

Catalyst Design for Biorefining

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Summary

The quest for sustainable resources to meet the demands of a rapidly rising global population while mitigating the risks of rising CO₂ emissions and associated climate change, represents a grand challenge for humanity. Biomass offers the most readily implemented and low cost solution for sustainable transportation fuels, and the only non-petroleum route to organic molecules for the manufacture of bulk, fine and speciality chemicals and polymers. To be considered truly sustainable, biomass must be derived from resources which do not compete with agricultural land use for food production, or compromise the environment e.g. via deforestation. Potential feedstocks include waste lignocellulosic or oil based materials derived from plant or aquatic sources, with the so-called biorefinery concept offering the co-production of biofuels, platform chemicals and energy; analogous to today's petroleum refineries which deliver both high volume/low value (e.g. fuels and commodity chemicals) and low volume/high value (e.g. fine/speciality chemicals) products, thereby maximising biomass valorisation. This article addresses the challenges to catalytic biomass processing, and highlights recent successes in the rational design of heterogeneous catalysts facilitated by advances in nanotechnology and the synthesis of templated porous materials, as well as the use of tailored catalyst surfaces to generate bifunctional solid acid/base materials or tune hydrophobicity.

1. Introduction

1.1. The Biorefinery concept

Tackling the current world energy crisis and increasing environmental concerns over global climate change is a top priority for both developed and developing nations in the 21st century. To be truly viable, such alternative feedstocks must be sustainable, that is “*have the ability to meet 21st century energy needs without compromising those of future generations.*” In the context of energy, despite significant growth in proven and predicted fossil fuel reserves over the next two decades, (e.g. heavy crude oil, tar sands, deep water wells, and shale oil and gas), there are great uncertainties in the economics of their exploitation via current extraction methodologies, and crucially, an increasing proportion of such carbon resources (estimates vary between 65-80 % [1, 2]) cannot be burned without breaching the UNFCCC targets for a 2 °C increase in mean global temperature relative to pre-industrial levels.[3-5] There is clearly a fine balance between meeting rising energy demands, predicted to rise 50 % globally by 2040 [6] and the requirement to mitigate current CO₂ emissions and hence climate change.

Biomass, derived from non-food sources of lignocellulose, sugars, and triglycerides, is the only sustainable source of carbon that can provide low cost solutions for transportation fuels and organic chemicals.[7] The US DoE identified a range of sugar derived Platform Chemicals produced via chemical or biochemical transformation of lignocellulosic biomass that would be potential targets for production in biorefineries. [8] Akin to petroleum refining, biorefining will integrate such biomass conversion processes so biofuels, chemicals and energy are coproduced to maximise waste biomass valorisation; an approach analogous to current petroleum refineries which deliver high volume/low value (fuels and commodity chemicals) and low volume/high value (fine/speciality chemicals) products in tandem, the latter underpinning the economic success of the industry [9]. Catalytic technologies have played a critical role in the economic development of the petrochemical industry and modern society, underpinning 90 % of chemical manufacturing processes and contributing to over 20% of all industrial products. [10, 11] In a post-petroleum era, catalysis will underpin analogous biorefinery technology, and researchers will need to rise to the challenge of synthesising chemical intermediates, advanced functional materials and fuels from non-petroleum feedstocks.

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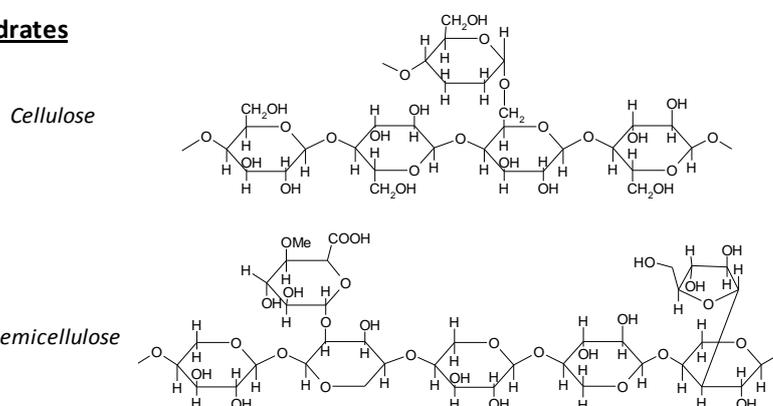
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1.2. Renewable Feedstocks

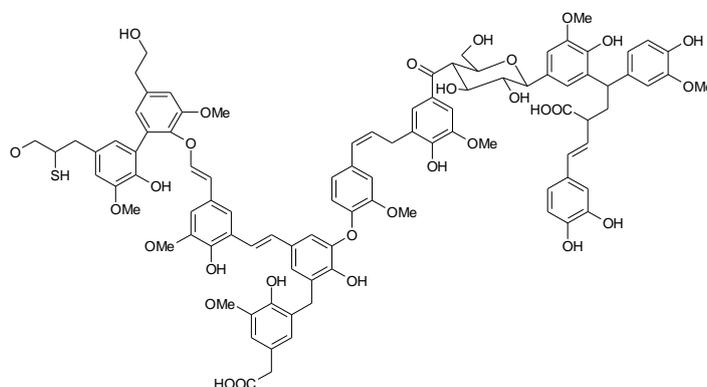
Feedstock selection for any bio-based process requires life-cycle and socio-economic assessments of attendant energy, resource and land use requirements to ensure sustainability. Polysaccharides sourced from starch ($C_6H_{10}O_5$)_n derived from wheat, corn or tuberous plants, or sugar cane [12] and sorghum [13], are most easily processed to glucose via hydrolysis, but such food crops are not considered sustainable. In this respect, lignocellulose derived from waste agricultural or forestry materials (e.g. logging or mill and manufacturing residues), or perennial herbaceous plants and short rotation woody crops (e.g. miscanthus, eucalyptus or willow), is considered a particularly viable option for sustainable fuels and chemicals production.[14],[15] The use of agricultural waste biomass residues [16], such as bagasse and rice husk and straw, also offers a very attractive means to valorise waste materials that would otherwise be left to decompose, or in the case of rice straw, simply burned thereby releasing atmospheric CO₂. [17] The use of such agricultural wastes must only be used in conjunction with sustainable land management practices to ensure that soil quality, biodiversity and water use is safeguarded; if such policies are abided by it is claimed that sustainably sourced waste residues could supply 16 % of road transport fuel by 2030, delivering green-house gas savings in excess of 60 per cent across the European Union.[18]

Lignocellulose is a biopolymer comprising cellulose (30–50% of total lignocellulosic dry mass) and hemicellulose (20–40% of total dry mass), themselves assembled from C₆ and C₅ sugars such as glucose, xylose and amylose, bound together by poly-phenolic lignin which makes up the remaining 15–25% of dry biomass and imparts rigidity to plants and trees (**Scheme 1**).

Carbohydrates



Lignin

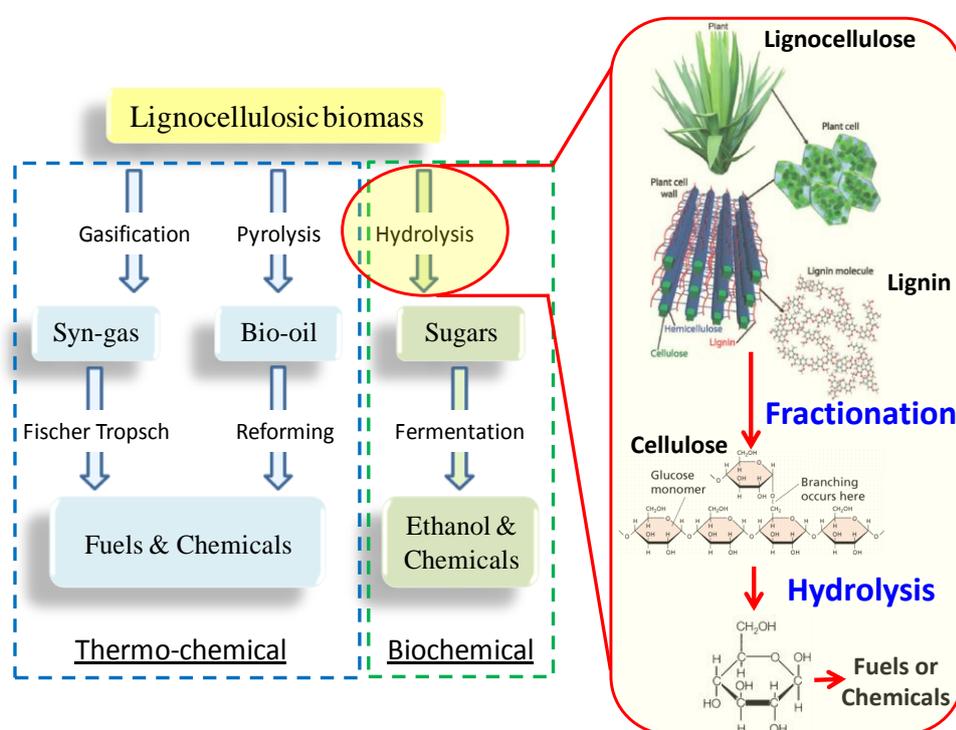


Scheme 1: Structure of lignin, hemicellulose and cellulose contained within woody biomass.

