Catalytic Conversion of Carbohydrates

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 Brønsted acidic catalyst, WOx/ZrO2. 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 thermolysis was investigated. A wide range of substrates could be converted with a high selectivity towards C1- to C3-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.

Integration of Chemical and Biological Catalysis: Production of Furylglycolic Acid from Glucose via Cortalcerone

Furylglycolic acid (FA), a pseudoaromatic hydroxy-acid suitable for copolymerization with lactic acid, can be produced from glucose via enzymatically derived cortalcerone using a combination of Bronsted and Lewis acid catalysts. Cortalcerone is first converted to furylglyoxal hydrate (FH) over a Bronsted acid site (HCl or Al-containing beta-zeolite), and FH is subsequently converted to FA over a Lewis acid site (Sn-beta zeolite). Selectivity for conversion of FH to FA is as high as 80% at 12% conversion using tetrahydrofuran (THF) as a solvent at 358 K. Higher conversion of FH leads to FA-catalyzed degradation of FH and subsequent deactivation of the catalyst by the deposition of carbonaceous residues. The deactivated catalyst can be regenerated by calcination. Cortalcerone can be produced from 10% glucose solution using recombinant Escherichia coli strains expressing pyranose 2-oxidase and aldose-2-ulosde dehydratase from the wood-decay fungus Phanerochaete chrysosporium BKM-F-1767. This enzymatically derived cortalcerone is converted in one pot to FA in a methanol/water solvent over an Al-containing Sn-beta zeolite possessing both Bronsted and Lewis acid sites, achieving 42% selectivity to FA at 53% cortalcerone conversion.
Selective production of aromatics from alkylfurans over solid acid catalysts

Solid acid catalysts were studied at temperatures near 523K 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., WOx-ZrO2, niobic acid, zeoliteY, silica-alumina) were more active than catalysts containing predominantly Lewis acid sites (γ-Al2O3, TiO2), 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 WOx-ZrO2 and niobic acid demonstrate superior activity for aromatics production than does zeoliteY. WOx-ZrO2 demonstrates a turnover frequency for p-xylene production that is 35 times higher than that demonstrated by zeoliteY. In addition, mesoporous materials such as WOx-ZrO2 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 WOx-ZrO2 catalysts are consistent with previous investigations of other acid-catalyzed reactions; this suggests that the high reactivity of WOx-ZrO2 is mainly associated with the presence of subnanometer WOx clusters mixed with zirconium, which reach a maximum surface concentration at intermediate tungsten coverage.
Trends and Challenges in Catalytic Biomass Conversion

The conversion of biomass to the plethora of chemicals used in modern society is one of the major challenges of the 21st century. Due to the significant differences between biomass resources and the current feedstock, crude oil, new technologies need to be developed encompassing all steps in the value chain, from pretreatment to purification. Heterogeneous catalysis is at the heart of the petrochemical refinery and will likely play an equally important role in the future biomass-based chemical industry. Three potentially important routes to chemicals from biomass are highlighted in this chapter. The conversion of biomass-derived substrates, such as glycerol, by hydrogenolysis to the important chemicals ethylene glycol and propane diols. Secondly, the conversion of carbohydrates by Lewis acidic zeolites to yield alkyl lactates, and finally the conversion of lignin, an abundant low value source of biomass, which could be a potential source of aromatics.

General information
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Tin-containing silicates: structure–activity relations

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.

General information
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Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.866 SNIP 1.279 CiteScore 2.07
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 0.949 SNIP 1.437 CiteScore 2.15
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.003 SNIP 1.589 CiteScore 2.35
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 0.969 SNIP 1.521 CiteScore 2.08
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
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Scopus rating (2011): SJR 0.867 SNIP 1.464 CiteScore 1.88
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Scopus rating (2007): SJR 1.139 SNIP 1.532
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 1.041 SNIP 1.456
Scopus rating (2005): SJR 1.14 SNIP 1.419
Scopus rating (2004): SJR 1.068 SNIP 1.339
Scopus rating (2003): SJR 1.146 SNIP 1.438
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 1.119 SNIP 1.414
Beyond petrochemicals: The renewable chemicals industry
From petroleum to bioleum: Since biomass is a limited resource, it is necessary to consider its best use. The production of select chemicals from biomass, rather than its use as fuel, could effectively replace the use of petroleum in the chemical industry, but the inherent functionality of biomass must be exploited.

General information
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Authors: Vennestrøm, P. (Ekstern), Osmundsen, C. M. (Intern), Christensen, C. (Ekstern), Taarning, E. (Ekstern)
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Web of Science (2016): Indexed yes
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Scopus rating (2013): SJR 5.681 SNIP 2.204 CiteScore 10.7
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Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 5.438 SNIP 2.115
Web of Science (2008): Indexed yes
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 4.71 SNIP 2.119
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 4.7 SNIP 2.295
Web of Science (2005): Indexed yes
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Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 3.41 SNIP 2.126
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 3.659 SNIP 2.146
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Zeolite-catalyzed biomass conversion to fuels and chemicals

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.
Projects:

**Catalytic Cracking of Sugars for Production of Chemicals**

Department of Chemical and Biochemical Engineering  
Period: 01/11/2017 → 31/10/2020  
Number of participants: 4  
Phd Student:  
Schandel, Christian Bækhøj (Intern)  
Supervisor:  
Høj, Martin (Intern)  
Osmundsen, Christian Mårup (Intern)  
Main Supervisor:  
Jensen, Anker Degn (Intern)  

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Samfinansieret - Andet  
Project: PhD

**Catalytic conversation of carbohydrates**

Department of Physics  
Period: 01/03/2010 → 19/04/2013  
Number of participants: 6  
Phd Student:  
Osmundsen, Christian Mårup (Intern)  
Supervisor:  
Taarning, Esben (Intern)  
Main Supervisor:  
Rossmeisl, Jan (Intern)  
Examiner:  
Fristrup, Peter (Intern)  
Skrydstrup, Troels (Ekstern)  
Svelle, Stian (Ekstern)  

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Institut stipendie (DTU)
Project: PhD