily be derived from biomass, and thus share the important characteristics of a platform chemical: Available in high volume at low cost.

Many biomass-derived chemicals have been suggested as suitable platform chemicals: In a study by the US Department of Energy [29], more than 300 potential platform chemicals, which can be produced from carbohydrates, were down selected to twelve top candidates (shown in Figure 2.2). This is not to be viewed as a final list, but rather an evaluation of potential, as it stood at the time of the report; indeed the same authors have suggested a revised list [30], which includes a greater number of furanic compounds, as well as ethanol and lactic acid. Despite the evolutionary nature of this type of ranking, it is beneficial to keep in mind, as it will help in identifying synergistic effects, which will be necessary for the success of the renewable chemical industry. Comparing the renewable...
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Figure 2.2: The twelve top candidates for platform chemicals in a biomass based chemical industry according to the US Department of Energy: 1,4-Diacids (succinic, fumaric, and malic acid) (a), 2,5-furan dicarboxylic acid (b), 3-hydroxypropionic acid (c), aspartic acid (d), glucaric acid (e), glutamic acid (f), itaconic acid (g), levulinic acid (h), 3-hydroxybutyrolactone (i), glycerol (j), sorbitol (k), and xylitol/arabitol (l) [29].

platform chemicals to those derived from fossil resources, clear differences are observed: These are all highly oxygenated chemicals, which retain a high degree of the functionality present in the parent carbohydrate. The production of target chemicals from these cannot be done using the conversion technologies currently employed in the petrochemical refinery, which rely heavily on gas phase conversion, due to the significantly different chemical properties of the two substrates: Where hydrocarbons are thermally stable molecules, requiring high temperatures to effect conversion, carbohydrates are thermally unstable; where introduction of functional groups are required for hydrocarbons, removal of excess functionality is the challenge from carbohydrates, and where hydrocarbons are apolar compounds, carbohydrates are highly polar. Thus a much greater focus on low temperature liquid phase conversions, especially aqueous phase, are required, at the very least in the initial conversion steps. As we, in a very literal sense, need to reinvent the chemical industry this should be taken as an opportunity to do so in a more sustainable manner, as defined by the Brundtland commission [31]:

“Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”
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To do this, certain guiding principles, which have been learned over the last many decades should be kept in mind.

**Atom economy**

The concept of atom economy [14, 32, 33], is a simple means for estimating the efficiency of a particular reaction path under ideal conditions. It is defined as the ratio between the mass of desired products to the total mass of products formed as written in the reaction scheme; it thus assumes 100% yield. Although somewhat crude, it can be a convenient tool as it allows one to evaluate the efficiency *a priori* from the overall reaction scheme. Maximizing the atom economy means striving to design a process, where all atoms of the substrates are incorporated into the product, which naturally leads to the aim of replacing stoichiometric reagents with catalysis. The concept does however fail on a number of important points: It does not take into account the actual yield, nor any solvents or excess of reagents needed. Finally it does not consider workup of the product nor the energy requirements of the process. Thus, the most atom efficient process is not necessarily the most sustainable solution.

**Environmental factor**

To make up for these deficiencies, the Environmental, or E-, factor was introduced [14, 26, 33]. This is given by the amount of waste generated in the actual process divided by the amount of product formed, while disregarding any water used. It also includes any waste generated to produce the energy needed for the process. Determination of the E-factor requires quite intimate knowledge of the process, however it is a powerful tool for comparing different processes, and for identifying steps where optimization is required. The shortfall off this method is of course the fact that it equates any type of waste generated, which is a rather unreasonable assumption. This problem has been attempted solved by multiplying the waste generated with an arbitrarily chosen “unfriendliness” quotient to better compare different types of waste, however this also makes the result somewhat arbitrary. To ultimately compare the environmental impact of different processes, a complete life cycle assessment is necessary, however the significant difficulties in reliably doing so makes this an inefficient tool for process design. Thus the atom economy and E-factor are important tools to consider, as long as one is not blind to their shortcomings.
Green chemistry

The term “Green Chemistry” was coined to describe a design philosophy of “benign by design” [14, 34]. The guidelines for designing a green chemical process are given in the 12 principles of green chemistry [33, 34], which can be summarized as:

“Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products.” [14]

Central to the idea of green chemistry are the notions of avoiding waste instead of cleaning it up, to replace stoichiometric reagents with catalysis and in all aspects of the process to avoid harmful, toxic, or persistent chemicals. The principles of green chemistry are thus ideals to strive for when designing a sustainable chemical process. The reasons for applying the principles of green chemistry should however not be considered limited to those based on ethics: Waste is product, which cannot be sold, lower energy requirements entails a lower production cost, and avoiding dangerous substances means that expensive safety precautions can be avoided. The possibility of improving process economics through green chemistry is likely a significant reason for why it has been embraced so broadly by industry [34].

2.2 The shift from crude oil to biomass

Although it is inevitable that fossil derived chemicals will eventually be replaced, it is desirable to accelerate this process. There are currently three motives for producing chemicals (and for that matter fuels) from biomass: The green premium, regulatory incentives, and profit.

There is currently a significant public focus on the problems of climate change due to green house gas emissions which can be capitalized upon, either through improved public relations or the willingness of consumers to pay an increased price, by creating sustainable products. The same focus, and the desire for energy independence, has caused governments to award tax deductions and favorable loans to companies engaged in creating sustainable solutions, while at the same
time increasing the tax burden on those that exacerbate the problems. Both of these are however fickle reasons; the economic crisis has decreased the publics willingness to pay the green premium, and the public relations benefits primarily influence products marketed directly to the public, while doing little to assuage investors. Similarly, basing an industry on tax breaks, which could be removed without much in the way of warning, or regulations, which may or may not come, is difficult. The idea of creating a process which can compete with fossil based analogs on market terms should however not be discounted. The price of crude oil routinely exceeds 100$/bbl, a price level which has not been reached since the 1860’s, in a time when the oil industry was still nascent\(^1\) [3], while projections only have the price increasing further. Focusing on processes that have the potential to become profitable in the current market, and expanding to new areas as these become viable, due to increasing oil prices and, equally important, increased experience with the handling and processing of biomass, seems to be the surest way of quickly replacing oil.

Two main strategies can be pursued to introduce biomass substrates in the chemical industry: Either identifying reaction pathways to yield current fossil-derived target chemicals starting from a different substrate (the drop-in strategy), or identifying target chemicals with similar or improved properties compared to the fossil counterpart (the emerging strategy) [11]. The two approaches are shown schematically in Figure 2.3. An example of the different approaches is the preparation of antifreeze: Ethylene glycol is a common antifreeze agent prepared by oxidation of ethylene [35]. Ethylene is currently derived mainly from steam cracking of petroleum, however it can also be produced by dehydration of fermentation based ethanol [36] (the drop-in strategy). Alternatively, instead of focusing on replicating the molecule, the function of ethylene glycol can be mimicked with propylene glycol, which can be derived from carbohydrates by hydrogenolysis [37–39] (the emerging strategy). Both approaches have distinct advantages and disadvantages [11], with the main advantage of the drop-in strategy being the possibility of using existing infrastructure and technology to a larger extent, while the emerging strategy can benefit from a better utilization of the inherent functionality of the substrate.

In any case, the sizable capital costs associated with the chemical industry and the significant technological challenges which still remain to be solved means that the biomass based and the petroleum based chemical industries will continue to exist side by side, or more likely intertwined, for the next many decades, with renewable resources slowly replacing more and more petroleum as alternative processes.

\(^1\)The oil crisis of the 1970’s is the one exception. Prices are adjusted for inflation.
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Drop-in strategy
• existing value chain • utilizing existing infrastructure • mature market

Emerging strategy
• new value chain • requires new infrastructure • emerging market

Figure 2.3: A schematic representation of the two approaches to forming a value-chain based on renewable resources: Either targeting chemicals in an existing value-chain, known as the “drop-in” strategy (top) or identifying novel chemicals with similar or improved properties compared to a current product, known as the “emerging” strategy (bottom) [11].

become financially viable or required by law. The identification of more efficient processes for producing chemicals from biomass is however a pressing need in order to initiate this transition.
One of the major technological breakthroughs in the petrochemical refinery was the introduction of Brønsted acidic zeolites [40]. Zeolites are crystalline aluminosilicates, composed of corner-sharing SiO$_4$ and AlO$_4$ tetrahedra. The inclusion of aluminum atoms in the framework introduces a charge imbalance which must be compensated for by the presence of a cation, e.g. a Brønsted acidic proton. Furthermore, zeolites are characterized by having a well-defined three dimensional pore system, with the diameter of the pores being in the Ångström-range, the same as small molecules. This property can be utilized to exclude certain molecules from the interior of the zeolite and thereby prevent them from interacting with active sites within; an effect known as shape-selectivity [41]. In the petrochemical refinery, this was recognized as a way to increase the selectivity of the fluid catalytic cracking (FCC) process, as only unbranched hydrocarbons would be able to diffuse to the Brønsted acidic sites, while branched hydrocarbons would be left intact, thereby producing gasoline with a higher octane number [40]. Today, the FCC process alone accounts for 95% of the zeolites used for catalytic purposes [42].

Although the majority of focus over the last 70 years, within zeolite science, has been on Brønsted acidic zeolites, the introduction of new types of functionality by the inclusion of heteroatoms has recently garnered an increasing amount of interest; the most well known example being TS-1 [43]. Titanium Silicalite-1 is based on the MFI framework, the same as the Brønsted acidic ZSM-5 employed in the FCC process, however it does not contain aluminum and is thus not Brønsted
acidic. Instead, the inclusion of titanium atoms in the framework makes it an efficient oxidation catalyst; a property which is utilized in the industrial production of catechol and hydroquinone from phenol by oxidation with hydrogen peroxide [44]. In addition to titanium, a range of different metals have been incorporated in zeolite structures, such as Sn, Zr, V, Ta, Nb, Fe, Ge, Ga, etc. [45–55]. In recent years, tin based zeolites in particular have been the focus of intense research, as these possess very strong Lewis acidic sites, which have been shown to catalyze a number of reactions, such as Meerwein-Ponndorf-Verley-Oppenauer (MPVO) redox reactions [56–58], Baeyer-Villiger oxidations [59–61], ketose-aldose isomerizations [62–69], and retro-aldol condensations [68, 69]. The ability of this type of materials to catalyze a range of different reactions has allowed for the development of a cascade reaction, converting normal table sugar, sucrose, into lactic acid (derivates) in a single reactor and in high yield [68], thus mimicking the anaerobic fermentation with inorganic catalysis.

3.1 Lactic acid

The main uses of lactic acid are currently in the food industry as a pH-modifier and a preservative, while its polymerization to polylactic acid, a biodegradable polymer, is a promising and rapidly growing application [70]. Future applications could be the dehydration to acrylic acid, an industrially important monomer [71], hydrogenation to propylene glycol, a non-toxic antifreeze [72–74], or esterification to alkyl lactates, which can be used as environmentally benign solvents [75]. Thus, lactic acid may find uses in a much wider range of industries than is the case today. As with most of the potential platform chemicals, the wider adoption is reliant on the identification of more efficient and less costly production methods. Lactic acid is currently produced almost exclusively through the fermentation of sugars, however the demands of the microorganisms impose certain restrictions on the process parameters, thus the volumetric production rates are rather low, and the continual addition of alkaline salts are required to maintain the pH of the fermentation broth with concomitant generation of significant amounts of waste [70]. The use of inorganic catalysis would allow for a much wider range of possible reaction parameters, which could allow for a more efficient process. One method for producing lactic acid by inorganic catalysis is by alkaline degradation of carbohydrates [76, 77], however low selectivity has precluded this as a viable industrial option. A more promising method is the Lewis acid catalyzed conversion of carbohydrates.
3.2 Inorganic fermentation

The production of lactic acid by Lewis acid catalysis proceeds by an initial retro-aldol condensation to produce triose sugars, which can then isomerize to lactic acid (derivates), as shown in Scheme 3.1. Although the reaction can be performed in aqueous solution, it is in general preferable to perform the conversion in alcohol solvents, as this leads to the formation of alkyl lactates, which do not acidify the solution. The presence of Brønsted acidity is unwanted as this catalyzes a number of side reactions, such as the dehydration of hexose and pentose sugars to furanic compounds [78], non-selective degradation of pyruvaldehyde [79], and, in the presence of alcohols, the formation of pyruvaldehyde acetal (as shown in Scheme 3.2) [56]. The isomerization/esterification of triose sugars can be effected with high selectivity using a range of different Lewis acid catalysts, e.g. traditional homogeneous Lewis acids, dealuminated zeolites, and metal substituted silicates [67, 79–84], however so far only the latter have been shown to

\[
\text{Sucrose} \xrightarrow{\text{Fructose, Glucose}} \text{Glyceraldehyde, Dihydroxyacetone} \xrightarrow{\text{H}_2\text{O}} \text{Lactic acid (derivate)}
\]

Scheme 3.1: Reaction scheme for the conversion of sucrose to alkyl lactates. The reaction occurs by an initial cleavage of the sucrose to the constituent monosaccharides. Fructose can then undergo a retro-aldol condensation to triose sugars, which can dehydrate to pyruvaldehyde. Pyruvaldehyde forms a hemiacetal, which isomerize to an alkyl lactate through a 1,2-hydride shift. As the presence of Lewis acids also catalyze the ketose-aldose isomerization, the theoretical carbon yield is 100%.
Lewis Acidic Silicates

Scheme 3.2: Reaction scheme for the conversion of pyruvaldehyde to either alkyl lactates or pyruvaldehyde acetal. In the presence of Lewis acids the intermediate hemiacetal is converted to an alkyl lactate by a 1,2-hydride shift, while the presence of Brønsted acidity favors the formation of pyruvaldehyde acetal.

efficiently catalyze the initial retro-aldol condensation, with Sn-BEA being by far the most active and selective [68]. The preparation of Sn-BEA is cumbersome however; the direct synthesis is performed by the so-called fluoride route, using hydrofluoric acid, and requires an expensive template and a long crystallization time [48]. Significant effort is currently being directed towards simplifying the synthesis, e.g. increasing the crystallization rate or preparing the catalyst by a post-treatment procedure of a conventional zeolite [85–87]. Another approach is the identification of catalysts structures, which can be produced using simpler synthesis methods. Regardless, a better fundamental understanding of the causes of the uniquely high activity of Sn-BEA is required.

3.3 Results and discussion

In an effort to better understand the influence of the silicate structure on the catalytic properties of stannosilicates, four different structures were investigated: Sn-BEA, Sn-MFI, Sn-MCM-41, and Sn-SBA-15 (as described in Appendix A.3). The first two are zeolitic materials, which have tin incorporated in the framework, with BEA being a large pore framework (5.95 Å) and MFI having a medium pore size (4.70 Å). The remaining are amorphous silicates, which are intersected by pores in the mesopore range (>20 Å). The last three can all be synthesized significantly faster than Sn-BEA and without the use of hydrofluoric acid. The catalytic performance of the materials were tested in the conversion of triose sugars to methyl lactate, the isomerization of glucose to fructose, and the conversion of sucrose to methyl lactate.
3.3.1 Influence of the silicate structure

The yield of methyl lactate from the conversion of 1,3-dihydroxyacetone, DHA, was studied as a function of temperature with the considered catalysts (see Figure 3.1). At 120 °C all four catalysts gave high yields (>80%), which is not surprising considering the wide range of catalysts which have previously been shown to catalyze this transformation. In methanol, and in the absence of strong Brønsted acidity, no significant byproduct formation is observed regardless of the catalyst, and the primary difference between catalysts is in terms of activity. While Sn-MFI, Sn-MCM-41 and Sn-SBA-15 gives similar yields at all temperatures, Sn-BEA shows a uniquely high activity at low temperatures, giving quantitative yields even at 40 °C.

Although the overall yield of methyl lactate does not differ significantly between the considered catalysts (with the exception of Sn-BEA), the distribution between intermediates show clear differences: While the amorphous silicates form primarily pyruvaldehyde, indicating that the hydride shift to form methyl lactate is the rate-limiting step, only relatively small amounts of this intermediate is present when Sn-MFI is used as catalyst, with the triose sugars instead being dominant. Thus it would appear that the dehydration of the triose sugars is the rate-limiting step in this case. This difference in activity could be explained by the larger concentration of silanols on the amorphous silicates, which would impart some

![Figure 3.1: Yield of methyl lactate obtained from the conversion of DHA catalyzed by stannosilicates [88]. (Reaction conditions: 110 mg of DHA, 80 mg of catalyst, 4.0 g of MeOH, 24 hr reaction time).](image-url)
Lewis Acidic Silicates

Figure 3.2: Carbon distribution after isomerization of glucose in either water (left) or methanol (right) catalyzed by stannosilicates [88]. Fructose and mannose are quantified together as they could not be sufficiently separated by the HPLC system to allow for individual quantification. (Reaction conditions: 100 mg or 50 mg of glucose in 5.0 g of water or methanol respectively, 50 mg of catalyst, 80 °C, 48 hr reaction time).

Brønsted acidity to the catalyst, and thus increase the dehydration activity, however it could also be due to a difference in the Lewis acid sites present in zeolitic and amorphous silicates.

Similar results are observed when examining the activity of the catalysts in the isomerization of glucose to fructose (and mannose), as shown in Scheme 3.3 (results shown in Figure 3.2), except that in this case Sn-MFI show almost no catalytic activity. As the pore diameter in the MFI structure is significantly smaller than in any of the other structures considered, diffusion of hexoses through the channel system is severely hindered [67]. The high activity of Sn-BEA is not limited to the isomerization, as significant side reactions are observed leading to a lowered hexose mass balance at high conversion. Such side reactions are not observed to any appreciable degree for the mesoporous silicates, which display close to 100% selectivity towards the isomerization products. Although the selectivity of Sn-BEA could potentially be increased by decreasing the reac-
Catalytic Conversion of Carbohydrates

tion temperature, this may not be desirable in all cases, due to issues relating to the solubility and equilibrium distribution of the hexose sugars, or because the reaction temperature needs to be matched to subsequent reaction steps (such as Brønsted acid catalyzed dehydration reactions). The ability to tailor the activity of the catalyst to the desired application through the choice of silicate structure is therefore an interesting possibility. One additional parameter which significantly influence the observed activity is the choice of solvent: With all investigated catalysts, the reaction proceeds significantly faster in methanol as compared to water, though the difference is less pronounced for Sn-BEA. The lowering of the activity could be due to deactivation of the active sites by interaction with water, where the zeolitic structures will be more resistant as the hydrophobic nature of the high-silica framework will prevent water from accessing the pores [58]. In the case of the mesoporous silicates, the high density of silanols on the pore walls means that a similar protection is not afforded to these.

With respect to the conversion of sucrose to methyl lactate, this relies on a combination of the two reactions mentioned above in addition to a retro-aldol condensation step, thus it is not surprising that similar trends with respect to the yield are observed. This is however not related to a higher conversion using Sn-BEA, as almost complete conversion was obtained with all catalysts under the used reaction conditions, but rather a significantly higher selectivity: With Sn-BEA a carbon yield in excess of 60% can be achieved, while the other considered catalysts all gave yields in the range of 20 to 30% (results shown in Figure 3.3). The range of byproducts which can be formed from hexoses at elevated temperatures, e.g. through dehydration reactions and oligomerization/polymerization reactions leading to humins and coke deposits, is much wider than is the case for trioses, and the higher yield obtained with Sn-BEA could therefore simply be related to a higher activity for retro-aldol condensations, directing the reaction along the desired path before thermal degradation can occur to a significant degree. The fact that Sn-BEA exhibits a significantly higher activity for the above mentioned reactions compared to the other stannosilicates, which all appear to have approx. the same catalytic properties, makes it unlikely that the difference can be explained simply in terms of diffusion properties or active site density, but rather that Sn-BEA possess an active site which is qualitatively different.

3.3.2 Probing the active site

To better understand the uniquely high activity displayed by Sn-BEA compared to other stannosilicates, the Lewis acidic site was characterized by FTIR spec-
Figure 3.3: Yield of methyl lactate obtained from the conversion of sucrose catalyzed by stannosilicates. The dotted line is the yield in a blank experiment [88]. (Reaction conditions: 450 mg of sucrose, 150 mg of catalyst, 15.0 g of MeOH, 160 °C, 16 hr reaction time).

When dosing deuterated acetonitrile (or another suitable probe molecule) onto Lewis acidic materials, the interaction with the acidic site causes a shift in the vibrational frequency of the nitrile. The extent of this shift has been used as a measure of the strength of the Lewis acid [51, 60, 61, 89, 90]. For all four silicates, bands at approx. 2266 and 2276 cm\(^{-1}\) are observed (for the mesoporous silicates the band at 2266 cm\(^{-1}\) only appears at very high acetonitrile loadings, which are not shown in Figure 3.4). These bands correspond to acetonitrile physisorbed on the surface of the silicate and interacting with silanols, respectively [90]. For all four catalysts, bands at higher wavenumbers are also observed caused by the presence of Lewis acidic tin sites. The spectra of the amorphous stannosilicates are very similar, as would be expected, as these structures mainly differ in the arrangement and dimensions of the pore system; features which are unlikely to significantly impact the local bonding environment of the tin sites and thereby their chemical properties. Furthermore, the bands assigned to acetonitrile interacting with the tin sites are relatively broad, which could indicate that a range of different sites are present in these structures, a situation which does not seem unreasonable as no well defined atomic ordering is present in these materials.

Conversely, the bands associated with tin sites appear much sharper for the zeolitic structures, with the shift observed for Sn-MFI being very similar to the amorphous silicates. Interaction with Sn-BEA however causes a much larger shift, presumably corresponding to a stronger Lewis acid site. This seems to correlate well with the much higher activity observed for Sn-BEA in a range of different reactions, as described above, as the stronger Lewis acid sites in Sn-BEA should be able to destabilize the carbonyl of the substrate to a much higher degree and thereby facilitate the reaction more efficiently. Thus the higher activity of Sn-BEA is related to a distinct difference in the active sites present. A further
Figure 3.4: The FTIR spectra of acetonitrile dosed onto different stannosilicates: The samples were saturated with acetonitrile, which was then desorbed by successive exposures to reduced pressure, with the spectrum measured between each desorption. The dashed line is the stannosilicate before dosing.
important feature of the Sn-BEA spectra is that two distinct bands assigned to tin sites are observed (at 2317 and 2308 cm$^{-1}$) indicating that at least two types of tin sites are present in the structure. This does not appear to be the case for the other structures.

### 3.3.3 The Lewis acid site in zeolite BEA

The cause of the dual sites observed in tin-substituted zeolite BEA have been explained by the presence of both isomorphously substituted tin sites and sites were one oxygen bridge has been hydrolyzed, as shown in Figure 3.5 [60].

![Figure 3.5: The two types of sites believed to be present in Sn-BEA: An isomorphous site (left) and a hydrolyzed site (right).](image)

assignment is primarily based on theoretical work, however the theoretical description of the active site in zeolite BEA is based almost exclusively on cluster models, where only a small cut-out of the zeolite structure is considered [57, 61, 91–94]. These calculations thus fail to include a significant portion of the interactions between the zeolite framework and the active site, as well as any differences between T-sites in the BEA structure. To elucidate the effect of these parameters, the metal substituted site was modeled by density functional theory calculations using a periodic structure. For these calculations the substitution with Sn, Zr, and Ti was considered.

If one initially considers the isomorphous substitution; exchanging silicon with larger ions causes a distortion of the MO$_4$ tetrahedra, which entails a lower stability, however the substitution energies do not follow the trend of the ionic radii (see Table 3.1); in fact the incorporation of Ti is even slightly favored compared to the purely siliceous zeolite BEA. The substitution energies were calculated as the energy difference between an MO$_2$ unit incorporated in its most stable oxide ($\alpha$-quartz, rutile, monoclinic zirconia, and cassiterite respectively) and incorporated in the zeolite structure. There are however differences between incorporation in different T-sites. The BEA framework is composed of 9 crystallographically different T-sites, however several of these are related by local symmetry and thus only three different types of site are present: $T_{1-4}$, $T_{5-6}$ and $T_{7-9}$. For substitution with Sn, no significant energy difference is observed between T-sites,
however this is not the case for Ti and Zr, where the T$_6$-site is energetically favored.

**Table 3.1:** Calculated substitution energies for Ti, Sn, and Zr inserted into the different types of T-sites in zeolite BEA.

<table>
<thead>
<tr>
<th>Metal</th>
<th>E$_{sub}$ [eV]</th>
<th>Θ$^a$</th>
<th>R$_i$$^b$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T1</td>
<td>T6</td>
<td>T7</td>
</tr>
<tr>
<td>Si</td>
<td>0.02$^c$</td>
<td>1.17</td>
<td>1.55</td>
</tr>
<tr>
<td>Ti</td>
<td>-0.12</td>
<td>-0.24</td>
<td>-0.09</td>
</tr>
<tr>
<td>Sn</td>
<td>1.01</td>
<td>1.05</td>
<td>1.03</td>
</tr>
<tr>
<td>Zr</td>
<td>0.62</td>
<td>0.49</td>
<td>0.69</td>
</tr>
</tbody>
</table>

a. Mean square deviation of the metal site from the ideal tetrahedra.
b. Ionic radii in crystals, from [95].
c. The stability of the individual T-sites could, for obvious reasons, not be determined.

To model the hydrolyzed site, several different representations can be used. Those considered in the current work are shown in Figure 3.6. In addition to the choice of representation, four different oxygen bridges can be hydrolyzed for each T-site$^1$; the choice of which oxygen bridge to hydrolyze can have a significant impact on the stability of the formed site, with energy differences of more than 1 eV (see Figure 3.7), clearly demonstrating the need to consider the entire structure of the zeolite. Of the hydrolyzed sites, the most simple is formed directly from the reaction of an oxygen bridge with water, giving a hydroxyl double bridge (site B). Due to the size of the double bridge, a significant distortion of the zeolite framework occurs, making this type of structure very unstable in a siliceous zeolite. The presence of heteroatoms greatly stabilize this structure, as an almost symmetric double bridge or a pentacoordinated metal atom are formed (as shown in Figure 3.8), depending on the local flexibility of the framework. As the formation of this type of structure is a step in the formation of any type of hydrolyzed site, or for desilication [96], it is interesting to note that the presence of heteroatoms clearly seem to ease the formation.