Cross-linking of the cellulose and hemicellulosic components with lignin via ester and ether linkages renders lignocellulose resistant towards hydrolysis, hampering its chemical conversion.[16] Popular approaches to lignocellulosic biomass utilisation for fuels and chemicals synthesis encompass sugar fermentation to ethanol, gasification to syngas (CO/H₂), or pyrolysis to bio-oils (**Scheme 2**). Given the rich functionality of biomass components, high temperature thermochemical methods such as gasification, are less desirable as they are crude, destructive methods that result in loss of potentially high value components that could add value to bio-based processes. The production of syngas from gasification of high quality biomass as a route to produce hydrocarbons (via e.g. Fisher Tropsch synthesis) cannot be rationalised unless the biomass fraction is particularly recalcitrant and unsuitable for processing via more economic methods. While biomass pyrolysis has good potential for the production of liquid fuels, generating a bio-oil which retains ~70% of the energy stored in the raw biomass, it has a high (> 40 wt%) oxygen and water (15 - 25 wt%) content and several other shortcomings, such as a relatively low heating value (16–19 MJ/Kg; less than half that of petroleum-derived fuels), strong corrosiveness (pH = 2–4), high viscosity, immiscibility with

conventional fuels and poor chemical stability which leads to polymerisation of components being observed on storage. Consequently, biomass pyrolysis into liquid fuels suffers from severe limitations that can be only overcome if the bio-oil is subjected to upgrading treatments to improve its properties, and is an area where significant developments are required in catalyst development, particularly in relation to pre-treatment processes and improved lifetime of deoxygenation catalysts.

The use of lignocellulose in bio-chemical processes is also particularly challenging as it cannot be used directly, and thus while enzymatic transformation of glucose to chemical and fuel feedstocks is an attractive prospect, extensive pre-processing of the raw materials is required. [19] Fractionation to isolate cellulose, lignin and hemicellulose is typically performed via acid or base hydrolysis, steam explosion [20] or organosolv treatments [21] to separate the polysaccharide from lignin components. [22] Once separated, the cellulose fractions are typically hydrolysed to fermentable sugars for further processing into fuels and/or chemicals via enzymatic, [23] chemical (acid or base) [24, 25], supercritical water [26] or more recently Ionic Liquid (IL) based [27] treatments. In an alternative approach, mechano-catalysis using H_2SO_4 -impregnated lignocellulosic substrates is showing enormous promise for cleaner and efficient depolymerisation of lignocellulose using a one-pot process, in which mechanical forces and acid catalysis converts dried lignocellulose into water-soluble products comprising oligosaccharides and lignin fragments.[28, 29]



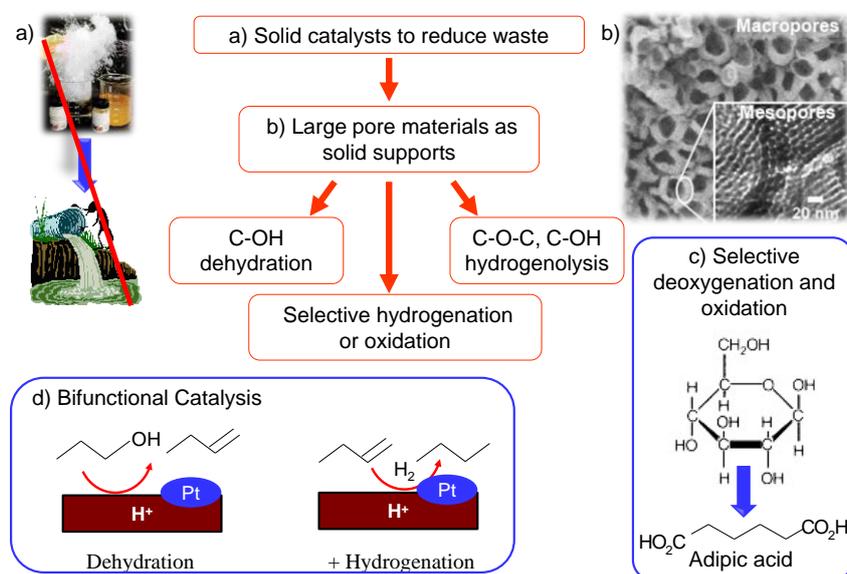
Scheme 2: Thermochemical and biochemical routes for lignocellulose conversion to chemicals and fuels; biochemical routes require fractionation of lignocellulose to isolate cellulose from lignin and hemicellulose for subsequent hydrolysis to glucose.

Current pre-treatment steps are energy intensive generating significant quantities of waste during acid/base neutralisation or enzyme separation; hence there is great scope for improved technology to enhance energy and atom economies. Furthermore, complete fractionation of lignocellulose often sacrifices one or more of the components e.g. lignin [30] or hemicellulose, [31] e.g. sulphuric acid treatments during the Kraft process results in a particularly intractable Kraft Lignin material. [32] Likewise, decomposition of hemicellulose during high temperature/pressure steam explosion leads to an aqueous fraction rich in furfural and C_1 - C_2 acids [33] derived from hemicellulose decomposition, which is problematic for subsequent fermentation since they can inhibit yeast growth. Biomass pre-treatment is thus an area of intensive research which may be expected to play an increasingly important role in the viability of biorefineries. In all these steps the processing cost and waste generated greatly offsets the potential energy benefits associated with low temperature enzymatic processing of the purified glucose. Furthermore as chemicals contained within fermentation broths are often produced in low concentrations their separation from biocatalytic processes can also be economically prohibitive. In this respect there is a growing interest in aqueous phase processing of cellulosic derived sugars using heterogeneous catalysis as a complementary processing method to enzymatic routes.

1.3. Catalyst Design Considerations

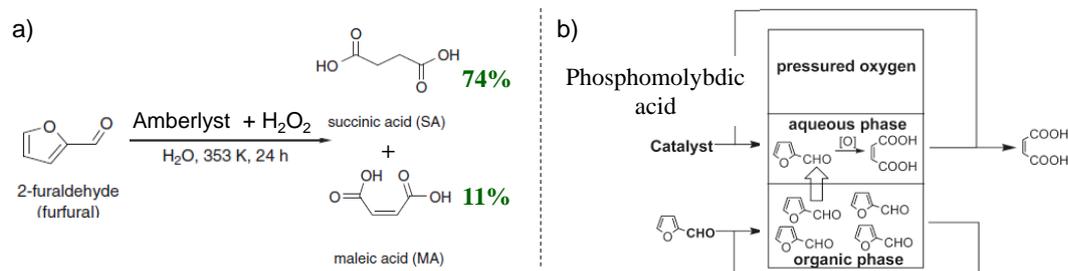
Conversion of bio-based feedstocks presents new challenges to the catalytic scientist, as the attendant reaction conditions are very different to those typical of petroleum processing, which occurs mainly through vapour phase processes $> 400\text{ }^\circ\text{C}$. The

utilisation of biomass-derived chemicals, whether from fermentation broths or sugars themselves, represents an area with extensive R&D potential for a renewable feedstock based technology platform. Biomass processing will be characterised by liquid phase, lower temperature [34] pathways such as hydrolysis, dehydration, isomerisation, oxidation, aldol condensation, and hydrogenation. [35] The design of catalysts for such biomass transformations requires careful tailoring of pore structure to minimise mass transport limitations, improve hydrothermal stability under aqueous operation, and tuneable hydrophobicity to aid product/reactant adsorption. [36] Platform molecules derived from fermentation are often present at low concentrations (typically <10 %) in aqueous solutions, alongside other polar molecules. Purification of such fermentation broths is particularly difficult,^{[37],[38]} and energetically demanding, hence, an ability to directly transform organic molecules contained within these aqueous solutions would be desirable,^{[39],[8],[40-43]} and requires the developments of water tolerant catalysts that are resistant to impurities present in the fermentation broth. [44] Corma *et al.* have extensively reviewed proposed methods for transforming platform molecules into chemicals. [41] Many approaches employ conventional homogeneous reagents which generate waste (**Scheme 3a**) and should be avoided, or attempt the use of commercial catalysts which are not optimised, hence there is enormous scope for rationally designing improved heterogeneously catalysed processes, tailored towards biomass-derived feedstocks. Catalyst development should thus focus on the use of tailored porous solids as high area supports to enhance reactant accessibility to active acid/basic groups. To function effectively catalysts will need to have tuneable hydrophobicity, be hydrothermally stable over a wide pH range, and resistant to in-situ leaching. Catalyst porosity will also be important to enable diffusion of bulky, viscous reactants to active sites; support materials with larger pores (compared to zeolites) are thus a promising starting point (**Scheme 3b**). Approaches to handling biomass-derived building blocks will be very different from petroleum processing, e.g. requiring reverse chemical transformations wherein highly functional bio-molecules are deoxygenated to their target product (**Scheme 3c**), instead of oxygenated as is usual when starting from crude oil.[45] New classes of catalyst are urgently required which are compatible with hydrophilic, bulky substrates to facilitate the move away from existing short-chain hydrocarbon supplies. Improvements and innovations in catalyst and processes design are thus needed in order to deliver high-value chemicals from biomass derived building blocks. Low temperature (< 200 °C), thermochemical aqueous phase processing of sugars is of particular interest, as this offers a viable method to generate highly functional intermediates via selective deoxygenation to produce aldehydes, alcohols, acids and esters via dehydration, hydrogenolysis or isomerisation.[46], [43], [47] Catalysts containing acid or base sites, will also be required that exhibit bi-functional character so that, for example, catalysts possessing acid sites for dehydration also contain metal sites for (de)hydrogenation (**Scheme 3d**). Organic-inorganic hybrid catalysts may also prove particularly interesting, as these allow catalyst hydrophobicity and acid-base character to be readily tuned, and in turn control the adsorption strengths of polar molecules. [48] Mesoporous carbons [49] are particularly popular supports for biomass conversion since they tend to be highly resistant to acidic and chelating media.



Scheme 3: Design considerations for heterogeneous catalysts in the conversion of sugars to platform chemicals.

A number of reports have described pathways to important chemical intermediates from platform molecules, [40-42, 50] with succinic acid one such valuable platform chemical, from which a range of chemical intermediates can be derived. Succinic acid may also afford new biopolymers based on polyesters, polyamides, and polyesteramides. [51] In this respect, carbon based solid acid catalysts have proven effective for succinic acid esterification with ethanol.[52],[53] Succinic acid production can be achieved via bacterial fermentation of glucose, which yields typically 40-60 gL⁻¹ succinic acid (SA) as salt [54], and is a powerful route to valorise bakery waste with yields of 0.55g SA reported as being produced per g bread waste.[55] In contrast while less frequently discussed there are catalytic routes to succinic and maleic acid from furfural.[56] A 34.5 % maleic acid yield obtained at 130 °C under 20 Bar O₂ when using a biphasic system [57] (**Scheme 4**), illustrating the potential of heterogeneous catalysts to offer alternative routes to platform chemicals conventionally produced via enzymatic processes.

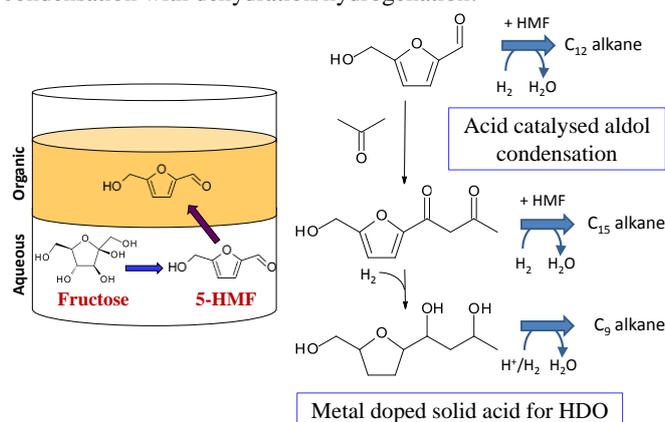


Scheme 4: Catalytic routes to succinic and maleic acid via the acid catalysed oxidative ring-opening of furfural

2. The catalytic conversion of sugars to 5-hydroxymethylfurfural (5-HMF)

2.1. Introduction

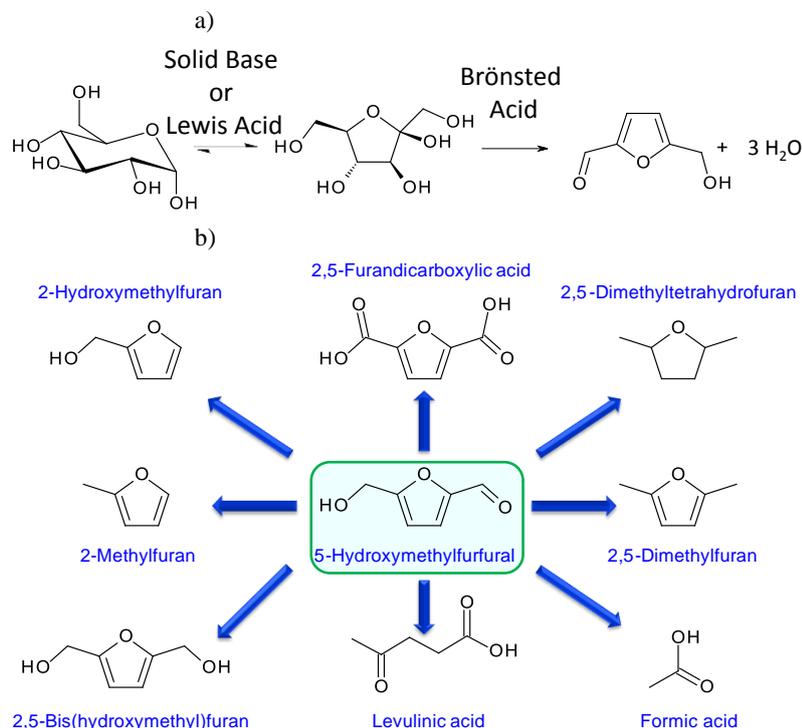
Among the platform chemicals identified by the US DoE [8, 58] 5-HMF [59] is widely recognised as a versatile intermediate for the production of value-added chemicals and high performance liquid fuels, and as a result its synthesis from sugars [8] has attracted significant academic and industrial interest.[60] 5-HMF can also be used as precursors for liquid hydrocarbon fuels via the production of linear alkanes aldol condensation and HDO generating hydrocarbons in the approximate molecular weight range for diesel and jet fuel (**Scheme 5**). Direct catalytic aqueous-phase reforming (APR) of cellulose has also been attempted for the conversion of carbohydrates into hydrogen and alkanes (C_1 to C_{15}) and could form a platform for fuels production within an integrated biorefinery. [34] APR typically involves the reaction of cellulose under acid conditions at ~ 200 °C to yield C_1 to C_6 alkanes by aqueous-phase dehydration/hydrogenation (APD/H) of sugars, or C_7 to C_{15} alkanes by combining aldol condensation with dehydration/hydrogenation.



Scheme 5: Biphasic system for the extraction of 5-HMF from the aqueous phase processing of hexoses, subsequent aldol condensation and hydrodeoxygenation of 5-HMF can be used to form synthetic alkane fuels.

5-HMF is also important as an intermediate for production of some useful chemicals such as levulinic acid, 2,5-furandicarboxylic acid (FDCA), [61] 2,5-diformylfuran (DFF), dihydroxymethylfuran, the promising fuel 2,5-dimethylfuran (DMF)[62] and 5-hydroxy-4-keto-2-pentenoic acid, which are potential intermediates for a variety of polymers and plastics.[41] The conversion of C_6 sugars to 5-HMF has been the topic of much interest, with liquid acids including H_2SO_4 , HCl , H_3PO_4 frequently used to catalyse the dehydration reaction, however current industrial use of 5-HMF as a chemical intermediate is impeded by high production costs.[63] Ideally, a heterogeneously catalysed process in which glucose could be converted directly to 5-HMF in aqueous media would be desirable, and requires a tandem process involving Lewis acid or base catalysed isomerisation of glucose to fructose followed by Brønsted acid catalysed dehydration of fructose to 5-HMF (**Scheme 6**). Unfortunately the lack of detailed analysis, reporting actual mass balances and systematic studies correlating catalyst acid/base properties with performance hampers the development of such catalysts, and many studies focus on the more facile conversion of fructose as a model saccharide.[64–74] To improve overall HMF yield, non-aqueous solvents such as dimethyl sulfoxide (DMSO) are often employed,[72] which while producing higher yields of 5-HMF by the aprotic solvent inhibiting the formation of levulinic acid and humins,[75] lead to problems for downstream processing and product separation due to the formation of toxic S-containing compounds during high temperature DMSO distillation.[76] Furthermore, the use of DMSO as a solvent should be treated with caution as high background rates of fructose dehydration are observed making comparison of catalyst

performance impossible when studies operate at elevated temperatures. [77] The use of alternative media such as ionic liquids as a processing solvent for carbohydrates and cellulose itself is attracting much interest and is reported to yield ~70% HMF from glucose when using a homogeneous metal halide catalysts, [78] however again, product separation is not facile.