$^1$For the T$_6$-site only the hydrolysis of the three oxygen bridges accessible from the pore system.
The hydrolyzed site can lower the steric strain by inverting either the metal atom or the adjacent silicon atom (Site C and D). Although no significant energy difference is observed depending on which atom is inverted, the difference between hydrolyzing different oxygen bridges is quite significant: Only in the case where the inversion directs the hydroxyl into the pore system is the inversion energetically favorable. The final site considered is formed by the introduction of a silicon vacancy, forming an adjacent silanol nest. This is the most stable of the considered representations, a results which is not surprising as the removal of a silicon atom removes all steric strain imposed by hydrolyzing the oxygen bridge, however it is interesting to note that this site is actually more stable than the isomorphous site. The most stable site of each representation for each metal atoms is shown in Figure 3.9; as can be seen the stability of the sites with respect to the isomorphous site, in general, follow the reverse trend of the ionic radii, with the larger ions being more stabilized (or less destabilized) by hydrolysis. Although the hydrolysis imposes some extra strain due to the larger size of two hydroxyls compared to one oxygen bridge, it also increases the flexibility of the framework was considered.
which makes it easier to accommodate the larger ions.

![Stability vs Site](image)

**Figure 3.9:** The stability of the most stable representation of each type of site with respect to the isomorphous site.

Thus, the above results seem to indicate that the desilicated site (site E) is the dominant among the hydrolyzed sites, and that the incorporation of larger ions, favor the formation of hydrolyzed sites. These results however only speak to the stability of the different metal sites in zeolite BEA, and thus fail to take into account any kinetic effects, which are highly important in zeolite synthesis, and furthermore does not account for the activity of the different sites. To gain further insights into the latter, calculations of the interaction between the sites and acetone was performed; acetone was chosen as probe molecule since it closely resembles the typical substrates converted using these types of catalysts, while at the same time is a suitable probe molecule for FTIR experiments.

The energy of acetone adsorption onto the isomorphous site (site A) does not appear to be dependent on the choice of T-site (see Table 3.2), however not surprisingly a significant difference is observed between the metals with the adsorption energy increasing in the order Si < Ti < Sn < Zr. The fact that Zr forms the strongest Lewis acid is in agreement with previous reports [91], however it does seem counterintuitive considering that Sn-BEA is typically considered the most active Lewis acid catalyst [68]. The cause of the higher Lewis acid
strength observed with the hydrolyzed site has been, at least partly, ascribed to the greater flexibility of the site upon hydrolysis, as the interaction between the probe molecule and the site causes a lengthening of the Sn-O bond distance \[97\]. Another factor is the change from a tetrahedral geometry to a trigonal bipyramide upon coordination of the probe molecule, which is more easily achieved with a more flexible site. The present calculations support this idea, as the formation of site B and C, both of which are highly strained due to the proximity of the adjacent silanol, have decreased adsorption energies compared to the isomorphous site. Furthermore, the metal attached hydroxyl becomes somewhat Brønsted acidic, and the adsorption energy onto this site is roughly identical or higher than the adsorption energy onto the metal site. For these reasons it seems highly unlikely that these are the active site in M-BEA. The desilicated site on the other hand increases in strength compared to the isomorphous site for all three metals, however an interesting difference is observed between the T-sites: Only the T\textsubscript{1} and T\textsubscript{7} sites increase in strength, while the T\textsubscript{6}-site slightly decreases in strength. This further emphasizes the need to consider the entire structure for these types of calculations.

Table 3.2: Calculated properties for the adsorption of acetone onto metal substituted zeolite BEA. The adsorption energy is given in eV. The distance between the metal atom and the oxygen of acetone, as well as the carbonyl bond length, are given in Å.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Site</th>
<th>T1</th>
<th></th>
<th>T6</th>
<th></th>
<th>T7</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>E\textsubscript{ads}</td>
<td>d(C=0)</td>
<td>E\textsubscript{ads}</td>
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</tr>
<tr>
<td>Sn</td>
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<td>-0.30</td>
<td>1.248</td>
<td>-0.26</td>
<td>1.243</td>
</tr>
<tr>
<td></td>
<td>B</td>
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</tr>
<tr>
<td></td>
<td>C</td>
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<td>1.250</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>D</td>
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<td>-0.17</td>
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<td>-0.32</td>
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</tr>
<tr>
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<td>Zr</td>
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<td>1.245</td>
<td>-0.55</td>
<td>1.243</td>
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</table>

\(^{a}\) The interaction between the metal site and acetone was to weak to allow for adsorption.
Although the adsorption energy, which is presumably related to the acid strength, is an important parameter, as it describes the coverage of the sites, the actual catalytic effect of the active site relies on the ability of the site to destabilize the carbonyl bond. The C=O bond lengths however do not correlate with the calculated adsorption energy, and in fact very little difference is observed between different sites. The lack of a correlation is supported by experimental results: Measurements of the FTIR spectra of acetone adsorbed onto Si-, Sn-, Zr-, and Ti-BEA (shown in Figure 3.10) do not show a correlation between the shift in the carbonyl vibrational frequency and the strength of the adsorption. While the shift in vibrational frequency for acetone adsorbed onto Zr-BEA and Ti-BEA are identical (1699cm$^{-1}$), the adsorption strength onto Ti-BEA is much weaker as the acetone can easily be removed by exposure to reduced pressure at room temperature. A similar observation can be made with Zr-BEA alone; two peaks are present (at 1699 and 1691cm$^{-1}$), however it is the one with the highest shift which is removed first. This is a quite surprising result as this would indicate that the Lewis acid strength in itself is not a good descriptor for the catalytic efficacy of the materials, but rather that the observed rate is a combination of the acid strength of the site, to determine coverage, and the ability of the site to destabilize the carbonyl bond, to determine the activation energy. Although several parameters were investigated to identify a suitable descriptor for the sites ability to activate the carbonyl bond, none was identified. The destabilization of the carbonyl bond occurs through back-donation of electron density from the metal site to the $\pi^*(CO)$ orbital upon coordination [94], and although the strength of the Lewis acid is therefore an important parameter, as the bonding facilitates the overlap of the antibonding orbital of the probe with the orbitals of the metal site, it is clearly not a sufficient descriptor on its own. Further investigation of the ability of the sites to effect the activation of the carbonyl is needed, e.g. by transition state calculations of relevant reactions, to elucidate the important parameters, and thereby guide catalyst design. Furthermore, the possibility that the actual active site is one not considered in the current work should not be overlooked.

### 3.4 Summary and outlook

The catalytic production of lactic acid has the potential to allow for a much more widespread use of this chemical, as a lower production cost would make a number of new applications economically feasible. Although improvements in reaction parameters, such as decreased operating temperature and increased selectivity, would be desirable, the main challenges are related to the catalyst; in particular
Figure 3.10: The FTIR spectra of acetone dosed onto different metal substituted zeolites: The samples were saturated with acetone, which was then desorbed by successive exposures to reduced pressure, with the spectrum measured between each desorption. The dashed line is the silicate before dosing.
the cumbersome preparation and the stability of the catalyst are issues which need to be addressed. Basing the catalyst on other silicate structures, such as amorphous mesoporous silicates, would help alleviate these concerns, as the preparation is simpler and the larger pore size would make the catalyst more resistant to deactivation by coke formation, however the BEA structure clearly induces a higher activity than observed with any other structure. Thus, a better understanding of the underlying causes of this greater ability of Sn-BEA to activate the substrates are required, if ways of transplanting these sites to other structures are to be realized. Although other avenues are currently being pursued to allow for simpler synthesis of Sn-BEA, e.g. through reduced synthesis time or post-synthesis introduction of the active site, these approaches are also reliant on the same basic understanding in order to be able to maximize the fraction of catalytically active tin sites.

The discussion of Lewis acidic silicates should however not be limited to the production of lactic acid; the action of the catalyst is to activate carbonyls, a moiety present in a wide range of biomass derived substrates, and these catalysts may therefore find wide application in the future. Thus, these materials constitute an exiting new class of materials, which could have the same significant role in the coming renewable chemical industry, as Brønsted acidic zeolites have in the current petrochemical industry.
3.5 Experimental

Computational method

Calculations were performed using the density functional theory code GPAW [98, 99], using the RPBE functional, and employing periodic boundary conditions. Only the Γ point of the Brillouin zone was sampled. Calculations were performed with a real-space grid spacing of 0.15 Å; the convergence criteria in all calculations was a force of less than 0.05 eV/Å on each atom. The position of all atoms in the unit cell was allowed to relax. The unit cell dimensions was determined, using a purely siliceous zeolite, by minimizing the energy of the fully relaxed structure with respect to an equal expansion of each unit cell axis, and this unit cell size was used for all calculations.

Spectroscopic measurements

Si-BEA, Sn-BEA, Zr-BEA, and Ti-BEA were synthesized according to published procedures [68]. FTIR spectra were obtained on a BioRad FTS 80 spectrometer equipped with a MCT detector operating in transmission mode. The samples were pressed into self-supporting wafers and mounted in a Pyrex measurement cell with NaCl windows, that was connected to a vacuum line. The sample was degassed at 375 °C for at least 2 hr. Acetone was dosed onto the sample in small aliquots, while measuring the IR spectrum. Once the sample had been saturated, the acetone was slowly desorbed by subjecting the sample to reduced pressure for short periods of time. The IR spectrum was measured between each desorption.
Aromatic compounds, in particular the so-called BTX compounds (benzene, toluene, and xylenes), are an important class of compounds: They are used as gasoline additives to increase octane number, as solvents, and as the starting point for the production of a range of different commodity chemicals, such as styrene and terephthalic acid [100–102]. Aromatics are currently produced exclusively from crude oil, *i.e.* by catalytic cracking or reforming of petroleum [100–102], however several methods for producing these from renewable resources are currently being investigated: Lignin, a biopolymer consisting mainly of aromatic subunits, can be deconstructed to the constituent molecules, thus affording a very direct route to a range of aromatic compounds [103]. Another approach is the catalytic fast pyrolysis of biomass using Brønsted acidic zeolites, which directly converts raw biomass into aromatics and olefins [104–111]. Finally, in an approach currently being commercialized by the company GEVO, iso-butanol, which can be obtained by fermentation of carbohydrates, is converted to *p*-xylene through a sequence of reaction steps consisting of dehydration, dimerization, and dehydrocyclization [112].

These approaches however all have significant challenges which remain to be solved: Due to the recalcitrant nature of lignin, harsh conditions are required for the conversion, and the product is a mixture of a wide range of compounds which need to be separated. Similarly, flash pyrolysis suffers from low selectivity towards any particular aromatic compound, and a significant portion of the substrate carbon is lost as coke. The process by GEVO is very interesting, however
it consists of a complex set of reaction steps, and is limited to the production of $p$-xylene. The basic problem faced when attempting to produce fossil platform chemicals from biomass (with lignin deconstruction being a possible exception) is the need for significant changes in the $H/C_{eff}$ of the feedstock, which invariably entails a loss of carbon efficiency as the change is effected either through a disproportionation reaction, as is the case with fermentation, or through the addition of hydrogen, currently produced exclusively by reforming. This issue can be circumvented by identifying chemical analogs, which can replace the function of the petrochemical, while retaining a significant fraction of the oxygen present in the feedstock, e.g. 2,5-furandicarboxylic acid, FDCA, obtained from the oxidation of 5-hydroxymethylfurfural (HMF), which could substitute terephthalic acid (produced from $p$-xylene) in the production of PET plastics. The use of alternate chemicals does however also come with a number of problems, such as the need for significant capital investments in research and equipment to integrate these in the established infrastructure, e.g. there are concerns related to the recycling of mixed PET and FDCA based plastics. Thus, while not ideal in the long term, the production of direct replacements could be preferable in the short term, as ideally no significant changes would be needed in downstream processing.

4.1 A general approach to aromatics

Identifying a synthetic approach for producing a wide range of aromatics with high selectivity from biomass derived substrates is challenging, however a possible method is the dehydrative aromatization of an oxabicyclic adduct. This type of adduct can be prepared by the Diels-Alder cycloaddition of a suitable dienophile to a furanic compound, e.g. the addition of acrolein to 2,5-dimethylfuran (DMF) [113]. Subsequently performing a dehydration and a decarbonylation step yields $p$-xylene, as shown in Scheme 4.1.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{[O]} \quad \text{CH}_2 \quad \text{O} \quad \text{C} \\
\Rightarrow & \quad \text{[O]} \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{[O]} \quad \text{CH}_3 \\
\text{H}_2\text{O} & \quad \text{H}_3\text{C} & \quad \text{H}_3\text{C}
\end{align*}
\]

Scheme 4.1: A reaction scheme for the cycloaddition of acrolein to DMF, followed by a dehydrative aromatization and decarbonylation.

Recently, a significant simplification of this approach was reported by Williams et al., who reacted DMF and ethylene over Brønsted acidic zeolites to yield $p$-
xylene directly, thereby avoiding the need for a decarbonylation step [114]. In addition to eliminating a reaction step, the use of ethylene is preferable as it is less expensive, more readily derived from renewable resources, and improves the carbon efficiency of the process. It is however rather surprising that ethylene can act as an efficient dienophile in a Diels-Alder reaction, as claimed by Williams et al., due to the lack of electron withdrawing substituent groups. Of the investigated catalysts, only Brønsted acidic zeolites were capable of efficiently producing p-xylene; this was attributed to the ability of these materials to activate ethylene through a confinement effect [115]. The framework type of the zeolite was found to be the most important factor in determining the activity of the catalyst, with the highest production rate obtained using zeolite FAU.

### 4.2 Results and discussion

Another very interesting aspect of the report by Williams et al. is that there does not appear to be any inherent reason to limit the choice of substrates to DMF and ethylene; a more general reaction scheme can be constructed, as shown in Scheme 4.2, which at the very least encompass the important BTX compounds. Thus, in the current work it was decided to investigate this type of chemistry for the production of the BTX compounds (see Appendix A.4).

![Scheme 4.2](image)

**Scheme 4.2:** A generalized reaction scheme for the cycloaddition of ethylene to a furanic compound, followed by a dehydrative aromatization.

The production of benzene and toluene requires the use of furan and 2-methylfuran (2-MF) respectively, however as will be described later, these are significantly less reactive than DMF for aromatics production. As the activity of Brønsted acidic zeolites was determined to be insufficient to efficiently catalyze these reactions, a range of acidic materials were investigated to elucidate the effect of the pore structure and the type of acidity present, and to identify more suitable catalysts.
4.2.1 Catalysts for the dehydrative aromatization

Both Lewis and Brønsted acidic materials are capable of catalyzing the dehydrative aromatization of the adduct [116, 117], thus materials of either type were tested for the production of $p$-xylene (results shown in Figure 4.1), however only Brønsted acids were found to be significantly catalytically active; $\gamma$-alumina and TiO$_2$, two common Lewis acidic solids, display only modest selectivity towards $p$-xylene and a very low turn-over-frequency. Thus, although Lewis acids can in principle catalyze the conversion, the rate is much lower than obtained with Brønsted acids; a result which was later corroborated by a theoretical study [118].

![Figure 4.1: Reactivity data for the conversion of DMF and ethylene to p-xylene over acid catalysts: Selectivity (left) and turn-over-frequency (right). The TOF is calculated as the number of p-xylene molecules formed at each Brønsted acid site per second (with the exception of $\gamma$-alumina and TiO$_2$, where the rate is normalized by the amount of Lewis acid sites). All reactions were allowed to proceed to 60% conversion.](image)

In the report by Williams et al. it was asserted that although the formation of the oxabicyclic adduct was an uncatalyzed process, the microporous structure of the catalyst was a crucial parameter as this activated ethylene through a confinement effect [114]. This assertion was based primarily on the fact that a Brønsted acidic amorphous SiO$_2$/Al$_2$O$_3$, which does not posses a microporous structure, displayed no selectivity towards $p$-xylene. Surprisingly, we find that SiO$_2$/Al$_2$O$_3$ display very similar activity and selectivity towards $p$-xylene compared to zeolite FAU. A microporous structure is thus not a requirement for an active catalyst, as clearly demonstrated by the fact that trifluoroacetic acid (TFA), a homogeneous Brønsted acid, display a selectivity comparable to zeolite FAU. The mechanism
of the adduct formation is therefore still very much an open question.

The highest activity and selectivity was obtained using $\text{WO}_x/\text{ZrO}_2$: This is a strongly Brønsted acidic material formed by dispersion of a tungsten-precursor on an amorphous zirconia support; upon calcination the precursor decomposes to tungsten oxide nanoparticles, into which zirconium atoms migrate from the support, thereby forming zirconium-stabilized distorted $\text{WO}_3$ nanoparticles, which are believed to be the cause of the Brønsted acidity [119]. If, as previously claimed, the cycloaddition occurs through a Diels-Alder cycloaddition, the presence of Brønsted acids would be unlikely to catalyze the formation of the adduct. This was confirmed by DFT calculations, performed by Nikbin et al. [118], which also indicated that Lewis acids are capable of activating ethylene, and thus facilitate the cycloaddition. Such a promoting effect was however not observed with a range of $\text{WO}_x/\text{ZrO}_2$ based catalysts [120], as no correlation between the production rate of $p$-xylene and the density of Lewis, nor Brønsted, acid sites was observed. Instead, the maximum activity of the catalyst was found to correlate with the maximum acid strength of the Brønsted acid sites. This would indicate, that either the overall reaction rate is not limited by the adduct formation or that strong Brønsted acids are capable of catalyzing the cycloaddition. Such a catalytic effect could arise if Brønsted acids are capable of activating the diene through a mechanism such as the one depicted in Scheme 4.3, which was not considered in the work by Nikbin et al.

Such a mechanism is speculative, as it is not possible to conclusively determine the cause of the increase in the observed reaction rate from the present data, however it would explain the significantly higher activity observed with $\text{WO}_x/\text{ZrO}_2$.

A further point relates to the stability of the catalyst. The presence of a mesoporous structure, rather than a microporous, is advantageous, as it increases the catalysts resistance towards deactivation due to coke deposition. Figure 4.2 shows the activity obtained with $\text{WO}_x/\text{ZrO}_2$ and zeolite FAU upon consecutive experiments. In the case of zeolite FAU, all activity is lost after the first experiment, due to blocking of the zeolite pores by coke deposits, as confirmed by the fact that the
activity can be restored by calcination. WO_x/ZrO_2 on the other hand, which only posses mesoporosity, does not suffer from a similar loss of activity, and retain the majority of the activity.

![Figure 4.2: Production rate of p-xylene from the reaction between DMF and ethylene over different catalysts. The catalyst was regenerated by washing with iso-propanol after the first use, and by calcination at 650°C after the second.]

### 4.2.2 Effect of furan substituents

A subset of the catalysts were investigated for the production of aromatics from furan and 2-MF. In general the reaction rate decreases significantly as the degree of substitution decreases (see Figure 4.3), with one exception being niobic acid, which somewhat surprisingly displays comparable rates for both p-xylene and toluene production. For all catalysts the rate of benzene production is very low.

![Figure 4.3: Production rate of aromatics (left), and cyclohexenone compounds (right) from different furanic substrates using different acidic catalysts.]

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The lower reaction rate is in agreement with previous results, which have shown that the lack of methyl substituents decrease the rate of dehydration of oxabicyclic compounds [117]. As is seen in Figure 4.3, the lower rate of dehydration of the adduct is accompanied by an increased production of cyclohexenone type compounds in the case of 2-MF. These compounds are likely formed by the isomerization of the adduct, and the ratio between dehydration and isomerization of the adduct is therefore an important parameter in deciding the ultimate yield of the desired aromatic. As the degree of substitution decreases, this ratio clearly shifts towards isomerization. Using γ-alumina as catalyst, the isomerization is heavily favored regardless of the substrate, which could indicate that the isomerization is catalyzed by Lewis acids, which would explain the lack of aromatics production over these types of materials.

In addition to the lower dehydration rate, byproduct formation directly from the furanic compound is more of a challenge with these substrates: One of the primary side reactions is the opening of the furanic ring to form a dicarbonyl, which can subsequently oligomerize; although the ring opening occurs more readily for DMF [120] the formed diketone is reasonably stable (≈ 5% yield at intermediate conversion) and can recyclize (primarily to DMF, but also to 3-methyl-2-cyclopentenone). The dicarboxyls formed from furan and 2-MF on the other hand quickly oligomerize [120], thereby lowering the overall yield of aromatics. Additionally, furan can react with itself in a Diels-Alder cycloaddition forming benzofuran, and some alkylation of the formed aromatic is observed. Based on the observed byproducts, the reaction network shown in Scheme 4.4 (for the conversion of DMF) is proposed. Due to the increased byproduct formation, the overall yield of benzene and toluene obtained by the present method is significantly reduced compared to that realized in p-xylene production, as shown in Figure 4.4, however it is demonstrated that appreciable yields can be obtained.

![Figure 4.4: Ultimate yield of aromatics obtained using WO_x/ZrO_2 as catalyst. (Reaction conditions: Temperature = 250 °C, P_ethylene = 20 bar, m_diene = 2.0 g, m_catalyst = 0.15 g, m_hexadecane = 18.0 g)](image-url)
Aromatics Production by Cycloaddition Reactions

4.3 Summary and outlook

Aromatics constitute an important class of compounds derived from crude oil, for which there currently does not exist a well-established and efficient route from renewable resources. Although processes for preparing chemicals which can substitute aromatics carries great promise, the introduction of these in the established infrastructure will not be an easy feat, and will require significant changes to the current value-chain; a process which will likely be slow. Thus, the identification of processes for preparing these fossil platform chemicals from renewable resources has the potential to greatly accelerate the replacement of crude oil with more sustainable alternatives.

The preparation of aromatics by dehydrative aromatization of oxabicyclic adduct formed by cycloaddition of ethylene to furanic compounds is an interesting path to this end, as both ethylene and furanic compounds can readily be obtained from carbohydrates [36, 78]. In the current work, it was demonstrated that the important BTX compounds could be produced in significant yields by the reaction of ethylene and a suitable furanic compound over WO$_x$/ZrO$_2$. The ultimate yield was however highly dependent on the degree of substitution of the substrate, and identification of reaction conditions which favor the desired reaction path is therefore required for this to become an industrially feasible production method. In particular the isomerization of the intermediate adduct to cyclohexenone type compounds was a significant cause of lowered selectivity, however the use of strong Brønsted acids was seen to favor the desired reaction path. Thus improvements in catalyst design is required; a development which requires an improved
understanding of the reaction mechanisms of both the dehydration to aromatics as well as the range of side reactions which are observed.
Selective High Temperature Thermolysis

The current paradigm for the conversion of biomass derived substrates into suitable platform chemicals relies heavily on liquid (possibly solid/liquid) phase reactions. This is mainly a consequence of the nature of typical biomass derived substrates, such as carbohydrates, lignin, and glycerol, which cannot easily be brought into the gas phase. Due to the high density of functional groups present, these compounds will invariably cross-react and/or decompose before vaporization, forming a complex mixture of reaction products. To overcome this problem, the feedstock is typically exposed to an initial liquid phase transformation to reduce the degree of functionalization, e.g. deoxygenation. The formed intermediates can then be further converted into the desired end products by a range of different approaches, such as gas phase conversion. The need to work in the liquid phase does however limit the temperature regime in which it is feasible to perform the desired transformation, due to the costs associated with high pressure reactors.

High temperature conversion of carbohydrates is basically limited to two processes; gasification and pyrolysis. Gasification is a high temperature (700-900°C) treatment of the feedstock, which affords the complete decomposition of the substrate to synthesis gas, which can be used as a starting point for the construction of desired target molecules [121]. Pyrolysis relies on heating the feedstock to intermediate temperatures (300-600°C), typically at high heating rates, whereby a partial deconstruction of the biomass occurs, forming a wide range of molecules, which is condensed as “bio-oil”; a supposed biomass analog to crude oil [122,
The characteristics of this bio-oil are however quite different as it retains the majority of the oxygen content of the parent feedstock; the removal of which is a significant challenge [123]. The overarching advantage of these thermochemical processes is their tolerance towards the type of feedstock converted, however this advantage is gained through a complete loss of the characteristics of the substrate. These approaches thus fail to capitalize on the inherent functionality of the substrate.

5.1 Glycolaldehyde

One of the products formed from biomass under pyrolysis conditions is glycolaldehyde (hydroxyacetalddehyde). This is the smallest compound containing both a hydroxy and a carbonyl group, thus making it structurally identical to a sugar (although, by definition, it is not). It can also be produced by dehydrogenation of ethylene glycol [124, 125], by hydroformylation of formaldehyde [126], or through retro-aldol condensation of carbohydrates in super-critical water [127]. Current world production is negligible as it is only utilized in a few niche applications, primarily as a food browning agent [128]. This can be attributed to the high cost of the compound as several commodity scale chemicals can conceivably be produced from glycolaldehyde (as shown in Scheme 5.1), such as the hydrogenation to ethylene glycol or ethanol or the isomerization to acetic acid. Glycolaldehyde is thus a potential platform chemical, however the identification of less costly production methods is required to realize this potential.

As stated above, glycolaldehyde is a common product observed from flash pyrolysis of biomass, however it typically constitutes only a relatively small fraction of the products (5-13%) [128, 133]. Furthermore, due to the difficulty in separating it from pyrolysis mixtures [128, 134] this production method is not economically feasible. If the selectivity towards glycolaldehyde could be increased significantly however, this could prove to be a simple method for large scale production, which would allow for the production of commodity chemicals starting from this compound.
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Scheme 5.1: Glycolaldehyde as a platform chemical. Potential transformation include hydrogenation to ethylene glycol [126, 129, 130], conversion to lactic acid [69, 131], isomerization to acetic acid, oxidation to oxalic acid, hydrogenation/dehydration to ethanol and ethylene, and reforming to synthesis gas [132].