Scheme 6. a) Glucose isomerisation to fructose and subsequent dehydration to 5-HMF, and b) potential uses of 5-HMF as a chemical feedstock

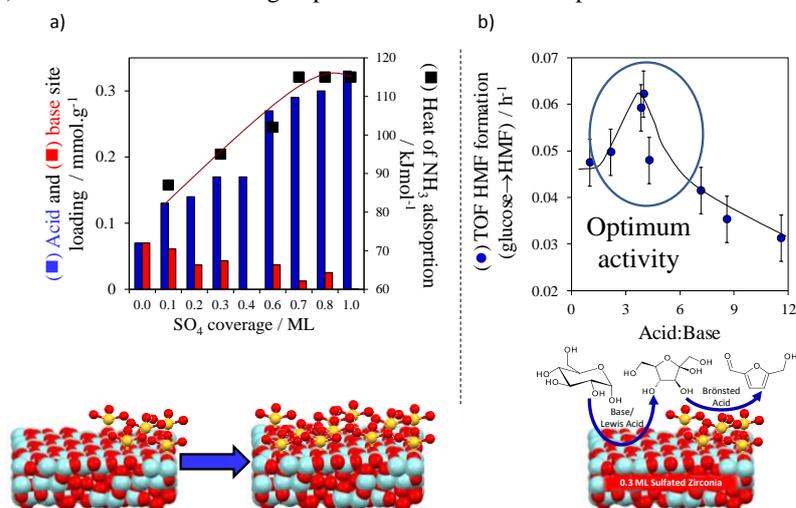
Biomass pre-treatments such as steam explosion [20] or enzymatic [23] and chemical (acid or base) [24, 25] routes to fractionate and hydrolyse cellulose will ultimately produce aqueous sugar sources, thus from a practical and environmental perspective aqueous phase, hydrothermal processing of cellulose and sugars offers an attractive method to produce platform chemicals and fuels.[79] The development of heterogeneous catalysts for aqueous phase conversion of sugars requires materials with improved hydrothermal stability,[80] such as carbon, zirconia and titania supports [81] which are amongst materials reported to exhibit excellent water tolerance. However, in their native form they exhibit low surface areas, or limited control over internal porosity, restricting their application in the chemical conversion of bulky bio-based molecules.

To reduce side reactions of 5-HMF, the use of biphasic systems (e.g. Water/MIBK) which allows reactive extraction of 5-HMF from the aqueous phase is proposed as a promising way to allow continuous production of 5-HMF, [64, 82] with both liquid [64, 83, 84] and solid acids.[85-87] Recently a tandem homogeneously Lewis/Brønsted acid catalysed process utilising AlCl_3 and HCl in a biphasic system of water/2-sec-butylphenol, was reported to respectively isomerise glucose to fructose and then dehydrate fructose giving a 62% yield of 5-HMF. [88] Other homogeneous metal halides [89, 90] including Cr(III), Zn(II) and Sn(IV) and more water tolerant lanthanide chlorides [91] were also explored, which while effective in converting glucose, yielded only a ~45-48% selectivity to 5-HMF. While an interesting concept, the use of soluble catalysts, particularly AlCl_3 (which reacts violently with water) is a concern due to the potential toxic waste that would result from a large scale process, and is at odds with the principles of Green Chemistry. The application of Lewis acidic Sn-Beta-Zeolite in conjunction with aqueous HCl can convert glucose to 5-HMF in a biphasic system at 180 °C with ~60% HMF selectivity reported, however again the use of corrosive HCl is undesirable. [92] The application of a 'one-pot' tandem reaction using hydrotalcite as the solid base with a solid acid resin also show potential, but in this instance reaction was conducted in N,N-dimethylformamide as a solvent rather than water.[93] Further development of catalysts for glucose to 5-HMF conversion really requires improved bi-functional solid acid and base catalysts which can operate efficiently in the aqueous phase.

2.2. Bifunctional Catalysts

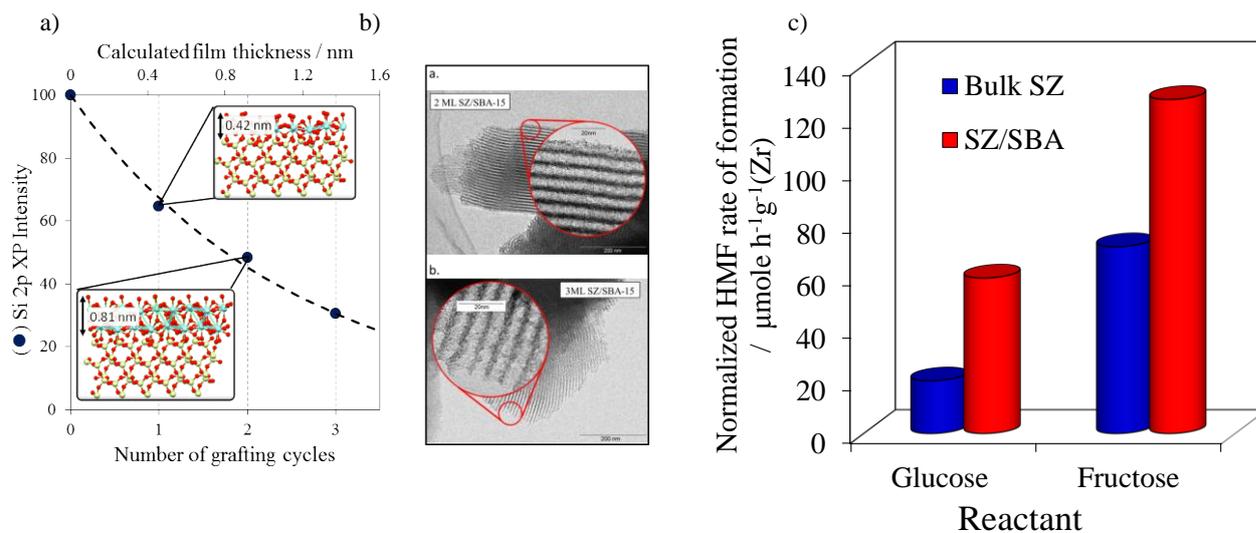
The amphoteric properties of zirconia make it an attractive catalytic material to employ in such a bifunctional process.[94, 95] Indeed zirconia has been reported as a catalyst for the isomerisation of glucose to fructose at 200 °C.[96] while sulfated zirconia (SZ) is also an attractive strong solid acid for alcohol dehydration processes. Initial reports relating to the performance of SZ in aqueous phase catalysis are somewhat disappointing due to instabilities of the SO_4^{2-} ion under high temperature hydrothermal conditions; most likely associated with dissolution of multi-layer sulfate species formed at the high S contents employed in

conventional materials.[72],[97] However, judicious control over sulfate coverages over bulk ZrO_2 materials can facilitate the 'one-pot' conversion of glucose to 5-HMF when fractional surface coverage of acid and base sites are tuned such that bare ZrO_2 sites are retained to impart some basicity. **Scheme 7** shows the detailed acid-base properties of SZ as the SO_4 coverage is varied from 0-1 monolayer (ML) on ZrO_2 and the resulting impact of acid:base ratio on production of 5-HMF in aqueous media.



Scheme 7. a) NH_3 and CO_2 titration of acid and base sites as a function of SO_4 coverage on ZrO_2 , and b) acid site normalised HMF productivity as a function of acid:base loading showing optimum activity for glucose isomerisation to fructose and subsequent dehydration to 5-HMF.