5.2 Pseudo gas phase carbohydrates

If sufficiently high heating rates can be achieved it is possible to obtain selective conversion of carbohydrates under pyrolysis-like conditions. This approach has been successfully applied in small scale, using a number of different reactor configurations, to investigate the chemistry of glucose at high temperatures [105, 135], however these methods cannot be translated to industrial scale. A more scalable solution is the use of fluidized bed reactors, which are used extensively when minimization of temperature gradients and high heating rates are paramount, e.g. the FCC process and for Fischer-Tropsch synthesis [136]. Such reactor systems can be used to achieve flash pyrolysis conditions for biomass conversion by introducing the feedstock as small particles (typically in the μm to mm range), however even though the particle exterior may be rapidly heated to the desired temperature, heat conduction through the particle can be markedly slower, leading to a lower actual heating rate [137]. This problem can obviously be avoided by introducing the substrate as even smaller particles, however mechanical size reduction is an inefficient method for achieving this [138]. Instead, smaller particles can be achieved by introducing the substrate as a solution which is injected directly into the bed through an atomization nozzle. Immediately upon entering the reactor, the liquid wets the bed particles, forming agglomerates, which are transported to the interior of the bed, where they are broken up due to the impact of other particles and the evaporation of the liquid [139]. In this manner very high heating
rates are achieved together with a very fine dispersion of the substrate in the re-
actor. Thus, this system can be viewed as approaching gas phase carbohydrates,
which is a very intriguing possibility.

5.3 Results and discussion

In this work, a fluidized bed reactor system, as shown in Figure 5.1, was operated
under flash pyrolysis conditions to investigate the thermolysis of carbohydrates.
An aqueous solution of glucose was injected directly into a bed of α-christobalite,
which was kept at 500-600 °C, along with a nitrogen flow sufficient to disperse the
feed and fluidize the bed (typical operating conditions are given in Section 5.5).
Under these conditions, the fluidization is estimated to be in the bubbling regime,

Figure 5.1: Schematic depiction of the fluidized bed setup used for the thermolytic conversion of
carbohydrates.

approaching turbulent fluidization [136]. Assuming bubbling fluidization, the
residence time is approx. 50 ms in the dense bed and 1.5 s in the freeboard
[140]. The calculation of residence time is however based on an assumption of
an isothermal bed; this is clearly not the case, as the feed and fluidization gas
are injected at room temperature. The gas velocity will increase through the bed
due to thermal expansion of gases and vaporization of water, and the residence
time will therefore be dependent on the temperature gradient. Furthermore, as
the substrate molecules wet the bed particles, these will be mixed along with
the particles and therefore most likely experience a residence time distribution.
The exact determination of residence time is thus not possible with the current
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experimental setup, except to say that a short residence time, with concurrent very high heating rate, is obtained.

The temperature profile in the bed during a typical experiment is given in Figure 5.2, as well as the carbon and mass balance obtained from the liquid condensate. The system reaches steady state within 1.5hr, at which point approx. 80% of the substrate carbon can be collected in the liquid condensate. Coke deposition on the catalyst is insignificant, accounting for no more than 5% of the carbon, and typically significantly less. Under these operating conditions, the system can maintain steady state operation for at least 20 hr if the feed is sufficiently dispersed upon injection and particle attrition is insignificant; up to 96 hr has been achieved without any changes to the product distribution. Upon extended time on stream the bed experiences a sudden defluidization, likely caused by coke build-up and particle agglomeration, at which point the required heating rate of the substrate can no longer be achieved.

![Figure 5.2: The mass and carbon balance obtained from the liquid condensate during the thermolytic conversion of glucose in an inert bed. (Reaction conditions: Feed = 10 wt.% glucose (aq), feed flow = 0.5 ml/min, \(N_2\) flow = 3.5 Nl/min, bed volume = 10.0 ml, bed material = \(\alpha\)-cristobalite).](image)

The composition of the condensate (shown in Figure 5.3), is dominated by a range of \(C_1\)- to \(C_3\)-oxygenates. These are the only compounds detected in significant amounts in the condensate by either GC og HPLC analysis. In all experiments, complete conversion of the substrate was observed. The primary product was glycolaldehyde, which under optimal reaction conditions could be collected in yields of approx. 60% based on carbon content.
5.3.1 Thermal retro-aldol condensation

When converting mono- instead of polysaccharides under pyrolysis-like conditions the production of glycolaldehyde is significantly favored compared to traditional pyrolysis [141–143]. Glycolaldehyde is believed to be formed through consecutive retro-aldol condensations, with erythrose as an intermediate, as shown in Scheme 5.2 [142]. An alternative reaction mechanism has been suggested, instead relying on a dehydration of the pyranose form of the hexose, followed by a retro-Diels-Alder reaction [133]. Although such a mechanism may play a role in raw biomass pyrolysis, where it would allow for the formation of glycolaldehyde directly from cellulose, it does not seem likely in this case, as it would limit the yield to 33% and should not be hindered by the use of disaccharides, both of which are contrary to the present results. The C$_1$- and C$_3$-oxygenates are formed due to isomerization of glucose to fructose (and possibly erythrose-erythrulose isomerization) before fragmentation can occur. Figure 5.4 shows the product distribution starting from either glucose or fructose. Changing the substrate to a ketose significantly increases the yield of pyruvaldehyde (formed by retro-aldol
Selective High Temperature Thermolysis

condensation and dehydration) and formaldehyde (from consecutive retro-aldol condensations with glyceraldehyde as intermediate), as expected. The overall yield of condensable products does not change significantly, as the increase in C$_1$- and C$_3$-compounds is at the expense of glycolaldehyde. The possibility of producing C$_3$-compounds from ketoses using the present method is also an interesting possibility, as for instance pyruvaldehyde is an intermediate in the catalytic production of lactic acid [56] and can potentially be hydrogenated to propylene glycol.

![Normalized product distribution from either an aldose or a ketose. The black bar is the total carbon yield in the condensate.](image)

**Figure 5.4:** Normalized product distribution from either an aldose or a ketose. The black bar is the total carbon yield in the condensate.

Although the thermolytic conversion of carbohydrates, as described above, occurs under pyrolysis-like conditions, indeed many of the same products are observed, and may resemble pyrolysis on a conceptual level, the chemistry is quite different. Pyrolysis of biomass occurs by a comparatively slow depolymerization of the cellulose and hemicellulose components forming a range of products, primarily anhydrosugars, which then either vaporize or react further, e.g. through dehydration to furanic compounds or fragmentation to form volatile products [144]. The wide range of substrates and intermediates present have different volatilization rates, making it impossible to ensure complete volatilization while avoiding secondary reactions. Conversely, the thermolytic conversion of carbohydrates is a selective conversion of a specific substrate molecule, and thus resemble typical liquid phase conversions, such as the Lewis acid catalyzed conversion of sugars to lactic acid, as described in Chapter 3, to a much higher degree.

The degradation of glycolaldehyde can occur by a number of pathways, thus a low residence time in the bed is paramount. The most important degradation reactions are the dehydration to ketene [145] (as will be described in more de-
Catalytic Conversion of Carbohydrates

tail in section 5.3.3) and oligomerization reactions of glycolaldehyde (and other intermediates/products). Ketene can decompose at high temperatures to hydrocarbons, CO and coke, or rehydrate to acetic acid, as shown in equations 5.1-5.4 [146]:

\[
\begin{align*}
2\text{CH}_2\text{CO} & \rightarrow \text{CH}_4 + \text{C} + 2\text{CO} \quad (5.1) \\
2\text{CH}_2\text{CO} & \rightarrow \text{C}_2\text{H}_4 + 2\text{CO} \quad (5.2) \\
\text{CH}_2\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{COOH} \quad (5.3) \\
\text{CH}_2\text{CO} + \text{CH}_3\text{COOH} & \rightarrow (\text{C}_3\text{CO})_2\text{O} \quad (5.4)
\end{align*}
\]

Oligomerization reactions are a significant loss-pathway when the residence time is increased (>150 ms), forming high-boiling tar like compounds, however these are not observed in appreciable quantities at typical reaction conditions.

In addition to the range of fragmentation reactions occurring, some changes in the oxidation state of the different products are observed, namely dehydrogenation of glycolaldehyde to glyoxal and hydrogenation of pyruvaldehyde to acetol. Based on the observed products the reaction network depicted in Scheme 5.3 is proposed.

### 5.3.2 Influence of the substrate

One of the major benefits of using a thermochemical process to effect the conversion of carbohydrates, as compared to biological or enzymatic processes, is the greater range of substrates which can be efficiently utilized. The composition of the condensate, as well as the yield of condensable products, are given in Figure 5.5 for a range of different substrates. The yield of liquid products does not appear to be dependent on the type of monosaccharide, irrespective of the length of the carbon chain, although the composition varies depending on the structure of the carbohydrate. One surprising observation is the high yield of glycolaldehyde obtained from xylose; despite the fact that the stoichiometric yield of glycolaldehyde is only 80% compared to glucose, the obtained yield is virtually identical. Xylose is an especially interesting substrate, since it is one of the major components of hemicellulose; as hemicellulose is more easily hydrolyzed than cellulose, due to its branched structure [144, 147], it is a very interesting substrate for the so-called 2nd generation bio-refinery, a potential which is currently
hampered by the fact that xylose cannot be converted by traditional fermentation processes [148].

Not surprisingly, disaccharides are more difficult to convert, as an initial hydrolysis step is required. The ability of the present method to convert oligosaccharides is an important parameter, as these will invariably be present in hydrolysates from lignocellulosic biomass. Significant differences are observed with respect to the ease with which different disaccharides are converted: Although both sucrose and maltose can be converted with similar yields of condensable species (with differences in the composition reflecting the difference in the constituent monosaccharides), the conversion of lactose proved difficult. In all attempts to convert lactose, defluidization due to coke formation occurred before steady state could be reached. A possible explanation for the difference could be the difference in the glycosidic bond, which differ between the investigated disaccharides. This would indicate that the $\beta-1 \rightarrow 4$ bond of lactose is more difficult to hydrolyze under these conditions; as the glucose chain in cellulose is also bound together by $\beta-1 \rightarrow 4$ glycosidic bonds [144], this would mean that careful depolymerization of cellulose is required before thermochemical conversion.

**Scheme 5.3:** Reaction network for the thermal fragmentation of hexose sugars to primarily glyco-laldehyde. Products and intermediates which have not been detected, or only tentatively identified, are shown in red.
Catalytic Conversion of Carbohydrates

Figure 5.5: Normalized product distribution from different substrates. The black bar is the total carbon yield in the condensate.

The necessity of a carbonyl moiety in the substrate is exemplified by the conversion of sorbitol. As sorbitol does not contain the carbonyl bond required for the retro-aldol condensation to occur, it is significantly more difficult to convert. Indeed, this is also what is observed: Significant amounts of unconverted sorbitol is present in the liquid condensate, accounting for more than 40% of the condensed species, while a significant amount of coke and unconverted sorbitol quickly deposits on the bed particles giving rise to a low liquid yield and a rapid defluidization of the bed (after approx. 6 hr on stream).

5.3.3 Effect of the bed material

Retro-aldol condensations are catalyzed by both alkali and acids [149], and the inclusion of this type of functionality in the bed material is therefore potentially a method for improving the yield of desired products or allowing for more desirable operating parameters. The bed material is however subject to strict requirement in a fluidized bed, specifically in relation to particle density, to avoid elutriation or defluidization, and mechanical strength, to minimize attrition. The active material therefore needs to be stabilized with a suitable carrier/support material, such as silica. Although silica is typically considered an inert material, the presence of hydroxyls impart a weak Brønsted acidity to the material [89], which can influence the yield of desired products. Figure 5.6 shows the composition of the product mixture using either silica gel (high surface area) or α-christobalite (low
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Figure 5.6: Normalized product distribution from glucose thermolysis over either a low surface area or a high surface area silica. The black bar is the total carbon yield in the condensate.

surface area). With high surface area silica, the yield of condensable products is significantly reduced; this is exclusively due to a lower yield of glycolaldehyde (in fact the yield of both C\textsubscript{1} and C\textsubscript{3}-compounds slightly increase). Glycolaldehyde is known to dehydrate to ketene at temperatures as low as 200 °C [145], although significantly longer reaction times are necessary than in the present case. The dehydration of the isomer, acetic acid, has however been shown to be catalyzed by hydroxyls under similar conditions [146], and thus it is reasonable to assume that a similar catalytic effect can occur for the much less thermodynamically stable glycolaldehyde. Increased ketene formation would also lead to increased acetic acid production, through rehydration, as is experimentally observed.

As the decrease in the yield of liquid product is mainly due to an increase in non-condensable species, analysis of the gas phase is required to gain an improved understanding of the effect of the bed material, however quantitative analysis of the non-condensable products is severely hampered by the high volumetric flow rate of N\textsubscript{2} required for sufficient dispersion of the feed and fluidization of the bed, which entails a low concentration of product species in the gas phase. Semi-quantitative determination of gas species was obtained using a mass spectrometer (a subset of these results are shown in Figure 5.7): Upon introduction of glucose in a bed composed of α-cristobalite, an increase of the intensity of m/z = 2, 42, 44 and 58 is observed; these ratios correspond to hydrogen, ketene, carbon dioxide/acetaldehyde, and glyoxal/acetone, respectively. Performing a similar experiment with a bed composed of silica gel, a significantly increased concentration of the last three signals are observed (as shown in Figure 5.7). This increase is likely related to increased dehydration activity of the bed material, which increases the
amount of ketene, acetaldehyde and acetone. Decomposition of ketene to carbon monoxide, followed by the water gas shift reaction, would explain the increased carbon dioxide production. Unfortunately, the carbon monoxide concentration could not be measured directly as the m/z ratio is identical to that of N₂.

![Graph showing MS signal intensity over time for compounds with m/z = 42, 44, and 58](image)

**Figure 5.7**: Intensity of the MS signal from compounds having a mass corresponding to (from the top) ketene, acetaldehyde/CO₂, and glyoxal/acetone. The signals have been normalized to the signal of N₂ and averaged over 1 min to minimize noise.

To further elucidate the effect of silanols on the decomposition of glycolaldehyde, a series of silicas with different concentrations of hydroxyls were prepared by varying degrees of calcination; the obtained yield of glycolaldehyde with these are shown in Figure 5.8. With silica gel, a very low initial yield of glycolaldehyde is obtained, however upon extended time-on-stream the yield increases steadily. In addition to the effect of Brønsted acidity imparted by hydroxyls, the porosity of the bed material can influence the observed yield, as this causes a slower evaporation of the liquid and an increased residence time in the dense bed: For a porous bed material, upon wetting the particles, the liquid absorbs into the pores, causing a slower evaporation of the liquid as pore diffusion will limit the evaporation rate [139]. Furthermore, the vaporized fragmentation products, i.e. glycolaldehyde, will need to diffuse out of the bed particles, and may adsorb on the particle
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surface, which will entail a longer residence time compared to the non-porous bed [139]. The combined effect of slower evaporation and longer residence time could explain the decrease in the observed yield of glycolaldehyde. In either case, due to increased dehydration activity, leading to increased ketene production, or increased residence time, leading to increased oligomerization, the end results will be an increase in the production rate of coke, which will deposit in the pore system and hinder access, thus improving the yield. Surprisingly, even small amount of hydroxyls/porosity significantly lowers the yield: The physiochemical characterization of the bed materials are given in Table 5.1; calcination at 500 °C reduces both the porosity of the materials and the volumetric density of silanols, however this does not increase the initial yield, as seen in Figure 5.8. Instead the calcination procedure causes the yield to increases significantly faster with time-on-stream. Calcination at 1000 °C leads to partial crystallization of the material and almost complete loss of pore volume/surface hydroxyls, and the process reaches steady state within 1.5 hr, as observed with α-cristobalite.

![Figure 5.8: Yield of glycolaldehyde as a function of time-on-stream with different silica bed materials.](image)

**Table 5.1: Results from the physiochemical characterization of silica materials.**

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{calc.}}$ [°C]</th>
<th>$A_{BET}$ [m$^2$/g]</th>
<th>$V_{\text{pore}}$ [ml/g]</th>
<th>$\rho_{\text{particle}}$ [g/ml]</th>
<th>$C_{\text{silanol}}$ [M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica gel</td>
<td>-</td>
<td>517</td>
<td>0.68</td>
<td>0.87</td>
<td>3.60</td>
</tr>
<tr>
<td>Silica gel</td>
<td>500</td>
<td>499</td>
<td>0.51</td>
<td>1.00</td>
<td>2.01</td>
</tr>
<tr>
<td>Silica gel</td>
<td>1000</td>
<td>4</td>
<td>0.01</td>
<td>2.17</td>
<td>0.20</td>
</tr>
<tr>
<td>α-cristobalite</td>
<td>-</td>
<td>4</td>
<td>0.01</td>
<td>1.94</td>
<td>0.00</td>
</tr>
</tbody>
</table>

a. Determined by N$_2$ sorption.
b. Determined by Hg porosimetry.
c. Determined by a combination of TGA and Hg porosimetry.

The fact that the bed material needs to be calcined at 1000 °C to avoid the cat-
Catalytic conversion of carbohydrates due to silanols severely limits the range of materials which can be employed as potential catalysts for the production of glycolaldehyde; the focus was therefore on using acidic and basic oxides. The bed materials were prepared by mixing colloids of the desired oxide with colloidal silica, evaporating to dryness, and calcining the material at 1000 °C. To prepare BaO/Silica an aqueous solution of BaNO₃ was used. SiC did not require stabilization with silica. The obtained selectivity and yield of condensable species are given in Figure 5.9. With the exception of CeO₂ all tested materials decrease the yield of condensable products, mainly due to a decrease in the yield of glycolaldehyde. The acid/base properties of the materials tested are summarized in Table 5.2; these are tentatively assigned by Busca [89] based on FTIR probe molecule studies and activity tests. As the surface properties of these materials are highly dependent on pretreatment and in situ conditions, care should be taken when attempting to rationalize the observed catalytic results based on these assignments. Furthermore, even though the material loading is identical in each case, the number of exposed acid/base sites may vary, which will also influence the obtained results.

![Figure 5.9](image-url)

**Figure 5.9:** Normalized product distribution obtained using different bed materials. The black bar is the total carbon yield in the condensate.

Nevertheless, the present results indicate that the formation of glycolaldehyde is not favored by any of the investigated materials. Glycolaldehyde is formed as the initial fragmentation product, thus to improve the yield a catalyst needs to favor the fragmentation over the isomerization. As the Lewis acid catalyzed reaction mechanisms of these two reactions are very similar, identifying a catalytic material which significantly favor the fragmentation may prove difficult. Furthermore, it is imperative that the catalyst does not unduly favor the further degradation of glycolaldehyde, such as by dehydration to ketene; a conditions which does not
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Table 5.2: Assignment of acid/base properties of binary oxides [89].

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Acidity type</th>
<th>Acid strength</th>
<th>Basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$_2$O$_5$</td>
<td>Brønsted/Lewis</td>
<td>Medium-strong</td>
<td>None</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Brønsted</td>
<td>Medium-weak</td>
<td>None</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Lewis</td>
<td>Medium</td>
<td>Medium-weak</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Lewis</td>
<td>Medium-weak</td>
<td>Medium-strong</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>Lewis</td>
<td>Medium-weak</td>
<td>Medium-strong</td>
</tr>
<tr>
<td>BaO</td>
<td>Lewis</td>
<td>Medium-very weak</td>
<td>Strong-very strong</td>
</tr>
</tbody>
</table>

appear fulfilled for materials with strong acid/base properties. Thus, although the identification of catalytic material, which can lead to improved yields, should not be completely discounted, the similarity in the reaction mechanisms leading to byproducts indicate that a more sensible approach could be the identification of more suitable reaction parameters, such as increased space-time velocity or changes to the reaction temperature, to favor the fragmentation reaction relative to the isomerization and degradation reactions. One surprising feature is the behavior of SiC; this is considered an inert material, and if the fragmentation is purely thermal one would expect the behavior to be very similar to that observed over $\alpha$-cristobalite. Although the observed yield is indeed very similar the resistance of the material towards defluidization caused by coking is significantly lower. The cause of this difference has not been identified, but it could be that small amounts of hydroxyls are beneficial in catalyzing the fragmentation, and thus avoiding coke formation, while not overly favoring the decomposition of glycolaldehyde.

5.4 Summary and outlook

High temperature, gas phase conversions are ubiquitous in the petrochemical refinery. This is partly a consequence of the nature of the feedstock, as hydrocarbons are thermally stable molecules that require relatively high temperatures to effect conversion, but also due to the fact that gas phase processes has a number of desired characteristics, namely high volumetric production rate and simple reactor design. The translation of these processes to the renewable chemical industry is difficult, and high temperature conversion of biomass derived substrates has therefore typically been limited either to downstream processes, or non-selective
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conversion.

The possibility of producing glycolaldehyde with high selectivity directly from any of the most abundant carbohydrates is therefore a very interesting possibility; even more so since the process follows many of the principles of green chemistry: Starting from renewable substrates, without using any precious or hazardous substances, and without the use of stoichiometric reagents, the substrate is converted in a reaction which has an atom economy of 100%. The process does however stumble on one point, as heating the feed solution requires a significant energy input, thus careful heat integration with other processes is required to reduce the impact of this shortcoming. A simple method for producing glycolaldehyde would however open up for its use as a starting point in the production of a wide range of commodity chemicals currently produced from fossil resources, such as acetic acid and ethylene glycol.

The identification of a suitable catalytic bed material could help in improving the selectivity of the process and allow for more desirable reaction parameters, however the advantages of performing the process with an inexpensive and abundantly available bed material, such as silica, should not be discounted. In addition to the direct economical benefits, the lack of specific active sites also means that deactivation from impurities present in biomass substrates, such as salts, are unlikely to be a significant problem. A further understanding of the effect of the bed material on the important reaction taking place in this process, namely fragmentation, isomerization, and degradation, is however needed as this will help in identifying the way forward for improved reaction design. This will in particular require a better determination of the distribution of gas phase products. Other important parameters which require investigation are the effect of using feedstocks that more closely resemble those industrially available. Finally, the chemistry of the product, glycolaldehyde, has up until now mainly been investigated for academic reasons as few practical applications existed outside of a few niche areas. If glycolaldehyde can be produced inexpensively by high temperature thermolysis we need to figure how to best use it.
5.5 Experimental

The thermolytic conversion of carbohydrates was investigated in a fluidized bed setup. The setup, depicted in Figure 5.1 on page 44, consists of a stainless steel reactor (i.d.: 22 mm, length: 80 cm) fitted with an air atomizing nozzle (Spraying Systems Co.), capable of delivering the liquid feed as a fine mist into the reactor (droplet size: <10 µm). The reaction temperature was monitored with a thermocouple extending from the top of the reactor into the bed. The top of the reactor was fitted with a disengager to prevent elutriation of the bed particles. Immediately after the outlet, the gas stream was directed through a condenser kept at 1°C to collect the liquid product.

In a typical experiment, the reactor was charged with 10 ml of bed material, having a particle size from 90 to 150 µm. A nitrogen flow of 3.5 Nl/min was used to fluidize the bed, while the reactor temperature was raised to the desired reaction temperature (typically 550°C). When the reactor reached the desired temperature water was pumped to the nozzle, using a tube pump, at a flow rate 0.5 ml/min and injected into the bed. The liquid flow was maintained for at least 20 min to obtain a stable temperature in the bed.

The experiment was started by changing the liquid to a 10 wt.% aqueous solution of the substrate, at which point the time was set as T₀. The dead time from the feed flask to the nozzle was approx. 20 min. Collection of the liquid product was started at T=30 min. The condensed liquid was collected over the entirety of the experiment to calculate mass balances. Each experiment was run for at least 6 hr.

Liquid products were quantified by HPLC analysis (Agilent, 1200 Series). The analytes were separated on a BioRad Aminex HPX-87H column operating at 65°C. The eluent was 0.005 M aqueous H₂SO₄, at a flow rate of 0.6 ml/min. The analytes were quantified using a RI detector against standard samples. Products were identified either by matching retention time with a known standard, or if possible by GC-MS analysis on an Agilent Technologies 6890 Plus series gas chromatograph with an Agilent Technologies 5973A series mass selective detector. Analysis of the gas phase products was performed by directing part of the gas stream, after the condenser, into a mass spectrometer (IPI, GAM 200 Multi Component Gas Analyser).

Determination of crystal structure was done by powder X-ray diffraction on a Phillips X’Pert diffractometer using Cu-Kα radiation. Pore volume and surface area measurements was performed by multipoint N₂ adsorption/desorption on a Quantachrome Autosorb automatic surface area and pore size analyser. The surface area was calculated using the BET method. The computer program Autosorb 3 was used for the data treatment. The dehydroxylation behavior of silica was measured on a Mettler TGA/DSC 1; the sample was dehydrated at 150°C for 60 min in a flow of 20% O₂, 26% He and 54% Ar at 50 ml/min; this gas flow was maintained for the duration of the analysis. The temperature was low-
ered to 40 °C and then increased to 1500 °C at 5 °C/min, while monitoring the weight of the sample. The density and porosity of the samples were determined by Hg porosimetry on a Micromeritics Autopore IV 9500Hg por.
One of the great challenges of the chemistry community in the 21st century will be the complete shift away from a chemical industry based on fossil derived feedstocks to one based on renewable resources. As these new substrates do not share many characteristics with the current, this will require a complete reinvention of the chemical industry; a process which will likely take several decades. This transformation should however be taken as an opportunity to create a more sustainable industry.

The first steps towards this end are already being taken, through the identification of renewable chemicals which can replace the current petrochemical platform chemicals. In the current work methods for producing two such potential platform chemicals, lactic acid and glycolaldehyde, have been investigated. Lactic acid is an established biomass-derived chemical, however the identification of more efficient production methods could allow for a much more widespread use. In this regard the stannosilicate catalyzed inorganic “fermentation” of carbohydrates is an interesting possibility. Much is however still unknown with respect to the active site in these materials, thus this knowledge needs to be developed to guide catalyst design. With respect to glycolaldehyde, very few reports exist detailing the chemistry, and methods for the preparation, of this compound. This is somewhat surprising as glycolaldehyde could have significant potential as a starting point for the production of a range of commodity chemicals. The lack of efficient production methods is most likely one of the factors, which have limited the interest in glycolaldehyde, a barrier which may be removed with further development
of the thermolytic production of glycolaldehyde. The knowledge of the chemistry of carbohydrates at temperatures of several hundred degrees is however limited and needs to be developed. The challenges faced when attempting to introduce biomass derived chemicals in an established industry goes beyond simply finding ways of producing alternative chemicals, as also institutional inertia needs to be overcome; a shortcut to replacing petroleum can therefore be the synthesis of the same chemicals as are currently employed, but from biomass substrates, such as the synthesis of aromatics by cycloaddition of ethylene to furans as described in this work. The lower reactivity of less substituted furans limits the yield which can be obtained with current catalysts, and this problem needs to be addressed, if this is to become a viable production method.

In any case, despite the fact that most people would probably agree that moving away from a dependence on oil would be desirable, if the reasons for doing so is primarily based on morality or effects which will only manifest in a potentially distant future, these can quickly be overshadowed by more immediate concerns, e.g. an economic crisis. Fortunately, we do not need to rely on such ephemeral reasons; we should focus on replacing oil with more sustainable solutions now, because it makes sense now, from a financial, a strategic, and an opportunity standpoint. Furthermore, we should focus on doing this in a sustainable way, because of the exact same reasons.
References


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References


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References


Catalytic Conversion of Carbohydrates


Publications

Papers included in this thesis


Other publications

Zeolite-catalyzed biomass conversion to fuels and chemicals

Esben Taarning,*a Christian M. Osmundsen,ab Xiaobo Yang,a Bodil Voss,a Simon I. Andersena and Claus H. Christensenb

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Heterogeneous catalysts have been a central element in the efficient conversion of fossil resources to fuels and chemicals, but their role in biomass utilization is more ambiguous. Zeolites constitute a promising class of heterogeneous catalysts and developments in recent years have demonstrated their potential to find broad use in the conversion of biomass. In this perspective we review and discuss the developments that have taken place in the field of biomass conversion using zeolites. Emphasis is put on the conversion of lignocellulosic material to fuels using conventional zeolites as well as conversion of sugars using Lewis acidic zeolites to produce useful chemicals.

Introduction

Zeolites are crystalline materials composed of SiO₄ and [AlO₄] tetrahedra. The negative charge of [AlO₄] tetrahedra is compensated by a cation, maintaining the overall electroneutrality of the zeolite. Charge compensation with H⁺ renders the zeolite highly acidic, which is useful for many catalytic applications. An important feature of zeolites is their microporosity. Many zeolites contain a multidimensional microporous system which has similar dimensions as small molecules. This microporous system allows small reactant molecules to diffuse into the zeolite crystal, thereby allowing access to internal acid sites. The microporous system also adds another important feature to the zeolites, namely shape-selectivity. The size-restraints of the micropore channels can in some cases restrict the formation of large and often unwanted products. This is the case for the isomerisation of xylene mixtures, where o- and p-xylene are formed predominantly over the more bulky and unwanted m-xylene isomer.¹ Alkylation of benzene with ethylene is another important industrial example.² However, most importantly, zeolites are some of the most widely used heterogeneous catalysts for the valorization of hydrocarbon streams in refineries and petrochemical facilities.³ The most important example is the use of zeolite catalysts in fluid catalytic cracking (FCC), which supplies about 45% of the global gasoline pool by the cracking of larger hydrocarbon into the gasoline range.⁴ Zeolites also find use as catalysts for the conversion of oxygen containing compounds, and there are many examples of zeolite catalyzed acylations, esterifications and dehydrations.⁵ Of particular importance is the zeolite catalyzed conversion of oxygenates to hydrocarbons. Most known is the conversion of methanol to gasoline (MTG) but many other oxygenates, including ethanol and pyrolysis oil, can also be converted into hydrocarbons that can be used as gasoline.

Biomass has in the past decade become an increasingly important resource for the production of transportation fuels and chemicals.⁶ This utilization is primarily based on biochemical transformations, such as fermentation to produce ethanol from sugars. Biomass conversion based on zeolite catalysis is an alternative approach which could find broad application, especially for the conversion of lignocellulose to transportation fuels and sugars to chemicals. This perspective describes recent developments in this area.

Lignocellulose

Lignocellulosic biomass is the most abundant bio-resource available and consists of three major components: cellulose, hemicellulose and lignin (Table 1). Cellulose is a linear crystalline polymer composed of glucose units. Due to its high crystallinity, cellulose is very difficult to hydrolyse to glucose. Hemihcellulose is different from cellulose since it is a branched amorphous polymer that is made of different pentose and hexose units. Due to the branching and its amorphous nature hemicellulose is easier to hydrolyse into monosaccharides than cellulose. Lignin is the largest

Broader context

We review the use of zeolites for the conversion of biomass to fuels and chemicals. Zeolites are crystalline microporous alumino-silicate materials that are useful in many applications ranging from use as detergents, ion exchange applications, adsorbents and catalysis. Zeolite catalysis has in particular found use in the upgrade of petroleum to high-quality fuels. However, since biomass is a very different feedstock from petroleum, new approaches are needed if zeolites are to play the same role in the conversion of biomass. In recent years, biomass conversion has attracted tremendous focus and zeolites could play a role in a thermochemical biomass conversion scenario. Selective transformation of sugars to lactic acid derivatives is another area where zeolites can be envisioned to become important catalysts in a future bio-based society.
non-carbohydrate component of lignocellulosic biomass. It is an amorphous polymer of aromatic allylic alcohols that is very resilient towards hydrolysis and cannot be utilized by fermentation. Many strategies exist for the conversion of lignocellulose to fuels. Second generation bioethanol can be produced by pretreating lignocellulose to open it up for a subsequent enzymatic hydrolysis. This facilitates the release of monosaccharides which can be fermented into ethanol. This process enables non-edible lignocellulose to be used as a source for ethanol, although lignin remains unutilized. Gasification of lignocellulose is a different strategy which enables all the carbon containing species present in the lignocellulose to be utilized, including lignin. The lignocellulose is heated to temperatures in the range of 800–1000 °C in the presence of a small amount of oxygen. This facilitates the complete break-down into CO/CO₂, H₂ and H₂O. The syngas thus produced can be converted into Fisher–Tropsch diesel or to

<table>
<thead>
<tr>
<th>Lignocellulosic material</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn cobs</td>
<td>45</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>30</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>Rice straw</td>
<td>32</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>Fresh bagasse</td>
<td>33</td>
<td>30</td>
<td>19</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>45</td>
<td>31</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 1. Composition of different lignocellulosic feedstocks.

Esben Taarning is a research chemist at Haldor Topsoe A/S, working on the conversion of biomass to fuels and chemicals using heterogeneous catalysis. He received an MSc degree in chemistry from the University of Copenhagen in 2005 and in 2009 the PhD degree from the Technical University of Denmark after which he has worked for Haldor Topsoe A/S. The topic of his PhD thesis is the development of green and sustainable chemical reactions.

Xiaobo Yang

Esben Taarning

Dr Xiaobo Yang, holding BSc and MSc degrees of Fudan University, Shanghai, China, obtained his PhD in Chemical Technology in 1999 from University of Kaiserslautern, Germany, under the supervision of Prof. Stefan Ernst with a thesis on the hostguest chemistry of zeolites. Then he held a number of research positions at academic and industrial institutions, working on zeolite synthesis and characterization, among them at ENSCMu with Prof. Henri Kessler, and at University of Pennsylvania with Dr David Olson. Since 2008 Dr Yang has been working at Haldor Topsoe A/S as a Research Chemist on catalytic conversion of biomass to chemicals.

Christian Osmundsen received an MSc in chemical engineering from the Technical University of Denmark (DTU). He is currently a PhD student at the department of physics at DTU under the Catalysis for Sustainable Energy (CASE) Initiative. The focus of the project is the development of methods for converting biomass, in particular carbohydrates, into chemicals and fuels by catalytic means. The work is performed in collaboration with Haldor Topsoe A/S.

Christian M. Osmundsen

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Christian Osmundsen received an MSc in chemical engineering from the Technical University of Denmark (DTU). He is currently a PhD student at the department of physics at DTU under the Catalysis for Sustainable Energy (CASE) Initiative. The focus of the project is the development of methods for converting biomass, in particular carbohydrates, into chemicals and fuels by catalytic means. The work is performed in collaboration with Haldor Topsoe A/S.

Bodil Voss

Bodil Voss (b. Feb. 14th 1967) is finishing an industrial PhD project in April 2011 on the conversion of biomass to chemicals by heterogeneous catalysis at Haldor Topsoe A/S (Denmark), a world leading supplier of catalysts and technological designs within the fields of bulk chemicals production and environmental processes and in collaboration with the Technical University of Denmark (DTU). Bodil Voss graduated as a Bachelor of Chemical Engineering from DTU in 1990 (Ingeniør-akademiet). She was employed at Haldor Topsoe A/S immediately after obtaining her degree and has been working there for 20 years.
methanol which can be used to produce gasoline using the MTG process.8

Pyrolysis oil from lignocellulose

Pyrolysis of biomass is yet another strategy for the utilization of lignocellulose. By heating lignocellulose in the absence of oxygen, it can be converted into gaseous, liquid and solid materials. The relative distribution of each depends on process parameters such as residence time, temperature and heating rate. In general, long residence times of 15–30 minutes and low temperatures, around 400 °C, favor the formation of solid charcoal whereas flash pyrolysis with residence times shorter than 1 second and temperatures around 500 °C favor the formation of the liquid pyrolysis oil.5,8 Pyrolysis facilitates the spontaneous occurrence of dehydration reactions, retro-aldol reactions and many radical reactions. In flash pyrolysis, high temperatures ensure efficient depolymerization while short residence time minimizes the effect of secondary reactions which otherwise would lead to further thermal decomposition of the pyrolysis oil, resulting in a reduced liquid yield. Yields of liquid pyrolysis oil in the range of 70–75% are obtainable using flash pyrolysis.

The most important reason to transform lignocelluloses into pyrolysis oil is that it becomes a liquid, which makes further processing less problematic. Pyrolysis achieves a partial breakdown of the macromolecular components of lignocellulose to smaller components such as sugar monomers and decomposition products of these. The lignin part is also depolymerized to some extent, and aromatics such as guaiacols and phenols are typical components found in pyrolysis oil. However, a large part of the lignin and some of the polysaccharides are converted into char, which is difficult to process further.

The elemental composition of pyrolysis oil generally resembles that of the parent lignocellulosic feedstock.9 Pyrolysis oil is a viscous black liquid with a similar appearance as crude oil. However, it is fundamentally different in many regards (Table 2). Pyrolysis oil can be considered a micro-emulsion of various oxygenates such as carboxylic acids, ketones and aldehydes in water and it is immiscible with hydrocarbons. The presence of carboxylic acids renders the pyrolysis oil acidic, with typical pH values in the range of 2–2.5. Over time, the aldehydes and ketones undergo aldol condensation reactions under these acidic conditions. This causes the pyrolysis oil to change composition and viscosity over time and its acidic nature makes storage difficult due to corrosion issues. Pyrolysis oil has a slightly higher energy density than its parent lignocellulosic precursor but only an energy density of about 40% of that of diesel at 25% water content.

Zeolite upgrading of pyrolysis oil

Through proper separation techniques a number of useful chemicals can be retrieved from pyrolysis oil.13 However, the sheer number of components present complicates this approach. Indeed, more than 400 different components have been identified in the oil, and the use of pyrolysis oil as a fuel substitute seems to be a more reasonable strategy.14,15 So far, pyrolysis oil has only been used as fuel in a limited number of applications, such as stationary ones.16,17 Pyrolysis oil is not useful as a liquid transportation fuel due to the many undesirable characteristics described unless it is upgraded to a more stable fuel product. One way to upgrade pyrolysis oil is by converting it to gasoline using a zeolite catalyst. This facilitates the conversion of pyrolysis oil to a hydrocarbon fraction which resembles gasoline.

When vapors of pyrolysis oil are passed through a bed of zeolite catalyst at 300–500 °C they are converted to hydrocarbons along with the formation of H2O, CO2 and coke. This process thus resembles the MTG process to a great extent. In general, coke formation is much more pronounced when pyrolysis oil is used as feed compared to methanol, and in the order of 30% of the carbon in the feed ends up as coke on the zeolite. The primary reason for this is that pyrolysis oil contains less effective

Simon Ivar Andersen is the Reservoir fluid chemistry discipline manager at Schlumberger DBR Technology Center, Edmonton, Canada. Previously he has been principal research scientist and responsible for a program on renewable chemistry at Haldor Topsoe A/S, Denmark. Before joining Topsoe he was an associate professor in applied thermodynamics Dept. Chem. Eng. Technical University of Denmark. His research interests have been within phase behavior, colloidal chemistry and analysis of complex mixtures such as petroleum as well as catalysis.

Claus Hviid Christensen is Chief Executive Officer at LORC (Lindoe Offshore Renewables Center) that is leading the turn-around of the Danish shipyard Lindoe from ship construction to renewable energy technology. Before this, Claus Hviid Christensen was Vice President, R&D at Haldor Topsoe A/S with responsibility for emerging technology. He came to this position after founding the Danish Center of Excellence for Sustainable and Green Chemistry at the Technical University of Denmark, where he was Professor of Chemistry. Claus Hviid Christensen is also co-founder of Amminex A/S that develops ammonia and hydrogen storage technologies.

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hydrogen than methanol or ethanol. It is simply a too highly oxidized feed to be converted solely into hydrocarbons, and excess carbon is therefore deposited as coke. The effective hydrogen of a feed can be assessed by the use of Chen’s effective H/C ratio concept as defined by (H – 2O)/C. Feeds having high H/C ratios in general lead to less coke formation than those having lower ratios. Thus, for methanol the effective H/C ratio is 2, while for pyrolysis oil it is below 0.5.

Oxygen is removed over the zeolites in the form of H2O, CO or CO2. The ideal situation for a highly oxidized feed such as pyrolysis oil is to remove most of oxygen in the form of CO2, as this would effectively enhance the H/C ratio and thus lead to reduced coke deposition. However, different organic components tend to lose oxygen in different ways (Table 3). In general, alcohols and phenols lose oxygen in the form of H2O, whereas alkaldyes, formates and carbohydrates primarily lose oxygen as CO and H2O. Carboxylic acids lose oxygen as CO2 and H2O. Acetic acid is therefore a useful component for the formation of hydrocarbons, even though its effective H/C ratio is 0.

Bakhshi and co-workers have tested different catalysts such as H-ZSM-5, H-Y, mordenite, silicalite-1, alumina–silica and various AlPO4 molecular sieves, for pyrolysis oil upgrading in a fixed-bed reactor at temperatures in the range of 290–410 °C. H-ZSM-5 was found to be superior to other catalysts, e.g. H-Y zeolite, has been studied by Vasalos et al. The use of FCC riser reactors could be employed where on-site regeneration of coked catalysts is an option. This approach is widely used in the petroleum industry when processing heavy feedstocks and the coke is not completely lost since the heat released by coking-burning is used to supply heat for the process. The use of FCC catalysts, e.g. H-Y zeolite, has been studied by Vasalos et al. In this study, the pyrolysis oil initially underwent a thermal pyrolysis-oil, at a mass ratio of 70/30. Here the yield of deoxygenated hydrocarbons increased from below 10% to ~40 wt%, illustrating the beneficial role of increasing the hydrogen content of the feed. Gayubo et al. have studied model compounds in order to investigate the molecular pathways taking place in the zeolites when processing pyrolysis oil. Using an H-ZSM-5 zeolite as the catalyst, model compounds representing most of the species present in pyrolysis oil were examined. Here it was found that alcohols undergo dehydration at low temperatures (~250 °C) to form olefins which are converted into alkanes and aromatics at higher temperatures. Acetaldehyde forms large amounts of thermal coke prior to contact with the H-ZSM-5 catalyst, illustrating the unstable nature of many aldehyde components. Acetone initially transforms into isobutene and at higher temperatures this is further transformed into heavier olefins and aromatics and alkanes. Acetic acid was found to undergo ketonization to aceto and CO2 and thus follows the reaction pathway of acetone. Phenol is much less reactive than the other substrates and is only partially converted to propene and butenes at temperatures of 400 °C; its conversion does not markedly change with temperature. 2-Methoxyphenol thermally decomposes in the heating zone, leading to the formation of coke, but it is not easily converted over the H-ZSM-5 even at 450 °C. From the insight gained when using these model compounds, it is speculated by Gayubo et al. that it could be worthwhile to remove aldehydes and phenolics from the pyrolysis oil prior to conversion over the zeolite in order to reduce the amount of coke formed.

Alternatively, from the view point of process design, FCC type riser reactors could be employed where on-site regeneration of coked catalysts is an option. This approach is widely used in the petroleum industry when processing heavy feedstocks and the coke is not completely lost since the heat released by coking-burning is used to supply heat for the process. The use of FCC catalysts, e.g. H-Y zeolite, has been studied by Vasalos et al. In this study, the pyrolysis oil initially underwent a thermal

### Table 2  Characteristics of pyrolysis oil and diesel fuel (40 °C and 25% water)1,3,4

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Pyrolysis oil</th>
<th>Diesel fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>20–30 wt%</td>
<td>0.1 wt%</td>
</tr>
<tr>
<td>pH</td>
<td>2.0–2.5</td>
<td>—</td>
</tr>
<tr>
<td>Density</td>
<td>1.2 kg L⁻¹</td>
<td>0.94 kg L⁻¹</td>
</tr>
<tr>
<td>Elementary analysis (wt%)</td>
<td>C      55–58</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>H            5–7</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>O            35–40</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>N            0–0.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Ash          0–0.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>IHV as produced 16–19 MJ kg⁻¹</td>
<td>40 MJ kg⁻¹</td>
</tr>
<tr>
<td>Viscosity</td>
<td>40–100 cp</td>
<td>180 cp</td>
</tr>
<tr>
<td>Solids (char) (wt%)</td>
<td>0.1–0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Vacuum distillation residue</td>
<td>Up to 50 wt%</td>
<td>1 wt%</td>
</tr>
</tbody>
</table>

### Table 3  Formation of H2O, CO and CO2 for various organic species over a H-ZSM-5 zeolite19

<table>
<thead>
<tr>
<th>Feed compound</th>
<th>H2O (%)</th>
<th>CO (%)</th>
<th>CO2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>96</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Glycerol</td>
<td>92</td>
<td>7.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Xylenol</td>
<td>93</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Eugenol</td>
<td>89</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>Anisole</td>
<td>88</td>
<td>12</td>
<td>Trace</td>
</tr>
<tr>
<td>2,4-Dimethyl phenol</td>
<td>87</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>o-Cresol</td>
<td>80</td>
<td>17</td>
<td>3</td>
</tr>
<tr>
<td>Starch</td>
<td>78</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Isougenol</td>
<td>77</td>
<td>19</td>
<td>4</td>
</tr>
<tr>
<td>Glucose</td>
<td>75</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Dimethoxymethane</td>
<td>73</td>
<td>6</td>
<td>21</td>
</tr>
<tr>
<td>Xylose</td>
<td>60</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td>Sucrose</td>
<td>56</td>
<td>36</td>
<td>8</td>
</tr>
<tr>
<td>n-Butyl formate</td>
<td>54</td>
<td>46</td>
<td>0</td>
</tr>
<tr>
<td>Diphenyl ether</td>
<td>46</td>
<td>46</td>
<td>8</td>
</tr>
<tr>
<td>Furfural</td>
<td>14–22</td>
<td>75–84</td>
<td>2.5–3.0</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>54</td>
<td>10</td>
<td>36</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>50</td>
<td>4</td>
<td>46</td>
</tr>
</tbody>
</table>
hydrodrcracking, resulting in a liquid yield of up to 42 wt%, with up to 85 wt% oxygen removed while 6.5 wt% oxygen remained in the hydrotreated product. The hydrotreated pyrolysis oil can be separated by distillation, with the light distillate having properties compatible with petroleum gasoline or diesel and can be used directly as blend stocks to the corresponding petroleum fractions. The heavy fraction of the hydrotreated pyrolysis oil can be mixed into the petroleum FCC feeds, such as vacuum gas oils. Experimental results show that co-feeding of this hydrotreated pyrolysis oil with vacuum gas oil at 2.5 wt% can increase the yields of light cycle oil by 1 wt% with the concurrent formation of 0.5 wt% more coke.

Catalytic fast pyrolysis

Pyrolysis processes can be carried out in the presence of a catalyst in order to obtain a more desirable hydrocarbon product in place of pyrolysis oil. An obvious benefit of using a catalyst such as a zeolite is that conversion of lignocellulose to gasoline takes place in a single step, thereby simplifying the process by avoiding condensation and re-evaporation of the pyrolysis oil. The principles in catalytic fast pyrolysis are the same as those for non-catalytic fast pyrolysis; lignocellulose is rapidly heated to a temperature between 300 and 700 °C using a short residence time and then rapidly cooled in order to achieve high liquid yields and prevent the formation of unwanted by-products. The catalyst ensures further cracking of the pyrolysis intermediates and oxygen removal in the form of H2O, CO or CO2 resulting in the formation of hydrocarbons.

Using a forestry residue biomass from beech wood, Lappas et al. carried out experiments to compare fast pyrolysis with catalytic fast pyrolysis using a FCC catalyst, i.e. Re-USY zeolite. With the catalyst, pyrolysis oil yields decreased from ca. 75% to 45–50%, while yields of both gas and char almost doubled. However, the oil product obtained in the catalytic process was found to contain 50% more hydrocarbons and significantly less oxygenates than in the absence of catalyst, thus illustrating that upgrade of the pyrolysis oil occurs simultaneously as the pyrolysis reaction. The oxygen was removed primarily in the form of water in this study, resulting from the zeolites’ ability to catalyze dehydration reactions due to its strong acidity. Samolada et al. have introduced a number of measurable factors which can be used as criteria to evaluate the effectiveness of the catalytic fast pyrolysis processes. These are: loss of organics (LO), stability index (SI) and water generation (WG). The LO criteria relates to carbon efficiency and the other factors define the efficiency of oxygen removal. Different catalysts, such as H-ZSM-5 and Re-USY, mesoporous Al-MCM-41, alumina, and supported Fe/Cr catalysts, were tested for catalytic fast pyrolysis using a model biomass mixture. Here it was found that alumina hardly exhibits any catalytic role with respect to improving the fuel property of the liquid product. MCM-41 was found to be comparably inactive, probably due to the poor structural stability and its low acidity. Zeolites, especially H-ZSM-5, are effective oxygen removal catalysts, although at the expense of organics yield; in comparison with e.g. aluminium containing Al-MCM-41 or Al-MCM-41 synthesized from zeolite seeds, H-ZSM-5 produces more H2O, indicating its stronger dehydration tendency due to its stronger acidity.

Catalytic fast pyrolysis of sugars is a topic that has been investigated by Huber and co-workers. Zeolites H-Y, β, and H-ZSM-5, silicalite-1 and a silica–alumina have been tested for the catalytic fast pyrolysis of glucose at 600 °C. H-ZSM-5 gives the highest yields of aromatics and other (partially) de-oxygenated organics, along with by-products such as CO, CO2, H2O and coke. The primary product on silica–alumina is coke. The highest achievable aromatic yield over H-ZSM-5 is ca. 30% based on carbon, while approximately a similar amount of carbon ending up as coke.

Using the same H-ZSM-5 catalyst Huber and co-workers further studied the conversion of xylitol, cellulose and cellobiose. The more reduced xylitol was found to give higher yields of hydrocarbons (48%) compared to the glucose-based substrates. This is highly interesting, since glucose can be viewed as being xylitol + CO. Thus, if glucose is first decarbonylated to xylitol, higher gasoline yields should be obtainable. The aromatic product was analyzed and found to contain ca. 45% naphthalene, 20% toluene, others are benzene, alkylbenzene, and up to 5% indene.

Fast pyrolysis and catalytic fast pyrolysis are currently hot topics of research and development, but no commercial scale technology has been demonstrated yet. Current state of the art gasoline yields are in the order of 50% of what is theoretically possible. Challenges are two-fold. On the one hand, highly efficient methods have to be developed to deal with the large amounts of coke. An adaptation of the riser reactor technology applied in FCC processes should be a solution under consideration. On the other hand, to realize rapid heating and short residence time on a reasonably large throughput of feedstock requires sophisticated reactor design. Many different ideas are under investigation, such as fluidized beds, rotating cones, microwave heating, etc. Realistic leads will soon emerge.

Conversion of pyrolysis oil to a hydrocarbon fuel that can be used as a transportation fuel is an important field of research. An interesting strategy that has not been discussed here is hydro-treatment of the pyrolysis oil using HDO catalysts to form a more fuel-like product. This is more desirable from a carbon-perspective, since more carbon ends up in the final hydrocarbon product rather than as coke on the catalyst. However, zeolite catalysis could take an important step forward by achieving a better control of how the oxygen is expelled from the pyrolysis oil. If a larger fraction of oxygen is expelled in the form of CO or CO2, more hydrogen would be accessible for hydrocarbon formation and consequently less carbon would deposit on the zeolite.

Catalytic conversion of sugars to lactates

The isomerisation of C4-sugars to lactic acid, which is thermodynamically more stable, is catalyzed by aqueous acids at temperatures of 250–300 °C. However, moderate yields are obtained at best. Lewis acidic catalysts such as SnCl3 have been demonstrated to be highly active and selective catalysts, achieving a methyl lactate yield of 89% for the conversion of glyceraldehyde in methanol at 90 °C. Unfortunately, the use of a homogeneous catalyst is not practical with respect to catalyst recycling and product purification, and a heterogeneous catalyst would therefore be preferable. It has recently been demonstrated that Lewis acidic zeolites such as Sn-β have unique catalytic...
activity and are capable of converting C₃- and C₆-sugars directly into lactate esters (Scheme 1). The solvent defines which lactate derivative is formed; water leads to the formation of lactic acid whereas methanol leads to methyl lactate.