Tailoring the acid:base distribution generates a material with the necessary base sites for glucose→fructose isomerisation, and Brønsted acid sites optimized for the subsequent conversion of reactively-formed fructose to 5-HMF. Although such non-porous zirconias are promising, their intrinsic rate of 5-HMF productivity requires significant enhancement to improve catalyst efficiency and methods to stabilize highly porous and/or more highly dispersed tuneable ZrO_2 phases are desirable. Poor thermal stability and associated pore-collapse during catalyst activation limits the utility of templated zirconias, [98, 99] hence high surface area nanostructured silicas (e.g. HMS-24,[100] MCM-41 and SBA-15) with well-defined mesoporosity are attractive scaffolds over which to disperse ZrO_2 . To maintain the internal pore network and hence molecular accessibility, it is critical that ZrO_2 is introduced in a layer-by-layer fashion to minimise three dimensional crystallite formation and/or pore blockage. Incipient wetness impregnation, [101-106] urea hydrolysis [107] and vapour induced hydrolysis (VIH) [99, 108] methods have been reported to prepare ZrO_2 coatings on SBA-15, typically employing zirconium propoxide [101-105] or acetate[106] precursors in an anhydrous organic solvent (e.g. dry hexane or 50:50 vol% anhydrous toluene:ethanol). However, simple variation of the precursor concentration to achieve different zirconia loadings invariably yields 3-4 nm crystallites, similar to the silica mesopore diameter. To address this, high area ZrO_2 /SBA-15 materials have been reported following a solution phase atomic layer deposition of $\text{Zr}(\text{iPrO}_4)$ from anhydrous hexane [109]. XPS verified the ZrO_2 growth mode using the attenuation of the Si 2p signal to provide a direct measure of film thickness (**Scheme 8a**), with the observed exponential decay in the SBA-15 substrate intensity with consecutive ZrO_2 depositions indicative of a layer-by-layer growth mode. The observed attenuation with each cycle is in excellent agreement with the thickness of a (111) oriented monolayer of monoclinic ZrO_2 (0.42 nm), indicating the conformal growth of ZrO_2 monolayers over SBA-15. Further characterisation by HRTEM (**Scheme 8b**) and XRD provided additional verification for film uniformity, ruling out the presence of 3D crystallites of ZrO_2 . The grafted ZrO_2 films were confirmed to exhibit amphoteric character similar to bulk ZrO_2 , with the Brønsted:Lewis acid site ratio increasing with sulfate loading at the expense of base sites. The optimum bilayer SO_4 - ZrO_2 /SBA-15 was found to afford an ordered mesoporous material with a high acid site loading, which delivers a three-fold enhancement in 5-HMF productivity from glucose over non-porous SZ counterparts (**Scheme 8c**) [110]. The co-existence of accessible solid basic/Lewis acid and Brønsted acid sites in grafted SZ/SBA-15 promote the respective isomerization of glucose to fructose and dehydration of reactively-formed fructose to the desired 5-HMF platform chemical.

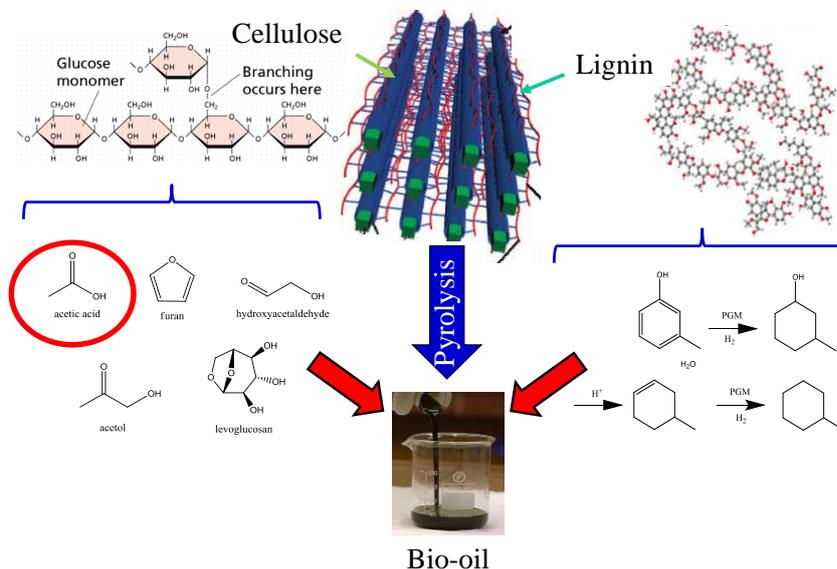


Scheme 8. a) Si 2p XP attenuation following 1-3 grafting cycles demonstrating layer-by-layer growth of ~ 0.42 nm thick ZrO_2 sheets. Dashed line shows the theoretical fit and associated film thickness to the observed attenuation, b) HRTEM of SBA-15 with 2-3 grafted ZrO_2 layers, and c) catalytic performance in HMF production from glucose and fructose using 2ML SZ/SBA-15.

3. Biofuel Synthesis

3.1 Catalysts for esterification pre-treatments of pyrolysis oil.

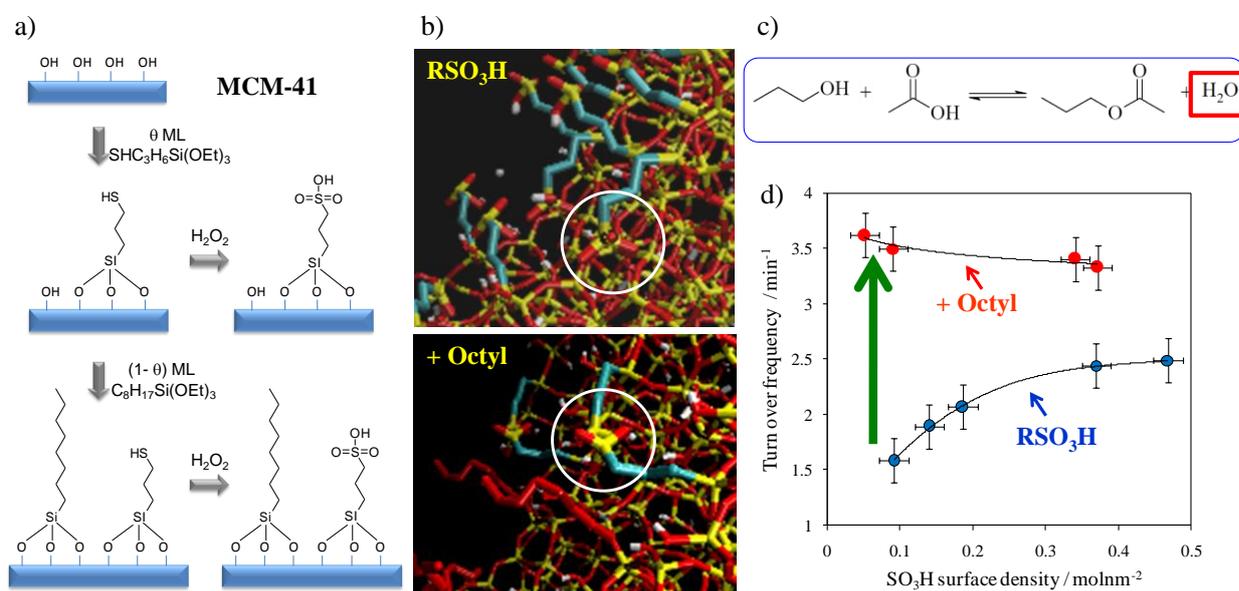
Pyrolytic thermal decomposition of biomass in the absence of oxygen is a commonly used approach to generate bio-oil, however this generates a broad product distribution which is sensitive to the feedstock, reaction temperature and residence time. Typical bio-oils are a mixture of acids, alcohols, furans, aldehydes, esters, ketones, sugars and multifunctional compounds such as hydroxyacetic acid, hydroxyl-acetaldehyde and hydroxyacetone (derived from cellulose and hemicellulose), together with 3-hydroxy-3-methoxy benzaldehyde, phenols, guaiacols and syringols derived from the lignin component (**Scheme 9**).



Scheme 9. Representative bio-oil components formed from lignin and (hemi)cellulose components during fast pyrolysis.