For C₃-sugars, a quantitative yield of methyl lactate can be obtained in methanol at 80 °C, while yields in the range of 40–65% are achieved when using glucose, fructose or sucrose as the substrate at somewhat higher temperatures (160 °C). Lower yields are generally obtained when water is used as solvent, which could be resulting from autocatalytic decomposition reactions catalyzed by the formed lactic acid. The reaction pathway from C₃-sugars to lactate products is believed to proceed through a preliminary dehydration step, leading to the formation of pyruvaldehyde. Since pyruvaldehyde is highly reactive, it will be present as its hydrate in water and its hemiacetal in methanol. Isomerisation of these species via a 1,2-hydride shift leads to the formation of lactic acid and methyl lactate (Scheme 2, path A).

It has been confirmed that aqueous pyruvaldehyde is also converted into lactic acid using Sn-β as a catalyst, thus supporting the hypothesis that this is a preliminary intermediate. In this context it was found that aqueous pyruvaldehyde is transformed at lower temperatures than the C₃-sugars, suggesting that the dehydration of C₃-sugars to pyruvaldehyde is the rate limiting step in the overall reaction. The 1,2-hydride shift resembles the MPVO-redox reaction to a great extent, and Sn-β has previously been demonstrated to be a highly active MPVO-catalyst. Low levels of tin oxide can be incorporated into the β structure during zeolite synthesis, and Si-Sn ratio is typically in the order of 90 : 1 to 200 : 1. Since tin is tetravalent, charge compensation is not an issue and Sn-β is therefore not Bronsted acidic. Instead, the discrete tin atoms have Lewis acidic properties and can coordinate to carbonyl and alcohol groups. These functional groups are widely found in natural compounds, and in particular in carbohydrates. A tentative mechanism for 1,2-hydride transfer mediated by a hydrolysed Sn-site is shown in Scheme 3.

Although Lewis acidic zeolites such as Sn-β and Ti-β are superior catalysts for the conversion of C₃-sugars to lactate derivaties, conventional aluminium containing Y and β zeolites can also be used. Higher reaction temperatures are generally required for conventional zeolites (110–120 °C) and the product selectivity depends greatly on the nature of the aluminium present in the zeolite. Strongly dealuminated zeolites containing a large degree of extra-framework aluminium have high selectivities towards lactate products. In contrast, zeolites which are Bronsted acidic in nature exhibit low selectivities towards lactates and increased selectivity for the formation of pyruvaldehyde dimethyl acetal. This effect has been illustrated for an Al-β zeolite (Si : Al 65 : 1) which yielded 74% pyruvaldehyde dimethyl acetal and 3% methyl lactate from dihydroxyacetone in methanol at 115 °C. The same zeolite was tested in a comparable experiment after steam treatment at 750 °C for 20 hours. Here, the pyruvaldehyde dimethyl acetal yield had dropped to 18% while 32% methyl lactate was formed. This difference in product selectivity is caused by the inability of framework aluminium to catalyze the 1,2-hydride shift of pyruvaldehyde methyl hemiacetal leading to methyl lactate. Instead, further acetalization occurs, and pyruvaldehyde dimethyl acetal becomes the main product (Scheme 2, path B).

C₆-Sugars decompose when heated with an aluminium containing zeolite such as Al-β. However, Lewis acidic zeolites such as Sn-β, Ti-β and Zr-β are capable of converting C₆-sugars into lactate acid derivatives. Since C₆-sugars such as glucose, fructose and sucrose are much more abundant than C₃-sugars, this increase in scope is highly important. The overall reaction pathway is believed to involve glucose-fructose isomerisation followed by a retro-aldol reaction of fructose forming the two C₆-sugars, glyceraldehyde and dihydroxyacetone (Scheme 4). The retro-aldol reaction is the rate determining step. These C₆-sugars are then converted into methyl lactate as described previously. This overall reaction pathway starting from glucose thus resembles the biological glycolysis pathway. Similar yields of methyl lactate are obtained when using either glucose (43%) or fructose (44%), suggesting that the two are in equilibrium under the reaction conditions. Surprisingly, higher yields of methyl lactate are achieved from sucrose (65%) compared to the monosaccharides. The ability of Sn-β to catalyze glucose-fructose isomerisation in water was recently reported by Moliner et al. When comparing different Lewis acidic materials, Sn-β and Ti-β were found to be more active than other tin and
titanium containing materials. This further illustrates how Lewis acidic zeolites might find use as catalysts in carbohydrate conversion.

Currently, little is known about the carbohydrate chemistry catalyzed by Lewis acidic zeolites. However, the ability of the materials to catalyze MPVO-type hydride shifts, retro-aldol reactions and facile dehydration reactions while not having the strong and destructive Brønsted acidic properties of conventional zeolites makes them useful catalysts for converting carbohydrates to different compounds. The Lewis acidic zeolites further have the advantage that they are thermally very stable and can be calcined and reused many times. These promising characteristics make them real alternatives to fermentation based processes for the production of lactic acid. Currently, lactic acid is produced by fermentation of primarily glucose.44 Since it is necessary to maintain a neutral pH in the fermentation broth, calcium hydroxide is added continuously to precipitate the formed lactic acid. After the fermentation has completed, sulfuric acid is added to reform the acid. The lactic acid is then converted to methyl lactate and purified by distillation.44–46 The need for stoichiometric amounts of sulfuric acids and the large amounts of calcium sulfate produced as a by-product (approx. 1 ton per ton of lactic acid)44 make this process less than ideal from an environmental standpoint. In comparison, catalytic production of methyl lactate does not result in the formation of stoichiometric amounts of salt waste and the fact that methyl lactate is formed directly could simplify the purification of it. However, a racemic lactate product is formed when using catalysts, where the fermentative approach yields a stereochemically pure product. This might limit the use of catalytically produced lactates to non-polymer applications.

Dehydration of sugars to furan compounds

Dehydration of pentoses to yield 2-furancarboxaldehyde, furfural, and hexoses to yield 5-hydroxymethylfurfural, HMF, has been studied for more than a hundred years. Furfural is produced on an industrial scale (approx. 200 000 t a⁻¹) from agricultural wastes, by hydrolysis followed by dehydration in aqueous acids at high temperatures.44 HMF in contrast is not produced in large scale, although much research has gone into finding viable production methods. HMF can be produced analogously to furfural by dehydration of fructose or hydrolysis of dehydration of inulin, but the high costs of the substrate compared with comparable chemicals derived from petroleum make large scale production of HMF unattractive, thus HMF is primarily produced for use in the production of a few high value chemicals.44 Both furfural and HMF, however, can be converted to a number of interesting chemicals by known processes, and thus have potential for use as platform chemicals.44 Scheme 5 shows a number of industrially interesting chemicals that can be produced from HMF. HMF can be oxidized to furan-2,5-dicarboxylic acid, FDCA, which can be used as a replacement for terephthalic acid in the production of polymers,45 making it interesting as a starting material for the production of biomass-derived polymers. Transportation fuels can be produced by hydrogelenolysis of C–O bonds over a copper–ruthenium catalyst to produce 2,5-dimethylfuran (DMF). This compound is insoluble in water, and has a 40% higher energy density than ethanol,46 making it an interesting alternative for gasoline blending. Alternately liquid alkanes can be produced by condensation reactions between acetone and either HMF or furfural, followed by hydrogenation, over a bi-functional catalyst, such as Pd/MgO–ZrO₄.47,48

The industrial production of HMF is typically performed in a homogeneous system using aqueous sulfuric acid as the catalyst. This approach leads to the formation of a number of by-products, formed by fragmentation and condensation reactions,45 as well as polymeric by-products, known as humins.44 The use of a homogeneous catalyst is not optimal, and much research has gone into finding alternative solid catalysts, such as zeolites or acidic resins. Rivalier et al. compared several different zeolites, such as zeolite β, ZSM5, Y, and mordenite, and found clear differences in conversion and selectivity, with mordenite...
giving the best selectivities at more than 90%\(^\text{49}\). In a study by Moreau \textit{et al.} the effect of the Si/Al ratio on the conversion and selectivity of the process was investigated;\(^\text{49}\) a maximum yield of 70\% was obtained, when using a zeolite with a Si/Al ratio of 11. In this process HMF was continuously extracted using methyl isobutylketone, MIBK. HMF can rehydrate to give levulinic acid,\(^\text{51}\) and since this reaction is also acid-catalyzed removal of the formed HMF to a neutral phase can be used to avoid further reaction. The partition coefficient in the used system, however, necessitates the use of large volumes of the extraction phase (1 : 5 water to MIBK) making purification of the product costly. An alternative approach relies on the use of other solvents than water to perform the reaction, coupled with continuous removal of the formed water. In a work by Shimizu \textit{et al.} water-free DMSO was used as solvent and the reaction was performed at reduced pressure to boil off any water formed during the reaction.\(^\text{43,44,46}\) Using zeolite H-\(\beta\), yields of up to 97\% HMF were achieved, when the reaction was performed in an inert atmosphere, while at standard atmospheric pressure, the yield dropped to 51\%. Both aldo- and ketohexoses can be utilized as substrate for HMF production. The reaction pathway from glucose and fructose is given in Scheme 6.

The dehydration can occur both through cyclic intermediates and through acyclic intermediates. Considering only the chemistry of the process, the use of ketohexoses, such as fructose, is generally preferred, as the reaction is both more efficient and selective.\(^\text{51}\) In the dehydration of glucose, the enolization step is very slow, and thus becomes the rate determining step. The use of glucose further complicates the process, in that oligosaccharides with reducing groups can form, which react with intermediates or HMF itself, thereby reducing the overall yield.\(^\text{51}\) However, glucose is much cheaper than fructose, and a change to a process based on glucose, or some polysaccharide of glucose, as substrate would go a long way in making the process more feasible from an industrial standpoint.

**Glycerol**

Glycerol is produced on large scale as a by-product in biodiesel production and its production is projected to grow even further as biodiesel production increases. Biodiesel production by transesterification is accompanied by the co-production of approximately 10\% glycerol. This currently results in the co-production of more than 1 million tons of crude glycerol per year. There is a limited market for high-purity glycerol in the pharmaceutical sector, but this is not able to absorb the large quantities of glycerol produced. In recent years, though, glycerol has found new applications and the chemical companies Solvay and Dow have started using glycerol for the production of epichlorohydrin. Much research has been aimed at converting glycerol into different high-value chemicals. Glycerol transformation using dehydration, hydrogenation, oxidation and etherification as well as acetal and ketal formations have been reported in the literature. Of these, acetalisation and esterification lead to products that can be used as fuel additives, cosmetics, surfactants, plasticizers and pharmaceuticals while the other reactions aim at bulk-type chemical products such as acrolein, 1,3- and 1,2-propandiol. Also acetol, 3-hydroxypropanol, propylene oxide, glyceraldehyde and lactic acid are possible products from glycerol.\(^\text{52–55}\)

Acid catalyzed dehydration of glycerol in liquid and gas phase has received much attention.\(^\text{44}\) Acrolein has limited use but it can be transformed into acrylic acid, a very important commodity chemical, by oxidation. Typical catalysts used for the dehydration of glycerol are metal oxides and zeolite catalysts. The boiling point of glycerol is 290 \(^\circ\)C and it is thermally unstable at this high temperature. Catalytic glycerol dehydration reactions, however, often require temperatures in the range of 250–350 \(^\circ\)C, so catalyst deactivation due to glycerol by-product formation, coke deposition and acrolein polymerization are all complicating issues. These issues are taken into account by the use of a catalyst that can be regenerated by calcination. The catalyst life-time can be

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**Scheme 5** Overview of industrially interesting chemicals that can be produced from HMF.\(^\text{43,44,46}\)

**Scheme 6** Pathways for the dehydration of glucose and fructose to HMF.\(^\text{44}\)
improved by using diluted glycerol rather than pure glycerol. This is particularly true in liquid phase dehydration of glycerol, but dilution with water can often also be used to minimize coke-formation in vapour phase dehydrations. Kartryniok et al. recently gave an excellent review on glycerol dehydration in gas phase showing that zeolites (H-ZSM-5, H-ZSM-11 and H-β) all give 100% glycerol conversion and acrolein selectivities in the range of 70–83% at temperatures of 330–360 °C.46 Corma et al. have used a FCC type reactor for glycerol conversion and showed that low temperatures (350 °C) give higher acrolein yields over H-ZSM-5 than using higher temperatures (500 °C). However, even at 350 °C there is a significant build-up of coke. Yoda and Ootawa showed by FT-1R analysis that on H-ZSM-5 the secondary hydroxy group in glycerol interacts preferentially with the OH of the zeolite, leading to acrolein being formed selectively.47 Liquid phase glycerol dehydration is somewhat slower and polymerization of acrolein may hamper the industrial application. The acrolein selectivity found for zeolite catalyzed dehydrations are generally slightly lower than those obtained when using many metal oxides. The lower selectivity is likely caused by the higher acidity of the zeolites compared to metal oxides. When operating in a temperature regime where zeolites are known to form hydrocarbons, coke and hydrocarbon formation is likely to occur simultaneously with the dehydration, thus lowering the acrolein selectivity.

Terpenes

Terpenes are hydrocarbon compounds found in many places in nature. The basic building block of terpenes is the isoprene unit; terpenes consisting of between 1 and 8 isoprene units are found in the resins secreted from a wide variety of plants, in essential oils, and in pigments, while higher terpenes, polyterpenes, are found in latexes. Derivatives of terpenes are known as terpenoids. Compared to other biomass resources, the available amount of terpenes is relatively low, and the price relatively high, thus most terpenes are used directly, e.g. as fragrances or flavors. Some terpenes, and terpenoids, are, however, produced on a large scale and find use as solvents and as starting materials for the production of fine chemicals.48

The isomerisation of citronellal to isopulegol (Scheme 7), an intermediate step in the industrial production of menthol, can be performed using Sn-β with almost quantitative yields of pulegols.49 Industrially, the production of isopulegol is much more interesting than the other pulegols, thus a high diasteroselectivity is important; using Sn-β it is possible to obtain approximately 85% isopulegol. The current industrial yield is 92%, however, this is achieved using a homogeneous, water-sensitive catalyst.

Another example is the isomerisation of α-pinene to camphene (Scheme 8); camphene has a large number of uses, e.g. as an intermediate for the production of fragrance materials, acrylates, terpene–phenol resins, as well as a solvent for varnishes. The industrial production is performed using a TiO2 catalyst, yielding a complex reaction mixture of camphene, limonene, tricyclic, fenchenes and bornylene.44 Due to the low reaction rate, a number of other catalysts have been investigated for the reaction, such as zeolites β, ZSM-5, mordenite, and Y. For zeolite Y, yields of over 40% camphene, along with 23% limonene, have been reported, at 85% conversion.41

Dehydration of alcohols

Ethanol is the largest biochemical produced today and its growth is estimated to continue for many years. Due to the large scale of ethanol production, ethanol can be viewed as a potential feedstock for the production of other compounds, in the same way as naphtha is today. In general, dehydration of ethanol using zeolites leads to the formation of diethyl ether, ethylene or gasoline, depending on the reaction conditions (Fig. 1).

Derouane et al. and others have studied the conversion of methanol and ethanol over H-ZSM-5 zeolite at different temperatures. At low temperatures (150–200 °C), diethyl ether is the dominant species formed, whereas higher temperatures (200–300 °C) lead to the formation of ethylene instead. At temperatures above 250 °C, higher hydrocarbons form and at temperatures above 300 °C the higher hydrocarbons constitute the majority of the product composition (Fig. 1). At temperatures above 350 °C, the product composition resembles that seen for methanol, where a large fraction of the hydrocarbons is aromatic species. The most notable difference is that ethylated aromatics are formed, rather than the methylated aromatics seen in the MTG reaction.

Diethyl ether is a diesel fuel with excellent cold-start properties and the ability to reduce NOX emissions in the exhaust gas from diesel engines and has the potential to be an important bio-fuel in the future.56 Diethyl ether formation is catalyzed by both Bronsted and Lewis acidic sites and even weakly acidic sites have been demonstrated to be effective catalysts for the formation of diethyl ether.57–59

Ethylene is the most important chemical produced, with an annual production exceeding 100 million tons. Currently, ethylene is produced from petroleum and natural gas, either by steam cracking of naphtha or from ethane dehydrogenation. Ethylene can also be obtained from ethanol by dehydration, and commercial scale production of bio-ethylene began in 2009 in
Brazil. Ethylene can be obtained in high selectivity over H-ZSM5 zeolite catalysts at temperatures in the range of 250–300 °C. As is the case for many zeolite catalyzed processes, catalyst deactivation due to coke formation eventually occurs and the catalyst has to be calcined in order to regenerate its activity. Hierarchical zeolites, such as nanocrystalline H-ZSM-5, exhibit significantly improved lifetimes compared to conventional H-ZSM-5 for ethylene production at 240 °C. Thus, a lifetime in the order of 500 hours has been reported for nanocrystalline H-ZSM-5, compared to a lifetime of 120 hours for conventional microcrystalline H-ZSM-5. The presence of water in the feed has been found to moderate the strongly acidic sites and enhance the catalyst activity and selectivity towards ethylene. Furthermore, water often has a diminishing effect on the rate of coke formation and can thus be an instrument to improve the catalyst lifetime. The use of aqueous rather than anhydrous ethanol will reduce the feed cost. However, ethylene production will likely only be viable in countries such as Brazil, where a large source of cheap ethanol is available.

Conversion of ethanol to gasoline has been studied in continuation of the findings of the MTG process. The ETG process leads to a hydrocarbon product similar to that obtained in the MTG reaction, consisting primarily of monocyclic aromatics in the C7–C10 range together with C5+ alkanes, which can be used directly as gasoline. According to the hydrocarbon pool theory the cavities of the zeolites host cyclic organic species from which the gasoline products originate through alkylation and cracking reactions. Analysis of the organic species present in spent H-ZSM-5 zeolites has been carried out by dissolution of the zeolite crystal in hydrofluoric acid followed by extraction and GC analysis. This analysis shows that they consist of both ethylated and methylated aromatics. This is slightly different from the MTG reaction, in which only methylated aromatics, such as hexamethylbenzene, are present in the micropores. The importance of the zeolite pore architecture has been investigated. Zeolites having large pores (FAU and BEA) undergo a rapid deactivation of the Bronsted acidic sites, resulting in very low C5+ activity. In comparison, H-ZSM-5 with its smaller pores exhibits a comparable slow deactivation, analogous with what is observed in the MTG process. However, deactivation on H-ZSM-5 is more pronounced for ETG relative to MTG. The deposited coke consists of polyaromatics and is more condensed on large pore zeolites than on H-ZSM-5. Using ion exchanged zeolites can also change the lifetime and product selectivity. In a recent study the yield of C5+ products was found to increase when 0.3–0.5 wt% Fe was exchanged into the H-ZSM-5 zeolite.

Conversion of higher alcohols such as butanol or propanol to gasoline can be achieved using a H-ZSM-5 zeolite. The production of gasoline from these higher alcohols is easier than from methanol or ethanol, since only mildly acidic sites are needed. Even after the strongly acidic sites have deactivated, production of highly branched C5–C9 olefins from 1-propanol takes place without the formation of aromatics. These olefins can be hydrogenated into high-octane gasoline. Co-feeding methanol with butanol has also been shown to have a beneficial effect on the production of gasoline from methanol, allowing lower reaction temperatures to be used. This increased activity for methanol conversion in the presence of butanol could be an effect of butanol being able to maintain the carbon-pool more effectively at lower temperatures than methanol.

**Outlook**

The discovery of zeolites has improved the global energy supply tremendously, allowing a higher gasoline production from oil than what was previously possible. Zeolites are today an integral part of any oil refinery and although zeolites initially emerged as catalysts for the conversion of petroleum, they are likely to play an important role in future bio-refineries as well. No matter how bio-refineries will be based, zeolites will have a role to play. Zeolites can be used for the production of gasoline from methanol (gasification), ethanol (fermentation) and oxygenates (pyrolysis), thereby covering the most likely bio-refineries. Zeolites can also be used for the production of olefins, either from methanol, in the MTO process, or by dehydration of ethanol, propanol and butanol. Finally, zeolites could replace, or supplement, biochemical processes in some cases, e.g. for the production of lactates from carbohydrates.

Gasoline production from pyrolysis oil is cost-attractive since this does not require a gasifier or a fermentation and distillation facility, which is the case for the gasification and fermentation based scenarios. However, the serious coking issues described illustrate that this is very difficult to realize. The fundamental problem is that too little hydrogen is available in pyrolysis oil, which results in the deposition of coke on the catalyst, rather than the formation of hydrocarbons. It would be a major breakthrough within zeolite catalysis if the fate of oxygen in the pyrolysis oil could be controlled to a greater extent. If oxygen was expelled primarily as CO2 rather than water, this would result in a higher hydrogen content of the feed and reduce the production of highly branched C5–C9 olefins from 1-propanol takes place. According to the hydrocarbon pool theory the cavities of the zeolites host cyclic organic species from which the gasoline products originate through alkylation and cracking reactions. Analysis of the organic species present in spent H-ZSM-5 zeolites has been carried out by dissolution of the zeolite crystal in hydrofluoric acid followed by extraction and GC analysis. This analysis shows that they consist of both ethylated and methylated aromatics. This is slightly different from the MTG reaction, in which only methylated aromatics, such as hexamethylbenzene, are present in the micropores. The importance of the zeolite pore architecture has been investigated. Zeolites having large pores (FAU and BEA) undergo a rapid deactivation of the Bronsted acidic sites, resulting in very low C5+ activity. In comparison, H-ZSM-5 with its smaller pores exhibits a comparable slow deactivation, analogous with what is observed in the MTG process. However, deactivation on H-ZSM-5 is more pronounced for ETG relative to MTG. The deposited coke consists of polyaromatics and is more condensed on large pore zeolites than on H-ZSM-5. Using ion exchanged zeolites can also change the lifetime and product selectivity. In a recent study the yield of C5+ products was found to increase when 0.3–0.5 wt% Fe was exchanged into the H-ZSM-5 zeolite.

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coking significantly. This could improve the productivity of gasoline from pyrolysis oil and improve the catalyst lifetime.

Other advances within zeolite catalysis are likely to emerge from new zeotype materials such as stannosilicates (Sn–β) and titanosilicates (TS–1, Ti–β) which have already been demonstrated to be highly active and selective catalysts for the conversion of carbohydrates. These materials have very different catalytic capabilities than conventional aluminosilicate zeolites and seem more compatible with the fragile nature of carbohydrates. These materials have the potential to be broadly applied within biomass conversion in the future.

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References


The use of renewable resources has attracted significant attention in recent years for many different reasons. Renewable resources include electricity made from kinetic energy stored in wind, potential energy stored in water, thermal energy stored as heat underground and as solar influx in the form of electromagnetic radiation, and energy stored in chemical bonds in the case of biomass. Although renewable resources have been used for various purposes for centuries, there is currently a significant focus on expanding and optimizing this use in the form of new technologies fit for the 21st century.

The use of biomass as a resource has developed rapidly in recent years, and it will become an important contributor to our available resources in the future. Biomass sets itself aside from the other renewable resources, since the energy it contains is stored as chemical bonds. This characteristic allows biomass to be used for several purposes apart from electricity and heat generation, such as the production of liquid fuels and chemicals. Indeed, biomass is the only renewable source of useful carbon atoms. Although biomass is annually renewable, it is still a scarce and limited resource, especially when produced in a sustainable manner, and it is important to use it in the most efficient way. This Essay argues for the production of select chemicals, thereby effectively replacing petroleum, as an efficient use and illustrates some of the current efforts that are made in the chemical industry towards adoption of biomass as a feedstock.

### Availability of Biomass Resources

In recent years, a large number of processes for producing fuels and chemicals from biomass have been demonstrated. When the potential of these processes is discussed, it is often done in the context of the current world situation. This approach gives an unclear picture of the actual merit of the process, as large-scale industrial production using biomass will drastically alter the premises. To consider the true potential of a process and its ability to substitute or compete with a fossil-based analogue, absolute numbers of the demand and the amount of potential feedstock must be considered. In the U.S., the total demand for crude oil is approximately one billion, i.e. $10^9$ metric tons per year ($\text{ty}^{-1}$). In comparison, the amount of biomass used for electricity generation and the production of biofuels and other nonfood bioproducts constitutes about 190 million tons. As a consequence, biomass production must be increased drastically to replace all products derived from petroleum with biomass. The total sustainable biomass potential is estimated by the U.S. Department of Energy to be at least 1.2 billion tons per year in the U.S., a target reachable within 50 years. This rough comparison illustrates how present demand for oil and future availability of biomass can become comparable on a weight basis, as shown in Figure 1, and although the quantities reported are based on U.S. statistics, and are thus not necessarily representative of other countries, the conclusions can be extrapolated to the rest of the industrialized world. The comparison on a weight basis is, however, somewhat misleading, as biomass has a lower energy and carbon density than crude oil; on a weight basis, oil contains approximately twice the amount of carbon atoms and chemically stored energy as biomass. Therefore, the proposed sevenfold increase of the U.S. biomass production will not constitute a large enough resource to completely replace the current demand for oil. Thus, as the use of biomass in industry increases, it will at some point become a scarce resource, and its utilization should for this reason be considered wisely.

Current economic feasibility studies of processes using biomass as feedstock, which use a zero or even negative...
feedstock price, are therefore unrealistic if these processes are to be carried out on a scale that is comparable to that of current petrochemical processes. Thus, for long-term planning, the mature market must be considered instead of the current market. This is of course by no means a simple task. Large-scale use of biomass as feedstock will drastically alter the market, and much of the biomass that is currently considered a waste product will eventually become a valuable feedstock as demand increases, since the quantities available are not sufficient to completely saturate the market. Thus, there will be no biomass waste in the future, only biomass resources.

For the reasons mentioned above it is necessary to consider the best use of biomass resources. As also shown in Figure 1, the amount of oil presently used in the chemical industry to produce fossil platform chemicals, that is, methanol, ethylene, propylene, butadiene, benzene, toluene, and the xylenes,[10] is comparable in volume to the total amount of biomass harvested for nonfood purposes. The potential biomass supply should therefore be sufficient to replace oil in this application, and a complete transition from petroleum to biomass feedstocks seems entirely feasible for the production of chemicals, although it implies significant technological and economic challenges. Currently, however, most of the available biomass is used directly for electricity production, and only a small fraction is upgraded to higher-value products, largely covered by ethanol. In fact, only a few biomass-based processes are currently able to compete with petrochemical processes on commercial terms.

**Biomass Utilization**

To further discuss how biomass is best utilized, we will use the effective H/C ratio, which is the ratio between hydrogen and carbon atoms in the molecule adjusted for heteroatoms. For a molecule containing only carbon, hydrogen, and oxygen, the ratio is calculated by the simple formula in Equation (1).

\[
H/C\text{ ratio} = \frac{n(H) - 2n(O)}{n(C)}
\]  

The formula provides a quantitative number for the overall degree of oxidation in a given molecule. In this way, carbohydrates can be regarded as “hydrated coal”. Figure 2 shows the most common fossil and biomass-based resources, as well as a number of platform, intermediate, and target chemicals. Horizontally they are arranged according to their degree of processing, with the target chemicals at the center. Vertically, the molecules are arranged according to their effective H/C ratio. Chemical reactions resulting in a horizontal shift in Figure 2 include isomerization reactions, (de)hydrations, and condensation or fragmentation reactions, while redox reactions imply a vertical shift.

Transportation fuels have an effective H/C ratio in the range of 1 to 2.3 (purple box), which is close to the ratio of crude oil. This ratio implies a high energy density, and it is thus ideal for liquid fuel purposes. Commodity chemicals, on
the other hand, span a much wider H/C ratio (blue box), which is more comparable to that of biomass. A wide gap in the effective H/C ratio between a resource and a target chemical implies that a lengthy process is needed for its conversion. Sugars, for example, have a similar effective H/C ratio to many functionalized high-value chemicals and should therefore be a more ideal feedstock than fossil resources in some cases. By utilizing biomass as feedstock for the production of chemicals instead of fuels, the necessity for deoxygenation, which is one of the biggest challenges when making fuels from biomass, is partially or completely avoided. Oxygen-rich chemicals such as ethylene glycol, acetic acid, and acrylic acid are examples of chemicals that could be obtained more efficiently from biomass than is possible from fossil resources. Since oxidation reactions typically involve product loss owing to overoxidation, it would be desirable if these reactions could be avoided, or at least their use minimized, when producing chemicals: an objective which seems simpler to achieve when starting from lignocellulosic biomass. Olefins, on the other hand, have an H/C ratio far from that of biomass, which implies that biomass is a poor starting point. It seems that the vast amounts of olefins produced by the chemical industry today will not be easy to directly replace by biomass-based olefins, and the ideal solution is to develop alternative materials with an effective H/C ratio in the range of 0 to 1, thereby indirectly replacing olefins.

These considerations mainly apply to the carbohydrate fraction of lignocellulosic biomass. Since lignin does not possess a well-defined structure, performing selective chemistry on this resource is particularly challenging. Currently, the best approach for converting lignin appears to involve gasification to yield synthesis gas. This approach presents a route either through methanol to olefins or hydrocarbons via the methanol-to-hydrocarbons (MTH) process or directly to hydrocarbons in the transportation fuel regime through Fischer–Tropsch synthesis.

The considerations above assume that processes exist that can convert biomass to desired products, which is not the situation in all cases. The fossil platform chemicals are produced in chemical reactions that utilize the inherent chemistry of naphtha, that is, its ability to undergo fragmentation reactions at high temperatures leading to olefins and cyclodehydrogenation reactions leading to aromatics. To efficiently convert biomass to fuels or chemicals, it is similarly necessary to exploit the chemical pathways that sugars are likely to undergo and identify catalysts and conditions that promote these. In biological systems, retroaldol condensation reactions are central for the conversion of hexoses (glycolysis), and nature has optimized this pathway with a series of enzymes, leading to the efficient production of compounds such as ethanol and lactic acid from biomass. It is also possible to use inorganic catalysts to promote this type of chemistry. An example is the conversion of fructose to lactic acid using Lewis acidic zeolites,[11] Here, the hexose first fragments to form two triose sugars, which are isomerized into lactic acid (Scheme 1). The lactic acid can be used directly,[12,13] or it can be dehydrated to produce acrylic acid, which is currently produced from propylene. This situation would represent an ideal use of biomass, since the effective H/C ratio of sugar and acrylic acid are both 0, thus negating the need for redox reactions.

Another pathway that sugars are likely to undergo is cyclodehydration leading to furan-type products such as furfural and 5-hydroxymethylfurfural (5-HMF).[14] These chemicals have little use in themselves, but they can be further converted into more useful compounds such as levulinic acid and γ-valerolactone (GVL, Scheme 2). GVL...
could be an interesting platform chemical for the production of polymers \[15,16\] as well as a central intermediate if the desired end products are hydrocarbons. \[17\] By removing oxygen in the form of fully oxidized species, such as carbon dioxide, which have no heating value, little energy is lost and the energy content of the product per carbon atom is effectively increased. \[18\] Further upgrade of GVL to butene can be achieved by the release of a second carbon dioxide molecule. \[19–22\] These combined reactions constitute a very elegant pathway from hexoses with an effective H/C ratio of 0 to hydrocarbons with a ratio of 2. The price for upgrading the biomass is paid by the co-production of carbon dioxide. This reaction pathway is well-suited for fuel production, since a significant energy densification has taken place.

In a scenario where there is a renewable electricity surplus or large fluctuations in the electricity production, yet other options may become attractive. In this case, storing the surplus energy as chemical energy in organic molecules, such as hydrocarbons, provides an ideal solution. This will require large amounts of hydrogen, which is currently produced almost exclusively by steam reforming of fossil natural gas, but which could also be supplied by electrolysis. For instance, sorbitol can be hydrodeoxygenated to yield alkanes in the C\textsubscript{1}–C\textsubscript{6} range using a bifunctional hydrogenation/acid catalyst. \[23\] In addition to allowing for relatively simple storage of energy in molecules, this approach has the further advantage that the products are compatible with the existing petrochemical infrastructure. Another approach is the hydrolysis of biomass feedstocks to yield propylene and ethylene glycols, as shown in Scheme 3. This conversion can be performed by combining basic and noble-metal catalysts. In this manner high-value chemicals, traditionally produced from crude oil, can be selectively prepared from carbohydrates. \[24–26\]

Additionally, concentrated carbon dioxide could be seen as a resource rather than a by-product, and the carbon dioxide formed in the upgrade of hexoses to hydrocarbons or during ethanol fermentation can be used to produce methanol. In this way the surplus energy can be used to increase the pool of useful carbon atoms for chemicals and fuel purposes.

**Different Value Chains in the Conversion of Biomass**

It is useful to discuss value chains of chemicals to get a simple overview of the necessary conversion and purification steps in the production of target chemicals from renewable resources. \[2\] When addressing the issue of how biomass can be converted into useful chemical products, we propose that two overall strategies can be undertaken. Figure 3 summarizes these two strategies through renewable chemical value chains and their fossil counterparts. The strategies differ in their compatibility with the existing fossil value chain and therefore also in the extent to which existing processing technology and infrastructure can be adapted (see also box). Both value chains start with a biomass resource, which is converted to a higher-value product by means of either a conversion or a purification step.

**Drop-in strategy**
- existing value chain
- utilizes existing infrastructure
- mature market

**Emerging strategy**
- new value chain
- requires new infrastructure
- emerging market

![Figure 3](https://example.com/figure3.png)

*Figure 3.* Two overall different value chains in the utilization of biomass depending on the compatibility with existing infrastructure and fossil value chain.

The “drop-in” strategy is characterized by the conversion of a biomass resource into a platform from which existing
intermediates can be obtained. Typically the challenges are to develop a competitive process targeted towards a predetermined end product and initially to compete with fossil equivalents. An example of this strategy is the conversion of sugar cane or corn (biomass resources) by fermentation into ethanol (platform chemical) and then by dehydration into ethylene, which can serve as an intermediate for polymerization, oxidation, halogenation, alkylation, or other reactions to produce target chemicals or products. In this approach the scene is already set; the product can enter a mature market, and furthermore a large part of the necessary infrastructure and technology already exists to capitalize upon the value-added chemical product. Note that the point of entry from the renewable value chain does not necessarily lie before the existing fossil intermediate. They may also converge later in the value chain. This is the case with target chemicals such as propylene glycol made from glycerol, for which the market may not yet be fully matured and which as such represent borderline cases.

The “emerging” strategy given in Figure 3 represents a completely new value chain with an emerging product in the end. This situation imposes several challenges as compared to the former, albeit also advantages. Typically the final product does not have to compete directly with existing products, and the inherent functionality present in the parent compound or biomass feedstock can be exploited to a much larger extent. The product may emerge as a consequence of utilization of the functionality of the feedstock or of the most suitable and cost-effective conversion route for the feedstock, rather than the resource needing to be converted into an already-existing product. In this case, new markets may have to be developed; the entire technology to produce the added-value chemical should be developed or, at best, extensive modification of existing technology is required. This approach therefore requires extensive initial investments and long-term commitment compared to the former “drop-in” strategy. At present, possible examples could include 2,5-furandicarboxylic acid or levulinic acid ketals, which are both products of hexose dehydration reactions. Both of these are, however, still at an early development stage.

Ethylene (“Drop-In” Strategy)

Ethylene is currently the organic chemical with the highest worldwide annual production (ca. 110 Mt y\(^{-1}\)). Almost 80% is used in the production of polymers, primarily polyethylene (PE), and 12% is used for ethylene oxide and glycol.[12] The production is primarily based on cracking of naphthas,[12] which induces only a small change in H/C ratio (< 0.33), however, it can also be produced from fermentation of carbohydrates into ethanol and subsequent dehydration, a process with large changes in H/C ratios from the starting material to the ethylene platform (\(\Delta(H/C) = 2.0\)) and with further fluctuations if the ethylene is converted to ethylene glycol or oxide, for example (\(\Sigma(\Delta(H/C)) \geq 3.0\)). The first move in this field came from the Brazilian company Braskem, who in 2010 launched a 200,000 ty\(^{-1}\) production of ethylene (0.17% of total world demand), with further processing into PE.[13] No modifications to downstream processing of ethyl-

eone are necessary, as existing infrastructure already exists, which is also what makes it a drop-in approach. Furthermore, the technology for fermentation of sugars into ethanol is well-known. These factors represent large advantages, as require relatively small capital investments are required and all steps are well known, including the dehydration step from ethanol into ethylene. However, it is also apparent that only a small fraction of the ethylene produced from petroleum can be replaced in this way owing to the sheer amount of ethylene produced.

Hexose Dehydration Products (“Emerging” Strategy)

The dehydration product of hexose sugars, 5-HMF, can be oxidized to furan-2,5-dicarboxylic acid, a possible alternative to terephthalic acid for polymer production,[13,36] or hydrogenated to 2,5-dimethylfuran, an octane booster with excellent blending properties.[33] Although a significant amount of research has gone into optimizing the process, no industrial or pilot-scale process has yet been demonstrated. A significant problem in the process is the rehydration of HMF to levulinic acid and formic acid, a reaction which is also catalyzed by acids. An alternative approach is to instead use levulinic acid as the platform chemical, thus avoiding the problem of stabilizing the intermediate. Recently, a large amount of research has gone into this approach.[15,36,37,38] Currently, the U.S. company Segitis has started up a process in which ketals are produced from the levulinic acid platform with a production of 136 ty\(^{-1}\) of levulinic acid ketals, with plans for a second plant.[37,38] Although no large-scale market currently exists for these ketals, they can possibly find use as non-petroleum-based plasticizers and solvents and as polyols for polymer production. Specifically, Segitis is working together with PolyOne to develop the use of these ketals as plasticizers. The need for extensive process development and construction of infrastructure defines this as an emerging strategy. As such, significant investments are necessary; however, the facile nature of the hexose dehydration reaction makes this an interesting route.

Propylene Glycol (A Strategy In Between)

Propylene glycol (PG) has a medium-size existing market (currently ca. 1.4 Mt y\(^{-1}\)),[39] but an even larger potential market can be envisioned (> 2 Mt y\(^{-1}\)) because it, among other uses, is suitable for deicing purposes. Compared to a currently produced deicer, ethylene glycol (EG), which is produced by conventional petrochemical methods and with a large existing production (> 6 Mt y\(^{-1}\)), PG is nontoxic and thus has a large advantage over its petrochemical analogue. PG can be produced from glycerol that today should be regarded as a renewable resource or perhaps even a renewable platform.[41] When the changes in H/C ratio are considered in the production of the two glycols, they are somewhat similar. For EG production, crude oil or naphtha is converted into ethylene and further into EG by oxycarboxylation, with an overall \(\Delta(H/C)\)of about 1.0. Starting from glycerol, the oxycarboxylation is, to a small extent, removed when it is converted into PG, leading to \(\Delta(H/C) = 0.67\). Several companies have announced their production of PG from glycerol, including Archer Daniels Midland (ADM),
Cargill/Ashland, and Senergy. ADM has furthermore developed a process where sorbitol, derived from corn, can also be used as a feedstock and thus introduced several renewable value chains ending with PG, allowing for a large flexibility in the feedstock. As the renewable value chain enters an existing value chain at a late stage, this way to PG can be placed in the borderline between the drop-in and emerging strategies and is a good example of how things are not always clear-cut.

Current Trends in Industry

Currently we observe the production and development of chemicals from biomass in industry to be motivated by at least three overall factors. In some cases, the knowledge and technology is already present to process one type of biomass resource, demanding only small capital investments, whereby the low-value nature of certain biomass feedstocks may be exploited. The results may also be products with no petrochemical equivalents, such as lactic acid or furfural, that can already compete on completely commercial terms. Especially microbial production of C2–C6 acids is a fast-evolving approach mainly driven by large developments in biotechnology and metabolic engineering.[27] A second factor is the answer to a general demand for renewable or “green” products from the consumer, exemplified by the PlantIBottle from the Coca-Cola company. Such initiatives furthermore give a sustainable image to all agents involved in the value chain—something everybody can benefit from. Thirdly, on the political side, subsidies and funding is provided to reduce the dependence on fossil resources and to decrease the environmental impact. This is most visible for the conversion of biomass to transportation fuels, owing to their large consumption, as exemplified by the U.S. ethanol industry.

As an analogue to the petrochemical refinery, the concept of a biorefinery has emerged to integrate production of fuels, power, and chemicals for maximum efficiency; a subject that has attracted much scientific interest during the last ten years. Although only about 5–10% of the crude oil is converted into chemicals, these generate roughly 50% of the profit in current petrochemical refineries.[28] Since this ratio will most likely not change drastically in future biorefineries, it indicates the large economic potential in producing chemicals from biomass. In general, the price of transportation fuels is determined by the feedstock price as an effect of more than 100 years of optimization in oil refineries, making them extremely efficient. The conversion of biomass has yet to undergo any significant optimization, and the price of fuels from biomass is still governed by the cost of processing, making it difficult to become competitive with fossil counterparts. On the other hand, the processing costs when chemicals are produced from oil account for a much larger portion of the total costs, which should make it easier for the renewable value chain to become competitive and thus be implemented in large scale.

The annual production of oleochemicals (chemicals produced from fats and vegetable oils) is in the range of 10–15 Mt · yr−1.[29–31] Although this volume is by no means as large as the petrochemical industry, it illustrates that large-scale production of chemicals is possible when biomass is used as a feedstock. It is interesting to note that some of the major oleochemical producers are joint ventures between traditional chemical producers and plantation operators. This situation further illustrates that the conversion of biomass requires a number of diverse competences; from the production and extraction of feed, thus ensuring a good raw material quality, to the more conventional chemical conversion of platform chemicals into target chemicals. Few corporations currently possess all of these competencies in-house, especially where lignocellulosic feedstocks are concerned. Therefore it is common to see strategic alliances formed between companies to ensure that all steps in the value chain are covered.

Table 1 lists a number of potential and current bulk chemicals that can be produced from biomass, together with some of the major players and alliances involved in the development and production from biomass resources. For each chemical, the market type is also indicated: either an existing market (typically of the petrochemical equivalent) or an emerging market, wherefrom the overall strategy and value chain (as discussed earlier) can be deduced. Large corporations active in the field of renewable chemicals have primarily chosen to focus on existing and large markets, such as ethylene, propylene, acrylic acid, and epichlorohydrin with little uncertainty of demand. As described earlier, these chemicals have to compete with the existing petrochemical products, which will require a high degree of optimization of the processing steps. Conversely, the development of products for emerging markets for example, C6 diacids, 5-HMF, and levulinic acid derivatives are governed by smaller budgets, and typically academia spin-offs are involved owing to the higher risks attributed to uncertainty and long-term commitment.

A Renewable Chemical Industry

As mentioned above, the vast majority of biomass used in industry today is burned to generate electricity. This use seems injudicious, as on-grid energy production is the sector where fossil resources can most easily be replaced by alternative sources such as wind, geothermal, or nuclear. Thus, upgrading of the biomass to higher-value products to replace crude oil seems a more sensible approach. As seen in Figure 1, the majority of crude oil is converted into transportation fuels, and it would therefore initially seem as though the replacement of this fraction would be the most crucial. There are, however, a number of problems with this approach, as outlined above: the amount of available biomass, the significantly different characteristics of transportation fuels and biomass, and lastly, the fact that transportation fuels are relatively low-value products. Instead, energy for transportation needs could be mediated through batteries or fuel cells, with the energy for these being produced by the above-mentioned on-grid energy sources. Fuel production from biomass should be limited to applications where electrical power is not a feasible alternative, for example, for aviation and marine applications. This approach will, however, require an extensive modification of the current transportation...
If biomass is instead used as a feedstock for the chemical industry, many of the problems associated with fuel production are avoided. The currently available biomass should be sufficient to replace fossil resources for the production of chemicals, and the characteristics of biomass and many bulk chemicals are similar. Furthermore, by sensible choice of target chemicals, the value addition could be significantly higher. Since the cost of developing the necessary processes can be significant, and because the initial process will inevitably be relatively inefficient, it makes sense to focus on high-value products, allowing for faster widespread adoption. The challenges in this case will be the development of efficient processes for the collection, handling, and pretreatment of biomass and for the selective conversion of biomass feedstocks; these are processes that in general only exist for the edible parts of biomass today. Since these challenges are present irrespective of the final use of the biomass resources as chemicals or fuels, the current research into second-generation biofuels will also benefit the future renewable chemical industry. This relationship is further emphasized by the fact that many of the compounds currently produced by the biofuels industry, either as the main product or as byproducts, could be interesting platform chemicals for the chemical industry: Ethanol could be used as a starting point for producing acetic acid, ethylene, or ethylene glycol, while glycerol can be dehydrated to acrolein, which can be further converted into acrylic acid.[2,31] Thus in the short term, the production of transportation fuels is a good way of establishing the infrastructure needed for large-scale industrial utilization of biomass while alternative uses of biomass are being developed and at the same time the consumption of fossil resources in the transportation sector is reduced.

The production of transportation fuels from biomass, however, relies on the premise that biomass is a resource available in excess amounts, a premise which will likely not hold in the future. Thus careful consideration is needed when determining how to utilize the available resources to the fullest, both in terms of maximizing profits and in terms of minimizing the consumption of fossil resources. For this decision the cumulative change in the effective H/C ratio of the overall process, from feedstock to target chemical, is a simple measure of the efficiency of a given reaction path; excessive fluctuations should be avoided to minimize energy and mass losses. Instead of attempting to forcefully convert the feedstock into platforms that were chosen because they were convenient to produce from fossil resources, the inherent functionality of the new feedstock should be utilized to the fullest extent possible by clever design of the reaction pathway and through catalytic control. When new value chains starting from biomass are developed, high-value chemicals should be targeted initially to ensure that the process is economically feasible despite the relatively high processing costs, which must be expected. As these value chains mature, they can be branched out to encompass an increasingly larger fraction of the chemical industry. The shift from a fossil-based chemical industry to one based on biomass still poses many challenges, but the possibilities are also great: to develop a more sustainable chemical industry utilizing a more versatile feedstock supply and producing products with superior properties.

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**Table 1: Overview of chemicals that are currently produced, or could be produced, from biomass together with their respective market type, size of the market, and potential biomass feedstock. Major players involved are also given.**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Market type</th>
<th>Market size (Mt y(^{-1}))[a]</th>
<th>Major player(s)</th>
<th>Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>existing</td>
<td>9.0</td>
<td>–</td>
<td>ethanol glycerol or glucose</td>
</tr>
<tr>
<td>acrylic acid</td>
<td>existing</td>
<td>4.2</td>
<td>Arkema, Cargill/Novozymes</td>
<td>glycerol or glucose</td>
</tr>
<tr>
<td>C4 diacids</td>
<td>emerging</td>
<td>(0.1–0.5)</td>
<td>BASF/Purac/CSM, Myriant</td>
<td>glucose</td>
</tr>
<tr>
<td>epichlorohydrin</td>
<td>existing</td>
<td>1.0</td>
<td>Solvay, DOW</td>
<td>glycerol or glucose</td>
</tr>
<tr>
<td>ethanol</td>
<td>existing</td>
<td>60</td>
<td>Cosan, Abengoa Bioenergy, ADM</td>
<td>glucose or ethanol</td>
</tr>
<tr>
<td>ethylene</td>
<td>existing</td>
<td>110</td>
<td>Braskem, DOW/Crystalsev, Borealis</td>
<td>glucose or xylitol</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>existing</td>
<td>20</td>
<td>India Glycols, Dacheng Industrial</td>
<td>glucose or xylitol</td>
</tr>
<tr>
<td>glycerol</td>
<td>existing</td>
<td>1.5</td>
<td>ADM, R&amp;G, Cargill</td>
<td>vegetable oil fructose</td>
</tr>
<tr>
<td>5-hydroxyethylfurufural</td>
<td>emerging</td>
<td>(≥0.5)</td>
<td>Novozymes/Cargill</td>
<td>fructose glucose</td>
</tr>
<tr>
<td>3-hydroxypropionic acid</td>
<td>emerging</td>
<td>(≥0.5)</td>
<td>–</td>
<td>glucose</td>
</tr>
<tr>
<td>isoprene</td>
<td>existing/emerging</td>
<td>0.1 (0.1–0.5)</td>
<td>Danisco/Goodyear</td>
<td>glucose</td>
</tr>
<tr>
<td>lactic acid</td>
<td>existing/emerging</td>
<td>0.3 (0.3–0.5)</td>
<td>Cargill, Purac/Akema, ADM, Galactic</td>
<td>glucose</td>
</tr>
<tr>
<td>levulinic acid</td>
<td>emerging</td>
<td>(≥0.5)</td>
<td>Segetis, Maine Bioproducts, Le Calorie</td>
<td>glucose</td>
</tr>
<tr>
<td>oleochemicals</td>
<td>existing</td>
<td>10–15</td>
<td>Emery, Croda, BASF, Vantage, Oleochemicals</td>
<td>vegetable oil fat</td>
</tr>
<tr>
<td>1,3-propanediol</td>
<td>emerging</td>
<td>(0.1–0.5)</td>
<td>Dupont/Tate &amp; Lyle</td>
<td>glucose</td>
</tr>
<tr>
<td>propylene</td>
<td>existing</td>
<td>80</td>
<td>Braskem/Novozymes</td>
<td>glucose</td>
</tr>
<tr>
<td>propylene glycol</td>
<td>emerging</td>
<td>(≥2.0)</td>
<td>ADM, Cargill/Ashland, Senergy, Dacheng Industrial</td>
<td>glycerol or sorbitol</td>
</tr>
<tr>
<td>polyhydroxyalkanoate</td>
<td>emerging</td>
<td>(0.1–0.5)</td>
<td>Metabolix/ADM</td>
<td>glucose</td>
</tr>
</tbody>
</table>

[a] Market size of an existing market is given as its current size including production from fossil resources; for emerging markets the expected market size is reported in parenthesis.
Tin-containing silicates: structure–activity relations

BY CHRISTIAN M. OSMUNDSEN1,2, MARTIN SPANGSBERG HOLM1, SØREN DAHL2 AND ESBEN TAARNING1,*

1Research and Development Division, Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs., Lyngby, Denmark
2Department of Physics, Technical University of Denmark, Lyngby, Denmark

The selective conversion of biomass-derived substrates is one of the major challenges facing the chemical industry. Recently, stannosilicates have been employed as highly active and selective Lewis acid catalysts for a number of industrially relevant reactions. In the present work, four different stannosilicates have been investigated: Sn-BEA, Sn-MFI, Sn-MCM-41 and Sn-SBA-15. When comparing the properties of tin sites in the structures, substantial differences are observed. Sn-beta displays the highest Lewis acid strength, as measured by probe molecule studies using infrared spectroscopy, which gives it a significantly higher activity at low temperatures than the other structures investigated. Furthermore, the increased acid strength translates into large differences in selectivity between the catalysts, thus demonstrating the influence of the structure on the active site, and pointing the way forward for tailoring the active site to the desired reaction.

Keywords: stannosilicate; biomass; catalysis; zeolite; infrared

1. Introduction

The selective conversion of biomass to fuels and chemicals is one of the major challenges facing the chemical industry in the twenty-first century (Ragauskas et al. 2006). Owing to the significantly different nature of biomass compared with fossil resources, current conversion technologies cannot be directly applied and new catalytic systems and catalysts need to be developed (Christensen et al. 2008; Vennestrøm et al. 2011). In this regard, stannosilicates have recently attracted significant attention as highly active and selective Lewis acid catalysts in a number of reactions involving biomass-derived substrates, such as monosaccharide isomerization (Moliner et al. 2010; Román-Leshkov et al. 2010; Nikolla et al. 2011), retro aldol condensations (Holm et al. 2010), hydride shifts (Taarning et al. 2009; Holm et al. 2010; Li, L. et al. 2011), as well as a number of other reactions including Meerwein–Ponndorf–Verley–Oppenauer (MPVO) redox reactions (Corma et al. 2002, 2003; Boronat et al. 2006a,b; Sasidharan et al. 2009) and Baeyer–Villiger oxidations (Boronat et al. 2005, 2006b, 2009; Sasidharan et al. 2009; Li, P. et al. 2011). In particular, tin atoms incorporated in zeolite beta have

*Author for correspondence (esta@topsoe.dk).