The pyrolysis oil is however highly acidic and corrosive (pH 2-3), and as a result, fresh bio-oil is inherently unstable at room temperature, deteriorating via polymerisation and condensation reactions on storage leading to increased viscosity and poor combustion. Furthermore, the strong acidity of bio-oils resulting from the presence of organic acids can cause problems for the stability and lifetime of the catalysts used in the hydrodeoxygenation process used to upgrade and reform the oil to fuel. Esterification of these corrosive acidic components in bio-oil is proposed as a simple pre-treatment to improve the stability of oils during storage and transportation prior to subsequent upgrading. While the use of strong mineral acids such as H_2SO_4 is effective at catalysing esterification, this is not recommended due to the corrosive and hazardous nature of the acid

Sulfonic acid silicas are promising solid acid catalysts for esterification reactions, however the hydrophilic nature of polar silica surfaces can be problematic as surface hydroxyl groups favour H₂O adsorption, which when formed during acid esterification can favour the reverse hydrolysis reaction and consequently reduce ester yields. Surface modification via the incorporation of organic functionality into polar oxide surfaces, or dehydroxylation, can lower their polarity and thereby increase initial rates of acid catalysed transformations of liquid phase organic molecules [111]. The incorporation of organic spectator groups (e.g. phenyl, methyl or propyl) during the sol-gel syntheses of SBA-15 [112] and MCM-41 [113] sulphonic acid silicas via co-grafting, or simple addition of the respective alkyl or aryltrimethoxysilane during co-condensation protocols has been suggested as a means to tune hydrophobicity of silica surfaces. The effect of co-functionalisation of sulphonic acid derivatised MCM-41 materials has been investigated to assess the effect of acid site density and surface hydrophobicity on catalyst acidity and associated performance in acetic acid esterification with butanol [114]. MCM-41 was selected due to the availability of accurate models for the pore structure from kinetic Monte Carlo simulations [115], enabling dynamic simulation of sulphonic acid and octyl groups co-attached within the MCM-41 pores to be modelled. In parallel experiments, two catalyst series were investigated towards acetic acid esterification with butanol (**Scheme 10a**). In one series, the propylsulphonic acid coverage was varied between $\theta(\text{RSO}_3\text{H}) = 0\text{--}100\%$ ML over the bare silica (MCM-SO₃H), while in the second octyl co-grafted series, both sulfonic acid and octyl coverages were tuned (MCM-Oc-SO₃H). Lateral interactions between acid head groups and also hydrogen bonding of sulphonic acid head groups with free surface silanols (**Scheme 10b**) could be assessed along with the role of hydrophobic octyl modifiers in altering the conformation of sulfonic acid groups [116].



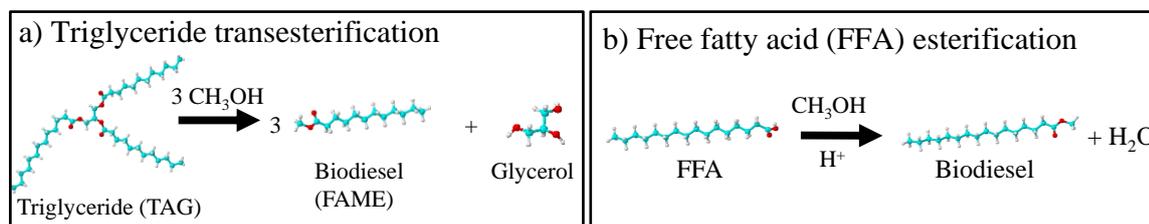
Scheme 10. a) Protocol for the synthesis of sulfonic acid and octyl co-functionalised sulfonic acid MCM-41 catalysts. Adapted from reference [116] with permission from The Royal Society of Chemistry. b) Molecular dynamics simulations of MCM-SO₃H and MCM-Oc-SO₃H pore models highlighting the interaction between surface sulfonic acid and hydroxyl groups in the absence of co-grafted octyl chains; (c-d) influence of PrSO₃H surface density and co-grafted octyl groups on catalytic performance in acetic acid esterification with butanol. Adapted from reference [116] with permission from The Royal Society of Chemistry.

Ammonia calorimetry revealed the acid strength of polar MCM-SO₃H materials increases from 87 to 118 kJ mol⁻¹ as a function of sulphonic acid loading. Octyl co-grafting dramatically enhances the acid strength of MCM-Oc-SO₃H for submonolayer SO₃H coverages, with $\Delta H_{\text{ads}}(\text{NH}_3)$ rising to 103 kJ mol⁻¹. While the per site activity of the MCM-SO₃H series in butanol esterification with acetic acid increases with SO₃H content, mirroring their acidity (**Scheme 10c**), octyl surface functionalisation promotes esterification for all MCM-Oc-SO₃H catalysts, doubling the turnover frequency of the lowest loading SO₃H material. Molecular dynamic simulations indicate that the interaction of isolated sulphonic acid moieties with surface silanol groups is the primary cause of the lower acidity and activity of sub-monolayer samples within the MCM-SO₃H series. Lateral interactions with octyl groups help to re-orient sulphonic acid head groups into the pore interior, thereby enhancing acid strength and associated esterification activity.

3.2 Biodiesel Synthesis using tailored porous catalysts

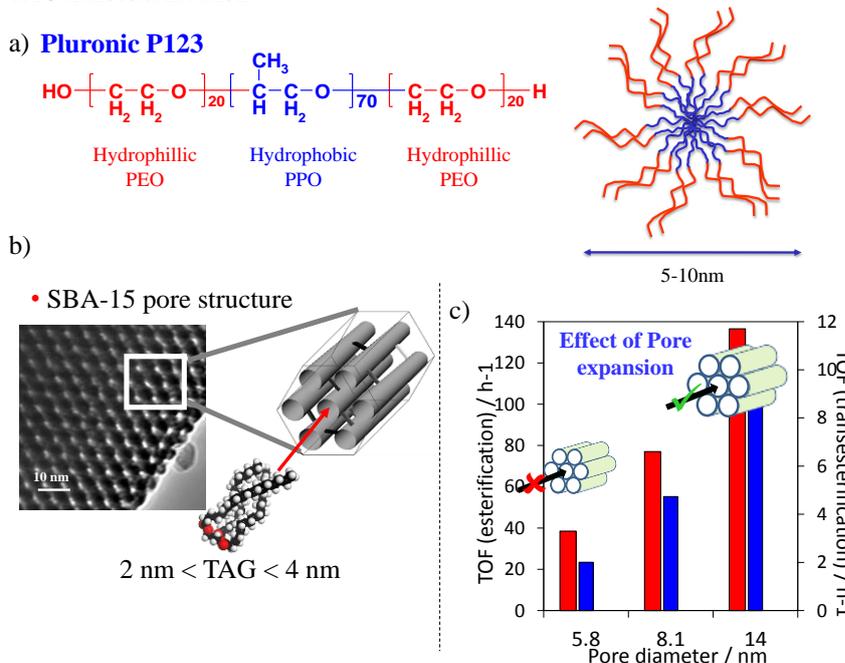
Biodiesel, produced by the transesterification of plant or algal oil triglycerides [117, 118] to form fatty acid methyl ester (FAME) (**Scheme 11a**), is a low cost solution to renewable transportation fuels which can be blended with or replace conventional diesel. [119] Commercial production typically employs homogeneous alkali or mineral acid catalysts to effect these transformations and consequently generates vast quantities of aqueous waste, detrimental to the economic feasibility and

environmental impact of biodiesel synthesis. Solid acid catalysts able to simultaneously perform these esterification and transesterification reactions under mild conditions would be particularly desirable to minimise processing steps and permit the use of high FFA containing waste oils.



Scheme 11 a) Triglyceride transesterification and b) fatty acid esterification with methanol.

In both conventional solid acid and base systems poor accessibility of the active site within micropore networks and associated mass transport/diffusion limitations hinders their performance in biodiesel synthesis. Further catalyst development and improved activity should prove possible through utilising tailored porous solids as high area mesoporous supports to enhance TAG and FFA diffusion to the active acid/basic groups [120, 121]. Templated mesoporous solids are widely used as catalyst supports [122, 123], with SBA-15 silica popular candidates for reactions pertinent to biodiesel synthesis [124-126]. The SBA family of materials generated from block copolymer surfactants (e.g. P123 (PEO₂₀PPO₇₀PEO₂₀) (**Scheme 12a** and **b**) typically give rise to larger pore diameters than those achieved with alkyl amines or ammonium surfactants used in HMS or MCM materials (**Scheme 12a**). However, conventionally synthesised sulfonic acid-functionalised SBA-15 silicas, with pore sizes below ~6 nm, possess long isolated parallel channels and suffer correspondingly slow in-pore diffusion and catalytic turnover in FFA esterification and TAG transesterification.



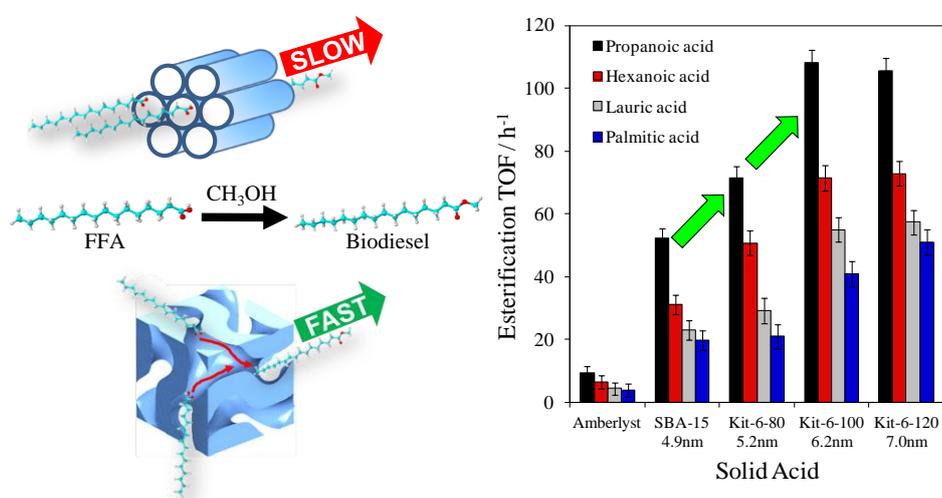
Scheme 12 a) Structure of Pluronic P123 template, b) hexagonal SBA-15 pore structure and typical TAG size, and c) effect of pore expansion on TOFs in palmitic acid esterification and triolein transesterification with methanol

The use of poragens such as trimethylbenzene [127] triethylbenzene or triisopropylbenzene [128] to induce swelling of the Pluronic P123 micelles can be used to produce highly-ordered periodic mesostructures with pore diameters of ~6, 8 and 14 nm [129]. When functionalised by mercaptopropyl trimethoxysilane (MPTS) and oxidised with H₂O₂ to yield expanded PrSO₃-SBA-15 catalysts these were effective in both palmitic acid esterification with methanol and tricaprylin and triolein transesterification with methanol under mild conditions. Enhancements in TOF were observed which were attributed to superior mass-transport of the bulky free fatty acid and triglycerides within the expanded PrSO₃-SBA-15 (**Scheme 12c**).

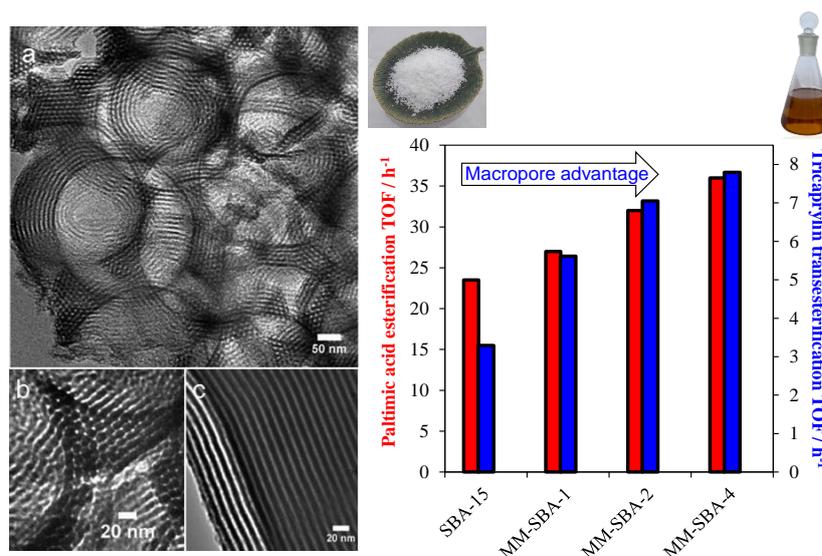
An alternative means to improve mass transport is to replace the two dimensional, micron-length channels characteristic of the SBA-15 *p6mm* structure with three dimensional interconnected channels associated with the *la3d* structure of KIT-6 mesoporous silica. This diversity of mesoporous silica architectures enables the impact of pore connectivity upon organic acid esterification to be quantified [130], using a family of pore-expanded propylsulfonic acid KIT-6 analogues, PrSO₃H-KIT-6, prepared via MPTS grafting and subsequent oxidation. Such a conventionally-prepared material exhibited 40 and 70 % TOF

enhancements for propanoic and hexanoic acid esterification respectively over an analogous $\text{PrSO}_3\text{H-SBA-15}$ catalyst of comparable (5 nm) pore diameter, attributed to faster mesopore diffusion. However, pore accessibility remained rate-limiting for esterification of the longer chain lauric and palmitic acids. Pore expansion of the KIT-6 mesopores up to 7 nm via hydrothermal ageing doubled the resulting TOFs for lauric and palmitic acid esterification with respect to an unexpanded $\text{PrSO}_3\text{H-SBA-15}$ (Scheme 13).

Simulations demonstrate that in the Knudsen diffusion regime [131], where reactants/products are able to diffuse enter/exit mesopores but experience moderate diffusion limitations, hierarchical pore structures may significantly improve catalyst activity. Materials with interpenetrating, bimodal meso-macropore networks have been prepared using microemulsion [132] or co-surfactant [133] templating routes and are particularly attractive for liquid phase, flow reactors wherein rapid pore diffusion is required. Liquid crystalline (soft) and colloidal polystyrene nanospheres (hard) templating methods have been combined to create highly organised, macro-mesoporous aluminas [134] and ‘SBA-15 like’ silicas [114] (Scheme 14), in which both macro- and mesopore diameters can be independently tuned over the range 200–500 nm and 5–20 nm respectively. Macropore incorporation in the mesopore network of a propylsulfonic acid functionalised SBA-15 confers a striking enhancement in the rates of tricaprylin transesterification and palmitic acid esterification with methanol, attributed to the macropores acting as transport conduits for reactants to rapidly access PrSO_3H active sites located within the mesopores



Scheme 13. Superior performance of interconnected, mesoporous propylsulfonic acid KIT-6 catalysts for biodiesel synthesis via free fatty acid esterification with methanol, versus non-interconnected mesoporous SBA-15 analogue. Adapted from reference [130] Copyright 2012 American Chemical Society.



Scheme 14. (left) (a) SEM and (b, c) low and high magnification TEM micrographs of a hierarchical macro-mesoporous $\text{Pr-SO}_3\text{H-SBA-15}$; (right) corresponding catalytic performance in palmitic acid esterification and tricaprylin transesterification with methanol as a function of macropore density, versus a purely mesoporous $\text{Pr-SO}_3\text{H-SBA-15}$. Adapted from reference [114] with permission from The Royal Society of Chemistry.

4. Concluding Remarks

The potential of lignocellulosic biomass for the production of renewable chemicals and advanced transportation fuels can only be unlocked via the development of tailored heterogeneous catalysts, in which advances in materials chemistry, nanoscience, surface chemistry and process engineering are exploited. Ultimately, catalytic chemists and engineers need to emulate the successes of heterogeneous catalysis in petroleum refining; achieving this necessitates an improved understanding of biomass properties and its impact on catalyst deactivation in order to accelerate biomass-to-chemicals and fuels production.

Widespread uptake and the development of next-generation biofuels and chemical feedstocks also requires progressive government policies and incentive schemes to place biomass-derived chemicals on a comparable footing with heavily subsidised fossil fuel-derived resources. [135][136] In the short- to medium-term it is likely that so called ‘drop-in’ replacements of crude oil derived chemicals, or methods to co-process biomass in conventional oil refineries will be most cost effective to circumvent high capital costs of new processing facilities.[137] Targeting processes that require ‘drop in’ chemical feedstocks that directly replace existing fossil derived chemicals, has the advantage of providing raw material for a mature market in which the necessary infrastructure and technology exists, thereby maximising the impact of the value added chemical. In parallel emerging chemicals will produce a completely new value chain with new products that may offer enhanced performance and potential for new business opportunities. [138] To overcome some of the infrastructure problems for biomass processing, economic models for biorefineries have proposed enhanced revenue that could be achieved by making more use of underutilised infrastructure in corn wet and dry mills or pulp and paper operations.[8]

Biomass pre-treatments employed to isolate sugars are some of the most wasteful steps in biorefineries, and new approaches are therefore desired to improve the atom- and energy efficiency of lignocellulose processing such that preliminary acid hydrolysis/extraction steps to sugars from lignocellulose can be performed under mild conditions and with minimal waste generation. Cellulose stability itself presents a major hurdle to such advances, with environmentally friendly and energy efficient means to break up this biopolymer an ongoing challenge. Conventional heterogeneous catalysts cannot be employed alone in solid phase reactions with biomass, although some recent reports propose ball milling as an effective means to induce ‘mechanocatalysis’ between cellulose and clay based catalysts possessing layered structures, [139] or carbon based catalysts [140]. Ultimately, the development of new heterogeneous catalysts, and integrated process optimisation, requires collaboration between catalytic chemists, chemical engineers and experts in molecular simulation to exploit innovative reactor designs; catalytic routes to convert biomass to chemicals and fuels will underpin renewable feedstock valorisation this century.

Additional Information

Information on the following should be included wherever relevant.

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Competing Interests

We have no competing interests.

Authors' Contributions

AFL and KW both made contributions to drafting sections of the article, revising it critically for important intellectual content, with KW giving final approval of the version to be published.