One contribution of 14 to a Special feature ‘Recent advances in single-site heterogeneous catalysis’.
been shown to be highly active sites for these reactions; however, owing to the
difficulty in preparing Sn-beta, other materials have been investigated, such as
the mesoporous stannosilicate Sn-MCM-41 (Li, L. et al. 2011).

The incorporation of acid functionality in silicates is most well known with
the incorporation of aluminium in zeolites to impart Brønsted acidity. Several
other heteroelements, such as Ti, Zr, Sn, Nb, Ta and V (Taramasso et al. 1983;
Valencia & Corma 2001; Corma et al. 2003, 2009; Zhu et al. 2004; de la Torre
et al. 2010), have been incorporated in zeolite structures, but these elements do
not introduce a charge imbalance like that responsible for the Brønsted acidic
behaviour of aluminium-containing zeolites. In some cases, other functionalities
can arise, such as the ability of titanium silicalite-1 (TS-1) to catalyse
epoxidations (Thomas et al. 2005; Fan et al. 2009). The incorporation of isolated
tin atoms has been shown to impart a strong Lewis acid functionality to silicates
(Corma et al. 2003). The tin atoms, substitute individual silicon atoms, giving
rise to electron-deficient active sites, which are able to coordinate to an electron
donor, e.g. the carbonyl oxygen of carbohydrates. Although direct isomorphous
substitution of silicon with tin is possible, several studies (Boronat et al. 2005,
2006a, 2007, 2009) have shown that the active site in Sn-beta is partially
hydrolysed, as shown in figure 1. It has further been claimed that the hydroxyl
group acts as a base, thereby creating a bifunctional active site, critical for the
activity of the catalyst (Boronat et al. 2007).

Furthermore, the partial hydrolysis of the tin site increases the Lewis acidity
of the tin site; a thesis that has been corroborated by both theoretical
calculations and experimental observations (Boronat et al. 2005). Whether other
stannosilicates possess several distinct tin sites in a similar fashion is less clear.
Studies of probe molecules dosed onto Sn-MCM-41 have indicated that, in
addition to the sites present in Sn-beta, doubly hydrolysed tin sites are also
present (Boronat et al. 2009). Conversely, in Sn-MFI, only fully incorporated tin
atoms were observed (Boronat et al. 2009). Although the catalytic properties of
stannosilicates differ significantly between structures, no thorough understanding
of the nature or causes of these differences has been developed—an understanding
that is necessary for the design of improved catalysts (Thomas et al. 2005, 2009).
Thus, the present work focuses on the comparison of different stannosilicates in
a range of carbohydrate conversion reactions, and on relating these results to the
Lewis acidity of the active sites as measured by infrared (IR) spectroscopy to
elucidate the effect of the structure on the catalytic properties of the materials.

2. Experimental

Tin atoms were incorporated into the framework of zeolites silicalite-1 (MFI)
and beta (BEA), with a Si/Sn ratio of 200. Furthermore, two mesoporous
stannosilicates, MCM-41 and SBA-15, were prepared with tin atoms incorporated
in the structure with Si/Sn ratios of 50 and 200, respectively.

Figure 1. Tin sites in zeolite Sn-beta: (a) isomorphously substituted and (b) partially hydrolysed.
Sn-BEA (Holm et al. 2010) was prepared by mixing 29.0 g of tetraethylammonium hydroxide (TEAOH; 40 wt.%) with 4.0 g of water. To this mixture, 30.6 g of tetraethyl orthosilicate (TEOS), was added and the mixture was stirred for 90 min. A solution of 0.26 g of SnCl$_4$·5H$_2$O in 4.0 g of water was added slowly. The mixture was stirred to allow the TEOS to hydrolyse and the formed ethanol to evaporate. A mixture of 3.1 g of HF (47–51 wt.%) and 3.0 g of water was added slowly, forming a white rigid gel. A suspension of 0.36 g of dealuminated zeolite beta seeds, prepared according to the procedure described in the patent of Valencia & Corma (2001), in 3.0 g of water was mixed with the synthesis gel. The final gel had an approximate composition of 1 Si : 0.005 Sn : 0.5 TEA$^+$ : 0.5 F$^-$ : 8 H$_2$O. The gel was transferred to a Teflon-lined autoclave and crystallized at 140°C for 12 days.

Sn-MFI (Mal et al. 1997) was prepared by dissolving 5.35 g of NH$_4$F in 25.0 g of water. A solution of 0.25 g of SnCl$_4$·5H$_2$O in 10.0 g of water was added slowly with rapid stirring, followed by a solution of 9.8 g of tetrapropylammonium bromide (TPABr) in 56.0 g of water. In this mixture, 8.6 g of fumed silica was dissolved. The mixture was stirred for 3 h to yield a gel with the approximate composition of 1 Si : 0.005 Sn : 0.26 TPA$^+$ : 1 F$^-$ : 35 H$_2$O. The gel was transferred to a Teflon-lined autoclave and crystallized at 200°C for 6 days.

Sn-MCM-41 (Li, L. et al. 2011) was prepared by dissolving 13.0 g of hexadecyltrimethylammonium bromide (CTAB) in 38.0 g of water. To this solution of 26.4 g of tetramethylammonium silicate (TMAS; 15–20 wt.%) was added slowly, and the mixture was stirred for 50 min. The desired amount of SnCl$_4$·5H$_2$O and HCl (37 wt.%) was dissolved in 2.1 g of water and the solution added slowly. The mixture was stirred for a further 1.5 h, at which point 12.2 g of TEOS was added. The mixture was stirred for 3 h to give a gel with an approximate composition of 1 Si : X Sn : 0.44 CTAB : 0.27 TMA : 0.08 Cl$^-$ : 46 H$_2$O, with X being either 0.02 or 0.005. The gel was transferred to a Teflon-lined autoclave and heated to 140°C for 15 h.

SBA-15 (Ramaswamy et al. 2008) was prepared by dissolving 8.0 g of Pluronic P-123 (PEG-PPG-PEG polymer, M$_w$ = 5800 g mol$^{-1}$) in 60.0 g of water. A solution of 1.0 g of HCl (37 wt.%) in 140 g of water was added, and the mixture stirred for 2 h. Then, 18.0 g of TEOS and the desired amount of SnCl$_4$·5H$_2$O dissolved in 2.0 g of water was added slowly. The mixture was stirred for 24 h at 40°C to give a gel with an approximate composition of 1 Si : X Sn : 0.016 P123 : (0.12 + X) Cl$^-$ : 134 H$_2$O, with X being either 0.005 or 0.02. The gel was transferred to a Teflon-lined autoclave and heated to 100°C for 24 h.

All of the catalysts were isolated by suction filtration and washed with ample water. The catalysts were dried overnight at 80°C and calcined in static air at 550°C for 10 h (heating rate: 2°C min$^{-1}$).

The diffraction pattern of the samples was measured by powder X-ray diffraction on a Phillips X’Pert diffractometer using Cu-Kα radiation. The elemental composition of the solid materials was determined by atomic emission spectroscopy (ICP-OES) measured on a Perkin Elmer model Optima 3000, Varian Vista. Elemental analysis of reaction liquids was performed on an Agilent 7500ce ICP-MS. Pore volume and surface area measurements were performed by multipoint N$_2$ adsorption/desorption on a Quantachrome Autosorb automatic surface area and pore size analyser. The surface area and micropore volume were calculated using the BET and $t$-plot methods, respectively. The computer
program AUTOSORB 3 was used for the data treatment. SEM pictures were taken with a Quanta scanning electron microscope. The samples were made conductive by depositing a silver layer. Measurements of the IR spectra of the samples were performed on a BioRad FTS 80 spectrometer equipped with an MCT detector operated in transmission mode. The samples were pressed into self-supporting wafers and mounted in a Pyrex measurement cell with NaCl windows that was connected to a vacuum line. Samples were dehydrated before analysis at 375°C for at least 2 h. Probe molecule studies were performed by subjecting the sample to small aliquots of deuterated acetonitrile. The probe molecule was then slowly desorbed by subjecting the sample to reduced pressure for short periods of time, and the spectrum recorded between each desorption.

The conversion of triose sugars to methyl lactate was performed by dissolving 110 mg of the triose dimer, either 1,3-dihydroxyacetone (DHA) or glyceraldehyde (GLA), in 4.0 g of methanol. A total of 80 mg of catalyst was added and the mixture sealed in a glass vial and heated to the desired reaction temperature. The reaction was allowed to proceed for 24 h with stirring. A blank experiment was performed with purely siliceous zeolite beta.

To test the conversion of sucrose to methyl lactate, 450 mg of sucrose was dissolved in 15.0 g of methanol and 150 mg of catalyst was added. The mixture was sealed in a stirred autoclave and heated to 160°C for 16 h. A blank experiment was performed with purely siliceous zeolite beta. The spent catalyst was regenerated by calcination at 550°C for 10 h.

The isomerization of glucose to fructose was performed by adding 50 mg of catalyst to 5.0 g of a glucose solution (2 wt.% in water or 1 wt.% in methanol). The mixture was sealed in a glass vial and heated to the desired reaction temperature with stirring. Individual experiments were performed for different sampling times.

After reaction, the catalyst was removed using a syringe filter, and the reaction mixtures were analysed by gas chromatography (GC) and high-performance liquid chromatography (HPLC). Methyl lactate was quantified by GC analysis on an Agilent 7890A gas chromatograph equipped with an HP-Innowax column and a flame ionization detector. All other compounds were separated by HPLC on an Agilent 1200 series liquid chromatograph equipped with an Aminex HPX-87H column operating at 65°C. The eluent was 0.004 M H₂SO₄ with a flow rate of 0.6 ml min⁻¹. The analytes were quantified with an refractive index detector. The column did not produce adequate separation of fructose and mannose; however, as the response factors of the two compounds are nearly identical, they were treated as a single compound, and quantified with the response factor of fructose. Owing to the acidic eluent, all acetals present in the reaction liquids were hydrolysed and thus quantified as such.

3. Results and discussion

The diffraction patterns of the zeolites, shown in figure 2, confirm that zeolites MFI and BEA have been formed with a high degree of crystallinity. No unassigned diffraction lines corresponding to tin oxide were observed. The diffraction patterns of the mesoporous stannosilicates (not shown) clearly demonstrate the amorphous nature of the samples as no diffraction lines were observed at angles higher than 5°. At lower angles, shown in figure 3, diffraction lines corresponding to
the (100), (110) and (200) reflections were observed, arising from the order of the mesopores. The measured angles correspond to a $d_{100}$ spacing of roughly 106 Å for the SBA-15 structures and 41 Å for the MCM-41 structures. A slight increase in the $d$-spacing is observed with increasing tin content for both structures. These results are in good agreement with previously reported values (Selvaraj & Choe 2010; Li, L. et al. 2011). Measurements of the surface area and pore volume of the materials further confirmed that highly porous structures had been formed, in agreement with the expected structures. Elemental analysis shows a high degree of incorporation of tin in the zeolite structures; however, in the case of the mesoporous stannosilicates, the incorporation varied significantly (table 1).

SEM pictures of the materials (figure 4) show distinctly different morphologies. The Sn-BEA crystals are very small (less than 1 μm) spherical particles, while Sn-MFI has large coffin-shaped crystals with a length in excess of 20 μm. The large particle size in combination with the narrow pore system of the MFI structure means that severe diffusion limitations must be expected for this catalyst. The appearance of the mesoporous stannosilicates also differs significantly; Sn-MCM-41 does not appear to have a distinct particle shape, which is not surprising owing to the amorphous nature of the sample. Sn-SBA-15, on the other hand, presents as hexagonal discs. This particle shape seems to fit well with the two-dimensional hexagonal ordering of the pore system in SBA-15.

The IR spectra taken of the zeolites (not shown) do not display any significant band around 3700 cm$^{-1}$, which is assigned to framework defects, indicating a very low defect concentration, as expected for zeolites prepared by the fluoride route. The IR spectra of deuterated acetonitrile dosed onto the materials are shown in figure 5. All of the spectra display a prominent band at approximately 2275 cm$^{-1}$, arising from acetonitrile interacting with the silanol groups of the material, and a second band at 2266 cm$^{-1}$, which is caused by physisorbed acetonitrile (Boronat et al. 2005). For the mesoporous stannosilicates, the second band was only observed at very high loadings of acetonitrile (not shown). The bands caused
Figure 3. Diffraction pattern of the mesoporous stannosilicates.

Table 1. Characterization of the prepared materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sn (wt.%)</th>
<th>DOI a (%)</th>
<th>Surface area (m² g⁻¹)</th>
<th>Pore volume (ml g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-BEA (200)</td>
<td>0.86</td>
<td>87</td>
<td>480 390</td>
<td>0.29 0.20</td>
</tr>
<tr>
<td>Sn-MFI (200)</td>
<td>0.82</td>
<td>82</td>
<td>365 190</td>
<td>0.20 0.10</td>
</tr>
<tr>
<td>Sn-MCM-41 (50)</td>
<td>2.70</td>
<td>68</td>
<td>1245 0</td>
<td>1.29 0</td>
</tr>
<tr>
<td>Sn-MCM-41 (200)</td>
<td>0.49</td>
<td>49</td>
<td>1114 0</td>
<td>1.26 0</td>
</tr>
<tr>
<td>Sn-SBA-15 (50)</td>
<td>0.99</td>
<td>25</td>
<td>1229 24</td>
<td>1.67 0.01</td>
</tr>
<tr>
<td>Sn-SBA-15 (200)</td>
<td>0.61</td>
<td>61</td>
<td>1354 52</td>
<td>1.80 0.03</td>
</tr>
</tbody>
</table>

aDegree of insertion; the ratio of Sn atoms detected by chemical analysis to the amount in the synthesis mixture.

bDetermined using the t-plot method.
by the tin sites were in the region 2305–2320 cm$^{-1}$. For Sn-BEA, two distinct bands were observed at 2308 and 2317 cm$^{-1}$, corresponding to the isomorphously substituted and hydrolysed tin sites, respectively (Boronat et al. 2005). The difference in adsorption strength between the sites is clearly seen in the difference in desorption rate; the intensity of the band arising from the isomorphously substituted site is rapidly reduced upon exposure to reduced pressure, while the other band remains virtually unchanged. A similar appearance is not observed for the other catalysts.

For Sn-MFI, a single band at 2310 cm$^{-1}$ was observed and a small band at 2290 cm$^{-1}$. The band at 2310 cm$^{-1}$ probably arises from isomorphously substituted tin, as is observed in Sn-BEA, but the lack of a band at higher wavenumbers indicates that the hydrolysed tin site is not present to any significant degree, demonstrating a significant difference between the BEA and MFI frameworks. The band at 2290 cm$^{-1}$ is unassigned, and it is thus not known whether this arises from a tin site or defects in the structure. The spectra of the two mesoporous stannosilicates look very similar, which is not surprising as the main difference between the structures is the size of the pores. They both
display a broad band centred at 2312 cm\(^{-1}\). Since the tin atoms are inserted in an amorphous structure, one would expect a broad range of possible local bonding arrangements, leading to a large variation in Lewis acid strength for the tin sites in the mesoporous stannosilicates, in agreement with the observed spectra. In this case, one would, however, also expect that the maximum of the band would gradually shift to higher wavenumbers as the probe molecules are desorbed (as is observed clearly for Sn-BEA) as the rate of desorption would be higher from the weaker sites. This does not appear to be the case, however—judging the adsorption strength simply from the observed shift may be an oversimplification.

Lactic acid is an important commodity chemical currently produced from carbohydrates by fermentation. The number of potential uses of lactic acid is vast (Gandini 2008; Serrano-Ruiz & Dumesic 2009; Pereira et al. 2011); however, the current relatively high price precludes many of these applications, thus improved processes for the production of lactic acid would be of great interest. An alternative catalytic process has been demonstrated, where lactic acid derivatives are prepared by the combined isomerization/esterification of triose sugars with a Lewis acid catalyst (Hayashi & Sasaki 2005; Janssen et al. 2007; Taarning et al.)
The reaction scheme is given in figure 6. The conversion was investigated over a wide range of temperatures with the prepared stannosilicate catalysts; the obtained yields are given in figure 7. As can be seen, at 120°C, all catalysts give high yields of methyl lactate (greater than 80%). The major compounds in the reaction mixture besides the product are the intermediate pyruvaldehyde (PA), present as the hemiacetal (PAHA), and the trioses. One of the major by-products typically produced is the diacetal PADA, formed by the Brønsted acid-catalysed second...

pathway shown in figure 6; however, this was not present in significant quantities. At a reaction temperature of 40°C, near quantitative yields are obtained with Sn-BEA, which is significantly better than all other tested catalysts, which gave less than 20 per cent. It is unlikely that this difference can be explained simply in terms of a higher number of active sites in the catalyst, but rather indicates that the active sites in Sn-BEA are capable of activating the substrate to a much greater extent. Even at 80°C, only Sn-MCM-41 (50) is able to give quantitative yields; however, this requires a tin content in the structure three times higher than in Sn-BEA. Using the bulk tin content of the samples as a measure of the number of active sites should however be done with great care, as the distribution between different types of sites is not necessarily identical between the structures, and furthermore, especially in the case of the mesoporous stannosilicates, not all tin atoms are necessarily accessible from the pore system. Finally, the effect of diffusion limitations should not be overlooked, although this will probably have a limited effect for this reaction owing to the small size of the substrate.

In figure 8, the composition of the product mixture obtained from the conversion of trioses at 40°C is given. It is very surprising to note the difference in distribution between the intermediates: for the Sn-SBA-15 and Sn-MCM-41 catalysts (and for Sn-BEA, although the high yield makes it difficult to conclude) the main intermediate is PA; however, for Sn-MFI, only relatively low amounts of this intermediate are present. Instead, a significantly larger fraction is present as the corresponding triose isomer of the substrate. The first step in the conversion of trioses to methyl lactate is the dehydration of the triose to PA, which appears to
Figure 9. Reaction scheme for the isomerization of glucose.

Figure 10. Distribution between hexoses after 48 h of reaction at 80°C in water.

Proceed rapidly for the SBA-15 and MCM-41 catalysts, followed by the formation of the PAHA. The significant amount of PAHA present indicates that the rate-limiting step is the hydride shift to yield methyl lactate. Conversely, for Sn-MFI, the large amount of the corresponding triose, and low amount of PAHA, indicates that the hydride shift to yield methyl lactate from PAHA and to interconvert the trioses is relatively fast and the rate-limiting step is instead the dehydration of the triose sugars. This difference in selectivity displayed by tin sites in different structures shows that the activity of the active sites cannot simply be judged from the strength of the Lewis acid sites, and may in fact indicate that different active sites are responsible for the dehydration and hydride shift reactions.

Sn-BEA is an effective catalyst for the isomerization of glucose to fructose and mannose in water (reaction scheme shown in figure 9; Moliner et al. (2010)). The isomerization was performed with a reaction time of 48 h and a reaction temperature of 80°C. The results are given figure 10. As can be seen, only Sn-BEA is capable of effectively catalysing the conversion; while Sn-BEA reached the equilibrium distribution within 8 h, none of the other catalysts was able to obtain conversions higher than 5 per cent in 48 h. The low conversion obtained by
Sn-MFI could be explained by severe diffusion limitations caused by the narrow pore system and the large crystal size. A similar explanation does, however, not hold for the mesoporous stannosilicates, where diffusion should not be a limiting factor. It could instead be caused by deactivation of the active sites by interaction with water. The active sites in the BEA zeolite, and for that matter in the MFI, will be more resistant to deactivation from water owing to the highly hydrophobic nature of the catalyst (Corma et al. 2003). Owing to the amorphous nature and large pore system of the mesoporous stannosilicates, a similar effect would not be observed for these.

To examine this further, we attempted to perform the isomerization in methanol (figure 11). Again, Sn-BEA displayed the highest activity, in this case reaching a maximum yield of 42 per cent within 4 h. However, in this case, conversion of hexoses to other compounds was significant, lowering the hexose mass balance to only 65 per cent at this reaction time. At longer reaction times, the mass balance was lowered further, to a point where only fructose and mannose were detected in the reaction mixture. This indicates that ketoses

Figure 11. Distribution between hexose sugars after isomerization at 80°C in methanol.
are significantly more stable than aldoses under these conditions. The significant decrease in hexose mass balance observed with Sn-BEA was not observed with the mesoporous stannosilicates, thus at longer reaction times higher yields of the isomerization products were obtained; Sn-MCM-41 gave a yield of approximately 75 per cent with no significant loss of hexoses after 17 h, while Sn-SBA-15 appears to approach a similar yield, although at a much slower rate. It thus appears that the deactivation of the active sites observed in water does not occur in methanol. Similarly to the results from the reaction run in water, Sn-MFI gave negligible conversion. Since Sn-MFI was demonstrated to efficiently catalyse the isomerization of trioses, the low conversion with the larger hexose substrate strongly indicates that the reaction is hampered by diffusion limitations.

The use of hexose sugars as the substrate for the production of methyl lactate (reaction scheme given in figures 6 and 12) is significantly more interesting owing to the lower cost of the feedstock compared with triose sugars, although it is also significantly more challenging; a number of alternative reaction pathways are possible, most notably dehydration to furanoic compounds and polymerization reactions leading to insoluble by-products, both of which lower the overall yield of methyl lactate significantly. The catalysts were tested for their activity in the conversion of sucrose to methyl lactate; the yields are given in figure 13. Again, Sn-BEA gives significantly higher yields—more than double the yield of the other catalysts. It is interesting to note the lack of difference between the other catalysts, all of them giving slightly more than 20 per cent yield. This further emphasizes the lack of correlation between the number of tin atoms in the structure and the number of active sites. The yield obtained using Sn-MFI is in fact surprisingly high; the size of the substrate, even after scission of the disaccharide to the constituent hexoses, will impose severe diffusion limitations, compounded by the size of the zeolite crystals. It is possible that the reaction only occurs at active sites located at the surface of the crystals or in the pore mouths.

Characterization of the catalyst used for the conversion of sucrose after regeneration showed no significant change in pore volume of the zeolite catalysts, as shown in table 2; however, the mesoporous stannosilicates lost a significant amount of their pore volume and BET surface area. This could simply be due to the deposition of carbon species in the pore system, which could not be removed by the regeneration procedure employed; however, since this procedure was identical for all catalysts, it seems more likely that the mesoporous structures are less stable at the conditions used for the hexose conversion. The stability of the zeolites and the mesoporous stannosilicates has previously been demonstrated, albeit at lower temperatures, in that the yield obtained with the catalysts did not
Tin-containing silicates

Figure 13. Obtained yield of methyl lactate from the conversion of sucrose at 160°C in methanol. The yield is calculated as the fraction of carbon atoms of the substrate that were incorporated in the product. The dashed line is the yield obtained using Si-BEA.

Table 2. Characterization of used catalyst after regeneration and elemental analysis of reaction liquid.

<table>
<thead>
<tr>
<th>sample</th>
<th>pore system retention</th>
<th>BET area (%)</th>
<th>pore volume (%)</th>
<th>leaching Sn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-BEA (200)</td>
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<td>100</td>
<td>100</td>
<td>5.9</td>
</tr>
<tr>
<td>Sn-MFI (200)</td>
<td></td>
<td>101</td>
<td>100</td>
<td>3.7</td>
</tr>
<tr>
<td>Sn-MCM-41 (50)</td>
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<td></td>
<td>88</td>
<td>88</td>
<td>4.1</td>
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<td>82</td>
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<tr>
<td>Sn-SBA-15 (200)</td>
<td></td>
<td>95</td>
<td>80</td>
<td>8.4</td>
</tr>
</tbody>
</table>

decrease upon re-use (Holm et al. 2010; Li, L. et al. 2011). This does not, however, conclusively demonstrate the stability of the active sites, as numerous factors influence the observed yield (Sheldon et al. 1998). To investigate the stability, the amount of metal which had leached into the reaction liquid was determined by elemental analysis. Significant amounts of tin species were present in the liquid, irrespective of the structure, and although this could possibly be partly ascribed to catalyst particles small enough not to be retained by the filtration or to the soluble extra-framework tin species, it indicates that the incorporated tin sites are not stable at the employed reaction temperature in liquid media. Previous
studies on similar materials have concluded that the active metal does not leach (Corma & Renz 2004; Li, L. et al. 2011); however, these were performed at lower temperatures, which could explain the discrepancy. To test whether leached tin species displayed catalytic activity, an experiment was performed where Sn-BEA was heated to 160°C in methanol for 3 h, and then removed by filtration. The substrate was added to the liquid and the reaction allowed to proceed. The yield obtained was identical to the blank run, thus the leached species are not catalytically active and the catalysis is truly heterogeneous; however, the loss of active sites draws the long-term stability of the catalysts, under these conditions, into question.

4. Conclusion

Stannosilicates have great potential as catalysts for use in a future biomass-based chemical industry, owing to the diverse range of reactions that can be catalysed with high activity and selectivity. Significantly different catalytic properties are, however, observed between structures, which cannot simply be explained by differences in diffusion properties. Thus, the type of structure influences the nature of the active site. This can be directly observed by measuring the change in vibrational frequency of a probe molecule adsorbed onto the active site. Sn-beta possesses an active site with a significantly higher acid strength than the other catalysts investigated; a difference that is probably responsible for the high catalytic activity at low temperature, as observed for the conversion of triose sugars into methyl lactate. In the conversion of hexose substrates, significantly higher yields of methyl lactate were obtained with Sn-beta. Thus, for the production of lactic acid, none of the other catalysts tested can match the activity and selectivity of Sn-beta. The high strength of the active site is, however, not necessarily an advantage, as observed when attempting to isomerize glucose, since alternative reactions begin to dominate at elevated temperatures. This could of course be compensated for by lowering the reaction temperature; however, this may not be desirable as the yield is limited by thermodynamics and a lower temperature would lead to a lower equilibrium yield (Moliner et al. 2010). Instead, matching the strength of the active site to favour the desired reaction can be done by choosing a different structure, and the range of structures can be thought of as a toolbox, where the optimal structure differs between applications. Further investigation of the influence of the structure on the active site is necessary, and, in particular, insights into the cause of the difference, on an atomic level, would be of great importance. The perspective of tailoring the active site to the desired application is exciting, and could potentially significantly improve the selectivity of these stannosilicate catalysts.

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References


Selective Production of Aromatics from Alkylfurans over Solid Acid Catalysts
Dong Wang, [a] Christian M. Osmundsen, [b, c] Esben Taarning, [b] and James A. Dumesic* [a]

Solid acid catalysts were studied at temperatures near 523 K for the production of benzene, toluene, and p-xylene by the reaction of ethylene with furan, 2-methylfuran, and 2,5-dimethylfuran, respectively, through the combination of cycloaddition and dehydrative aromatization reactions. Catalysts containing Brønsted acid and Lewis acid sites (i.e., WO$_x$-ZrO$_2$, niobic acid, zeolite Y, silica–alumina) were more active than catalysts containing predominantly Lewis acid sites ($\gamma$-Al$_2$O$_3$, TiO$_2$), which indicates the importance of Brønsted acidity in the production of aromatics. Microporosity is not required for this reaction, because amorphous solid acids and homogeneous Brønsted acids demonstrate significant activity for p-xylene production. The production of p-xylene from 2,5-dimethylfuran proceeded at higher rates compared with the production of toluene and benzene from 2-methylfuran and furan, respectively. Both WO$_x$-ZrO$_2$ and niobic acid demonstrate superior activity for aromatics production than does zeolite Y. WO$_x$-ZrO$_2$ demonstrates a turnover frequency for p-xylene production that is 35 times higher than that demonstrated by zeolite Y. In addition, mesoporous materials such as WO$_x$-ZrO$_2$ offer higher resistance to deactivation by carbon deposition than do microporous materials. Results from Raman spectroscopy and the trend of turnover frequency with varying tungsten surface densities for a series of WO$_x$-ZrO$_2$ catalysts are consistent with previous investigations of other acid-catalyzed reactions; this suggests that the high reactivity of WO$_x$-ZrO$_2$ is mainly associated with the presence of subnanometer WO$_x$ clusters mixed with zirconium, which reach a maximum surface concentration at intermediate tungsten coverage.

Introduction

The development of processes that convert biomass and biomass-derived molecules to bulk chemicals is essential to ensure continued supply of feedstocks for the chemical industry in an era of diminishing fossil fuel reserves. In this regard, the production of key platform aromatic compounds, such as benzene, toluene, and the xlenes (BTX compounds), has received increasing attention. [1] Interesting approaches have recently been demonstrated for the production of p-xylene. [3–5] Shiramizu and Toste reported the conversion of 2,5-dimethylfuran (DMF) and acrolein to terephthalic acid through a route described the one-pot catalytic conversion of DMF and ethylene to p-xylene with good selectivity through a combination of cycloaddition and dehydration reactions over acidic zeolites, such as H-Y, H-ZSM-5, and H-BEA. [4] Substituting DMF with 2-methylfuran (2-MF) or furan, which are also readily obtained from lignocellulosic biomass, [5] enables the production of toluene and benzene, respectively. However, the presence of substituent groups significantly affects the reactivity of furans toward the desired [4+2] cycloaddition reaction as well as competing side reactions, such as opening of the furan ring. [7–9] Therefore, a comparative study of substrates differing in the degree of substitution is necessary to provide insight into the essential factors that control the reactivity and selectivity of these systems toward the desired aromatic compounds. It is also necessary to identify more active and selective catalysts to improve the efficiency of the production of BTX compounds.

Herein, we investigate the combination of cycloaddition and dehydration reactions between ethylene and furan, 2-MF, or DMF for the selective production of BTX compounds. Reaction networks are proposed, with key reaction intermediates identified for all three substrates. Acidic oxides such as tungstated zirconia (WO$_x$-ZrO$_2$) and niobic acid demonstrate superior activity and selectivity for the production of aromatics than do zeolites. A series of WO$_x$-ZrO$_2$ catalysts with different surface compositions are investigated, and the observed catalytic properties indicate that the higher activity of these materials is at least partly due to the enhanced strength of Brønsted acid sites.
Results and Discussion

Production of p-xylene from DMF

The conversion of DMF to p-xylene by the reaction with ethylene proceeds by initially forming a 7-oxabicyclo[2.2.1]hept-2-ene-type adduct, as depicted in Scheme 1. The adduct is thermally unstable owing to ring strain in the bicyclic system, and it decomposes into DMF and ethylene unless refrigerated conditions are maintained. Given its low equilibrium concentration at temperatures close to or above room temperature, the dehydration of the cycloadduct to yield the more stable aromatic compound is necessary to drive the product distribution toward p-xylene. Both Brønsted acid and Lewis acid catalysts promote the dehydrative aromatization of the cycloadduct.\(^{[11,12]}\)

The selectivity for the production of p-xylene from DMF measured at 523 K over seven acid catalysts at 60% DMF conversion is illustrated in Figure 1. \(\gamma\)-Al\(_2\)O\(_3\) and TiO\(_2\) which possess predominantly Lewis acidity, demonstrated low selectivity of 10 and 17% toward p-xylene, respectively. A homogeneous Bronsted acid, trifluoroacetic acid, showed 40% selectivity toward p-xylene. A selectivity of 40% was also obtained over amorphous SiO\(_2\)/Al\(_2\)O\(_3\) which has both Brønsted and Lewis acid sites but lacks a crystalline microporous structure. H-Y zeolite, which was studied as a catalyst for this reaction in a previous study,\(^{[4]}\) demonstrated an increased selectivity of 52%. The p-xylene selectivity increased slightly to 57% over niobic acid, an amorphous acidic oxide. The highest selectivity was observed with WO\(_3\)/ZrO\(_2\) (calcined at 923 K), which demonstrated a remarkable selectivity of 77% toward the desired product. Major byproducts formed included 2,5-hexanedione, dimethylcyclohexenone, and uncharacterized soluble oligomers (see Table S1 for mass balances). In control experiments with p-xylene as the reactant, isomerization to form o- or m-xylene was not observed under our reaction conditions. The oligomerization of ethylene was not observed in control experiments, in which only ethylene was charged into the reactor with the solvent and the catalyst.

The turnover frequency (TOF) for the production of p-xylene over each catalyst was calculated by normalizing the rate by the number of acid sites, as determined by NH\(_3\)-temperature-programmed desorption (NH\(_3\)-TPD) and FTIR spectroscopy of adsorbed pyridine (Table S1). The Lewis acid sites on \(\gamma\)-Al\(_2\)O\(_3\) and TiO\(_2\) showed low selectivity and activity toward p-xylene production, with TOF values of 0.0015 and 0.0020 s\(^{-1}\), which are significantly lower than on all other considered catalysts (Figure 1b). Thus, Lewis acid sites are inefficient in catalyzing the dehydrative aromatization compared with Brønsted acid sites, and the TOF values for aromatics production will be reported only with respect to the number of Brønsted acid sites. The TOF values for WO\(_3\)/ZrO\(_2\) and niobic acid are 0.34 and 0.14 s\(^{-1}\), respectively, which are substantially higher than the rates observed over zeolite Y and SiO\(_2\)/Al\(_2\)O\(_3\) (0.0088 and 0.0090 s\(^{-1}\)). The effect of reaction temperature on the rate of p-xylene production from DMF and ethylene was investigated over WO\(_3\)/ZrO\(_2\), which was the most promising catalyst identified (see the Arrhenius plot in Figure S1). The rate of p-xylene production increases monotonically with increasing temperature, which indicates that the promoting effect of higher temperatures on the dehydration of the cycloadduct intermediate outweighs the lowering of the concentration of the adduct owing to its thermal instability, within the considered temperature range (453–548 K). The apparent activation energy for p-xylene production was determined to be 76 kJ mol\(^{-1}\).

Toluene and benzene production from 2-MF and furan

Substituting DMF with 2-MF or furan in the aforementioned reaction enables the production of toluene and benzene, respectively. The combined reaction mechanism for the conversion of all three substrates to aromatics is presented in Scheme 2. The presence of methyl substituents enhances the reactivity of the furan ring toward [4+2] cycloaddition reactions.\(^{[9,13]}\) Furthermore, the methyl groups stabilize charged intermediates in the dehydration of the bicyclic adduct, which thus facilitates the dehydration step.\(^{[12]}\) Upon combining these effects, the overall production rate of aromatics is expected to decrease by
moving from two methyl substituents in DMF to zero in furan. In addition, side reactions can take place that lower the selectivity toward aromatic products, such as opening of the furan ring to form γ-dicarbonyl compounds and the subsequent degradation of these species, for example, by oligomerization.[7,14] Although the ring opening of DMF occurs more readily than that of either 2-MF or furan,[8,9] the product 2,5-hexanediol is stable, which leads to an equilibrium situation (the diketone is observed with a yield of ~5% at 60% conversion). The intramolecular aldol reaction of 2,5-hexanediol yields 3-methyl-2-cyclopentenone, as observed in small quantities at high conversions. In contrast, the ring-opening products from furan and 2-MF are more reactive and oligomerize quickly,[7,9] which thereby lowers the carbon balance. (Because of their high reactivity, these compounds were not observed in experiments starting from 2-MF or furan.) In addition to the desired dehydration reaction to produce the aromatic ring, the adduct can react through an isomerization step to form an unsaturated cyclohexanone. The production of 1-ethyl-2,5-dimethylbenzene through the alkylation of p-xylene with ethylene is also observed to low extents at high conversions. Finally, two furan molecules undergo Diels–Alder cycloaddition to form benzofuran in the presence of solid acid catalysts, such as zeolites.[15]

The rates of the production of aromatics and major byproducts for the reaction of ethylene with DMF, 2-MF, and furan over zeolite Y, WO$_3$–ZrO$_2$, niobic acid, and γ-Al$_2$O$_3$ are illustrated in Figure 2. The rate of aromatic production decreases significantly by moving from two methyl substituents in DMF to zero in furan (Figure 2a) over all four catalysts. In contrast, the rates of the production of cyclohexenone-type compounds (Figure 2b) are highest for 2-MF, followed by DMF and furan. For both DMF and 2-MF, the production rate of the cycloadduct intermediate is sufficiently high to lead to high rates of the production of aromatics. The higher rate of the production of cyclohexenone compound from 2-MF can be explained by its lower rate of aromatization owing to the lower extent of alkyl substitution, as noted above. In the case of furan, the production rate of the cycloadduct becomes the limiting factor, which leads to low rates for benzene and cyclohexenone production. These trends suggest that aromatics and cyclohexenones are formed via the same cycloadduct intermediate. With DMF, the apparent activation energy for cyclohexenone production was determined to be 56 kJ mol$^{-1}$, compared with 76 kJ mol$^{-1}$ for p-xylene production (Figure S1).

Catalysts that are more active for DMF conversion demonstrate higher activity for 2-MF and furan conversion, which reflects analogous reaction pathways for all three substrates, as depicted in Scheme 2. Notably, the rate of cyclohexenone production (Figure 2b) is lower than that of dehydration over all catalysts except for γ-Al$_2$O$_3$. Because γ-Al$_2$O$_3$ possesses only Lewis acidity, this trend suggests that the rearrangement reaction to form cyclohexenone derivatives is catalyzed more effectively by Lewis acid sites. It is possible that Brensted acid sites catalyze the dehydration of the adduct more efficiently, which shifts the selectivity toward the dehydration direction on introducing Brensted acidity in addition to Lewis acidity. Also, zeolite Y shows a rearrangement rate higher than the dehydration rate.

The production of benzofuran-type compounds was not detected for DMF and 2-MF. However, when furan was reacted, it demonstrated similar rates for the production of benzene, 2-
cyclohexen-1-one, and benzofuran (Figure 2c). This result shows that the steric hindrance imposed by the substituent groups on the furan ring prevents effectively the coupling between furan rings to form benzofuran.

The high rates of the production of aromatics observed with WO$_x$–ZrO$_2$ and niobic acid enable the efficient use of these catalysts. Although WO$_x$–ZrO$_2$ is significantly more active than niobic acid for p-xylene production, the activity for toluene and benzene production is similar, with niobic acid demonstrating a slightly higher activity than WO$_x$–ZrO$_2$ for benzene production. Conversions of DMF, 2-MF, and furan were run to completion over the most active catalyst WO$_x$–ZrO$_2$, calcined at 923 K, and yields of 80, 34, and 18% were obtained for p-xylene, toluene, and benzene, respectively, at 523 K and 20 bar (2000 kPa) ethylene charged at room temperature.

The role of Brønsted acidity

Our finding that Brønsted acidity is essential for the dehydration of the adduct is consistent with previous reports that used acidic zeolites.

The stability of WO$_x$–ZrO$_2$, niobic acid, and zeolite Y was investigated for the production of p-xylene from DMF and ethylene.

The adduct is then formed through a stepwise mechanism instead of the concerted mechanism of Diels–Alder cycloaddition.

Catalyst stability for aromatics production

The stability of WO$_x$–ZrO$_2$, niobic acid, and zeolite Y was investigated for the production of p-xylene from DMF and ethylene.

The reactions were run to 60% DMF conversion over fresh catalysts. The spent catalysts were then recovered through centrifugation and washing with 2-propanol before drying in an oven. Without further calcination, these catalysts were reused in the reaction for the same reaction time as the previous runs with the fresh catalysts. In a third run, spent catalysts from the second run were washed, dried, and calcined under flowing air at 923 K for 3 h before they were reused in the reaction. As shown in Figure 3, zeolite Y deactivated significantly after the first run and simple washing could not recover its activity. In contrast, WO$_x$–ZrO$_2$ and niobic acid, respectively, retained 83 and 60% of their initial activity. Upon high-temperature calcination, however, both zeolite Y and WO$_x$–ZrO$_2$ recovered essentially all the catalytic activity, whereas niobic acid, which crystallized and lost most of its surface area (S.A.) upon high-temperature treatment, became even less active (showing 15% of its initial activity). These results suggest that the mesoporosity of WO$_x$–ZrO$_2$ (Table 1) offers higher resistance to deactivation by carbon deposition than that of microporous materials, such as zeolites, which thus requires less frequent regeneration in a continuous process.

Effect of tungsten surface density on the activity of WO$_x$–ZrO$_2$

WO$_x$–ZrO$_2$ is generally agreed to possess stronger Brønsted acidity than do zeolites. For example, WO$_x$–ZrO$_2$ is more active than acidic zeolites for reactions such as hydration, isomerization, and esterification. Using n-hexane isomerization as the probe reaction, the protonation energy, which provides a reliable metric of Brønsted acid site strength, is determined to be 1120 and 1185 kJ mol$^{-1}$ for WO$_x$–ZrO$_2$ and zeolite Beta, respectively, which indicates stronger acid strength of the former and hence its superior activity.
Generally, the surface density of WO\(_x\) species, expressed as the average number of tungsten atoms per unit area, is a key parameter that controls the surface morphology, surface acidity, and the catalytic properties of these materials\([22,23]\). To investigate the nature of active sites and the acidity requirement to achieve high selectivity toward aromatics, we prepared a series of WO\(_x\)-ZrO\(_2\) catalysts with a representative range of tungsten surface densities by varying the calcination temperatures (723–1223 K) for materials with the same initial tungsten loading (15 wt.% WO\(_x\)). Higher calcination temperatures lead to a progressive decrease in total surface area and a corresponding increase in pore size and tungsten surface density, as reported previously (Table 1)\([23]\). The most active catalyst for \(p\)-xylene production is produced by calcination at 923 K (Figure 4), which is consistent with the range previously found for other acid-catalyzed reactions\([25]\).

In situ Raman spectroscopy (Figure 5; see the detailed interpretation in the Supporting Information) measurements reveal the presence of distorted zirconium-containing WO\(_x\) clusters that are 0.8–1 nm in size (Raman bands 820–920 cm\(^{-1}\)) on the most active WO\(_x\)-ZrO\(_2\) materials. These clusters have been identified as the most acidic surface tungsten species that demonstrate high activity for methanol dehydration, and they reach maximum surface concentration at intermediate tungsten coverage because of the aggregation of mononitrogenses and the increasing extent of zirconium migration\([23,24]\). These WO\(_x\) clusters are more effective in dispersing the electron density transferred to the catalyst surface during catalysis, which thus stabilizes the transition states and leads to higher reaction rates\([25]\). At higher calcination temperatures (1123 and 1223 K), the concentration of these clusters decreases as surface tungsten species aggregate further to form well-ordered WO\(_x\) nanocrystallites (strong Raman bands at 270, 714, and 805 cm\(^{-1}\)). The density of Lewis acid sites decreases significantly with increasing calcination temperature, as reported previously\([26]\). The increase in TOF is not likely due to the decrease in Lewis site density, because the TOF value demonstrates a maximum while the Lewis site density decreases monotonically. Bronsted acid sites with varying strengths are collectively titrated by using NH\(_3\)-TPD, which thus gives similar densities of total Bronsted sites (Table 1). The overall acid strengths of materials calcined at different temperatures, however, can be distinguished by the TOF values. The TOF for \(p\)-xylene increases initially (Table 1), which indicates an increase in the acid strength of surface tungsten species with an increase in the surface concentration of zirconium-containing nanocrystal clusters. The TOF reaches a maximum at a surface density of approximately 4 Watom nm\(^{-2}\) and then decreases as the surface density of tungsten increases, which is consistent with the disappearance of zirconium-containing WO\(_x\) clusters owing to the production of WO\(_x\) crystallites seen in the Raman spectra.

**Table 1.** Phsyiochemical and catalytic properties of WO\(_x\)-ZrO\(_2\) with varying tungsten surface densities for \(p\)-xylene production.

<table>
<thead>
<tr>
<th>Sample(^{[a]})</th>
<th>S.A.</th>
<th>(D_p)</th>
<th>(\rho_{\text{cat}})</th>
<th>(\rho_{\text{Brønsted}})</th>
<th>(\rho_{\text{Lewis}})</th>
<th>TOF(^{(b)})</th>
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<td>1.6</td>
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<td>160</td>
<td>152</td>
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<td>5.0</td>
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<td>6.4</td>
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</tr>
<tr>
<td>WO(_x)-ZrO(_2)-1223</td>
<td>20</td>
<td>23.2</td>
<td>19.5</td>
<td>15</td>
<td>27</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^{[a]}\) WO\(_x\)-ZrO\(_2\)-T denotes the sample calcined at T K; all samples have an initial loading of 15 wt.% WO\(_x\); \(^{(b)}\) Normalized by Bronsted acid site density. S.A. = surface area; \(D_p\) = pore diameter; \(\rho\) = w/s/Bronsted/Lewis = surface density of tungsten species, Bronsted acid sites, and Lewis acid sites, respectively; TOF = turnover frequency.

Figure 4. Effect of calcination temperature on the conversion of 2,5-di-methylfuran (DMF) and selectivity toward \(p\)-xylene (\(p\)-xylene selectivity \(\downarrow\)). DMF conversion \(\uparrow\). Reaction conditions: 10 wt. % dienes in anhydrous hexane, 0.15 g catalyst, 253 K, 20 bar (2000 kPa) ethylene charged at 298 K in 50 mL batch reactor.

Figure 5. In situ Raman spectra of WO\(_x\)-ZrO\(_2\) catalysts calcined at different temperatures acquired under dehydrated conditions.

**Conclusions**

In summary, Bronsted acid sites are active for the production of benzene, toluene, and \(p\)-xylene by the reaction of ethylene with furan, 2-methylfuran, and 2,5-dimethylfuran, respectively, through the combination of cycloaddition and dehydrative ar-
omatization reactions. Microporous catalysts are not required for these reactions, as amorphous solid acids and homogeneously Brønsted acids also demonstrate significant activity for p-xylene production. WO$_3$–ZrO$_2$ demonstrates a turnover frequency for p-xylene production that is 35 times higher than that demonstrated by zeolite Y. In addition, mesoporous materials such as WO$_3$–ZrO$_2$ offer higher resistance to deactivation by carbon deposition than do microporous materials. Results from Raman spectroscopy and the changes in turnover frequency with the changes in the tungsten surface density for a series of WO$_3$–ZrO$_2$ catalysts are consistent with the conclusion from previous investigations that the high activity of WO$_3$–ZrO$_2$ is mainly associated with the presence of subnanometer WO$_x$ clusters mixed with zirconium, which reach a maximum surface concentration at intermediate tungsten coverage. Thus, the development of new catalysts for the production of aromatic compounds from biomass-derived furans can be guided by the fundamental concepts of Brønsted acidity developed for petroleum chemistry.

**Experimental Section**

**Catalyst preparation**

The zirconia-supported tungsten oxide catalyst was prepared by calcining commercial tungstated zirconium hydride (15 wt.%) WO$_3$ loading, MEL Chemicals, ZX01251/01) precursors at temperatures from 723 to 1223 K for 3 h in static air before use. A sample calcined at temperature $T$ was denoted as WO$_3$–ZrO$_2$–$T$; for example, WO$_3$–ZrO$_2$–923 was the sample calcined at 923 K. Commercial zelite H-Y (Zeolyst, CBV400, Si/Al $=2.55$, S.A. = 730 m$^2$ g$^{-1}$) was calcined at 823 K for 4 h before use. Niobic acid (CBMM, HY-340, S.A. = 118 m$^2$ g$^{-1}$) was used without further pretreatment; γ-Alumina was obtained from STREM Chemicals, and amorphous SiO$_2$/Al$_2$O$_3$ was obtained from Grace Davison (SIAL 3113, Si/Al = 3.40, S.A. = 450 m$^2$ g$^{-1}$). Both catalysts were calcined at 773 K in static air for 3 h before use.

**Catalytic activity measurements**

Reaction kinetics studies were conducted in a 50 mL, high-pressure Hastelloy Parr reactor (Parr Instruments, Co.) furnished with graphite gaskets and tapes. The reactor was heated to 523 K with a homemade furnace controlled by a 16A series programmable temperature controller (Love Controls), and stirring was done with a high-temperature SmCo (29 MGO) magnetic stir bar (V&P Scientific, Inc.). The reactor was charged with the catalyst (0.15 g) and diene (2 g, 99%, Sigma–Aldrich) dissolved in hexadecane (18 g, anhydrous grade, Sigma–Aldrich). The reactor was purged at RT with argon twice before it was pressurized with ethylene (Praxair) to 20 bar (2000 kPa) under vigorous stirring to ensure that the liquid was saturated with ethylene. It was estimated from the solubility data that an excess of ethylene was present in the reactor (ethylene/diene > 2) and thus the conversion was not limited by ethylene. The reactor was brought to the reaction temperature and maintained for the desired reaction time ($\approx$ 1.5–6 h) before liquid samples were collected. Products were identified with a GC–MS system (Shimazu GCMS-QP2010), and quantifications were performed with a GC (Shimazu GC-2010) equipped with a flame ionization detector. Spent catalysts were recovered through centrifugation. They were washed with 2-propanol (300 mL) to remove residual solvents and then dried in an oven (373 K) for 3 h before reuse.

When regeneration was needed, catalysts were calcined under flowing air at 923 K for 3 h.

**FTIR spectroscopy of adsorbed pyridine**

The distribution of Brønsted and Lewis acid sites on the solid acid catalysts studied was determined from FTIR measurements of adsorbed pyridine. The catalyst (≈ 10 mg) was placed in a 1.2 cm dia and pressed into a self-supporting wafer, which was placed in a treatment/sampling cell in which it was heated to 648 K under flowing dry helium (Airgas, industrial grade) for 2 h. (The niobic acid was degassed at 573 K to avoid crystallization.) A reference spectrum of the catalyst was then recorded. Pyridine was introduced into the cell through a bubbler at RT for 30 min, followed by purging under flowing helium for 1 h before another spectrum was recorded. The sample was held at 423 K for 1 h under flowing helium and then cooled to RT, and the final spectrum was recorded. The areas of the pyridine peaks at 1455 and 1540 cm$^{-1}$ assigned to Lewis and Brønsted acid sites, respectively, were determined by subtracting the spectra of the sample before pyridine exposure and after desorption at 423 K to remove weakly adsorbed pyridine. The Brønsted/Lewis acid ratios were obtained by normalizing the areas with integrated molar extinction coefficients reported in the literature: 1.67 cm m$^{-1}$ mol$^{-1}$ for Brønsted sites and 2.22 cm m$^{-1}$ mol$^{-1}$ for Lewis sites.

**NH$_3$-TPD**

NH$_3$-TPD was used to determine the total acid site density by loading the catalyst (100–200 mg) in a glass flow-through cell. Before NH$_3$ adsorption, samples were held at 538 K under flowing helium (120 cm$^3$ STP min$^{-1}$) for 1 h to remove adsorbed moisture. NH$_3$ was then adsorbed by exposing the sample to a flowing gas mixture of 1 mol% NH$_3$ in helium (100 cm$^3$ STP min$^{-1}$) at 423 K for approximately 45 min. Physisorbed NH$_3$ was removed by holding the sample at 423 K under flowing helium (120 cm$^3$ STP min$^{-1}$) for 45 min. TPD was performed with a temperature ramp of 10 K min$^{-1}$ from RT to 1073 K under flowing helium (40 cm$^3$ STP min$^{-1}$). The desorbed NH$_3$ was quantified with an online mass spectrometer (RGA 200, Stanford Research Systems).

**In situ Raman spectroscopy**

Raman spectroscopy was performed with a visible laser (532 nm) excitation on a LabRAM ARAMIS Horiba Jobin Yvon Raman spectrometer. The spectrometer was equipped with an in situ treatment cell (Linkam, THMS600), which allowed for control of both temperature and atmosphere within the cell chamber. The catalyst samples, in the form of loose powder (10–20 mg), were loaded into the cell chamber. The samples were dehydrated at 723 K for 1 h under flowing dry air (Airgas, dry grade, 50 mL min$^{-1}$) to desorb moisture and then cooled to 393 K. Spectra were recorded at 393 K with 10 scans of 10 s scan$^{-1}$ for a total acquisition time of 4 min spectrum$^{-1}$. System alignment was verified by using the characteristic 520 cm$^{-1}$ band from a silicon reference standard.

**N$_2$ adsorption**

N$_2$ adsorption–desorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 system. Sample pretreatment involved
evacuation at 393 K for 12 h. Surface areas were determined by using the BET method.

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