References

- [1] Authority, C.C. 2013 Reducing Australia's Greenhouse Gas Emissions –Targets and Progress Review Draft Report. (Commonwealth of Australia).
- [2] Secretariat, C.C. 2013 The critical decade 2013 Climate change science, risks and responses. (Commonwealth of Australia).
- [3] Agency, I.E. 2011 Prospect of limiting the global increase in temperature to 2°C is getting bleaker.
- [4] Agency, I.E. 2013 Redrawing the Energy Climate Map.
- [5] Jakob, M. & Hilaire, J. 2015 Climate science: Unburnable fossil-fuel reserves. *Nature* **517**, 150-152. (doi:10.1038/517150a).
- [6] Administration, U.S.E.I. 2013 International Energy Outlook 2013.
- [7] Armaroli, N. & Balzani, V. 2007 The future of energy supply: Challenges and opportunities. *Angew. Chem.-Int. Edit.* **46**, 52-66. (doi:10.1002/anie.200602373).
- [8] Bozell, J.J. & Petersen, G.R. 2010 Technology development for the production of biobased products from biorefinery carbohydrates-the US Department of Energy's "Top 10" revisited. *Green Chemistry* **12**, 539-554. (doi:10.1039/b922014c).
- [9] Lipinsky, E.S. 1981 Chemicals from Biomass: Petrochemical Substitution Options. *Science* **212**, 1465-1471. (doi:10.1126/science.212.4502.1465).
- [10] Thomas, J.M. 2012 The societal significance of catalysis and the growing practical importance of single-site heterogeneous catalysts. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science* **468**, 1884-1903. (doi:10.1098/rspa.2012.0196).
- [11] Somorjai, G.A., Frei, H. & Park, J.Y. 2009 Advancing the Frontiers in Nanocatalysis, Bionterfaces, and Renewable Energy Conversion by Innovations of Surface Techniques. *Journal of the American Chemical Society* **131**, 16589-16605. (doi:10.1021/ja9061954).
- [12] Kim, M. & Day, D.F. 2011 Composition of sugar cane, energy cane, and sweet sorghum suitable for ethanol production at Louisiana sugar mills. *J. Ind. Microbiol. Biotechnol.* **38**, 803-807. (doi:10.1007/s10295-010-0812-8).
- [13] Tew, T.L., Cobill, R.M. & Richard, E.P. 2008 Evaluation of Sweet Sorghum and Sorghum x Sudangrass Hybrids as Feedstocks for Ethanol Production. *BioEnergy Res.* **1**, 147-152. (doi:10.1007/s12155-008-9013-y).
- [14] Cherubini, F. 2010 The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Conversion and Management* **51**, 1412-1421. (doi:<http://dx.doi.org/10.1016/j.enconman.2010.01.015>).
- [15] Menon, V. & Rao, M. 2012 Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science* **38**, 522-550. (doi:<http://dx.doi.org/10.1016/j.pecs.2012.02.002>).
- [16] Hoogwijk, M., Faaij, A., van den Broek, R., Berndes, G., Gielen, D. & Turkenburg, W. 2003 Exploration of the ranges of the global potential of biomass for energy. *Biomass and Bioenergy* **25**, 119-133. (doi:[http://dx.doi.org/10.1016/S0961-9534\(02\)00191-5](http://dx.doi.org/10.1016/S0961-9534(02)00191-5)).
- [17] Kadam, K.L., Forrest, L.H. & Jacobson, W.A. 2000 Rice straw as a lignocellulosic resource: collection, processing, transportation, and environmental aspects. *Biomass and Bioenergy* **18**, 369-389. (doi:[http://dx.doi.org/10.1016/S0961-9534\(00\)00005-2](http://dx.doi.org/10.1016/S0961-9534(00)00005-2)).
- [18] 2014 Wasted: Europes untapped resource (<http://europeanclimate.org/wp-content/uploads/2014/02/WASTED-final.pdf>). (
- [19] Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M. & Ladisch, M. 2005 Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology* **96**, 673-686. (doi:<http://dx.doi.org/10.1016/j.biortech.2004.06.025>).
- [20] Glasser, W.G. & Wright, R.S. 1998 Steam-assisted biomass fractionation. II. fractionation behavior of various biomass resources. *Biomass and Bioenergy* **14**, 219-235. (doi:[http://dx.doi.org/10.1016/S0961-9534\(97\)10037-X](http://dx.doi.org/10.1016/S0961-9534(97)10037-X)).
- [21] Zhao, X., Cheng, K. & Liu, D. 2009 Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. *Appl. Microbiol. Biotechnol.* **82**, 815-827. (doi:10.1007/s00253-009-1883-1).
- [22] Fatih Demirbas, M. 2009 Biorefineries for biofuel upgrading: A critical review. *Appl. Energy* **86**, Supplement 1, S151-S161. (doi:<http://dx.doi.org/10.1016/j.apenergy.2009.04.043>).
- [23] Alvira, P., Tomás-Pejó, E., Ballesteros, M. & Negro, M.J. 2010 Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology* **101**, 4851-4861. (doi:<http://dx.doi.org/10.1016/j.biortech.2009.11.093>).
- [24] Mok, W.S., Antal, M.J. & Varhegyi, G. 1992 Productive and parasitic pathways in dilute acid-catalyzed hydrolysis of cellulose. *Industrial & Engineering Chemistry Research* **31**, 94-100. (doi:10.1021/ie00001a014).
- [25] Rinaldi, R. & Schüth, F. 2009 Acid Hydrolysis of Cellulose as the Entry Point into Biorefinery Schemes. *ChemSusChem* **2**, 1096-1107. (doi:10.1002/cssc.200900188).

- [26] Sasaki, M., Kabyemela, B., Malaluan, R., Hirose, S., Takeda, N., Adschiri, T. & Arai, K. 1998 Cellulose hydrolysis in subcritical and supercritical water. *The Journal of Supercritical Fluids* **13**, 261-268. (doi:[http://dx.doi.org/10.1016/S0896-8446\(98\)00060-6](http://dx.doi.org/10.1016/S0896-8446(98)00060-6)).
- [27] Binder, J.B. & Raines, R.T. 2010 Fermentable sugars by chemical hydrolysis of biomass. *Proceedings of the National Academy of Sciences of the United States of America* **107**, 4516-4521. (doi:10.1073/pnas.0912073107).
- [28] Kaufman Rechulski, M.D., Källdström, M., Richter, U., Schüth, F. & Rinaldi, R. 2015 Mechanocatalytic Depolymerization of Lignocellulose Performed on Hectogram and Kilogram Scales. *Industrial & Engineering Chemistry Research* **54**, 4581-4592. (doi:10.1021/acs.iecr.5b00224).
- [29] Carrasquillo-Flores, R., Kaeldstroem, M., Schueth, F., Dumesic, J.A. & Rinaldi, R. 2013 Mechanocatalytic Depolymerization of Dry (Ligno)cellulose As an Entry Process for High-Yield Production of Furfurals. *ACS Catalysis* **3**, 993-997. (doi:10.1021/cs4001333).
- [30] Suhas, Carrott, P.J.M. & Ribeiro Carrott, M.M.L. 2007 Lignin – from natural adsorbent to activated carbon: A review. *Bioresource Technology* **98**, 2301-2312. (doi:<http://dx.doi.org/10.1016/j.biortech.2006.08.008>).
- [31] Gírio, F.M., Fonseca, C., Carvalheiro, F., Duarte, L.C., Marques, S. & Bogel-Lukasik, R. 2010 Hemicelluloses for fuel ethanol: A review. *Bioresource Technology* **101**, 4775-4800. (doi:<http://dx.doi.org/10.1016/j.biortech.2010.01.088>).
- [32] Chakar, F.S. & Ragauskas, A.J. 2004 Review of current and future softwood kraft lignin process chemistry. *Industrial Crops and Products* **20**, 131-141. (doi:<http://dx.doi.org/10.1016/j.indcrop.2004.04.016>).
- [33] Ruiz, E., Cara, C., Manzanares, P., Ballesteros, M. & Castro, E. 2008 Evaluation of steam explosion pre-treatment for enzymatic hydrolysis of sunflower stalks. *Enzyme and Microbial Technology* **42**, 160-166. (doi:<http://dx.doi.org/10.1016/j.enzmictec.2007.09.002>).
- [34] Huber, G.W. & Dumesic, J.A. 2006 An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. *Catalysis Today* **111**, 119-132. (doi:<http://dx.doi.org/10.1016/j.cattod.2005.10.010>).
- [35] Lin, Y.-C. & Huber, G.W. 2009 The critical role of heterogeneous catalysis in lignocellulosic biomass conversion. *Energy & Environmental Science* **2**, 68-80.
- [36] Dacquin, J.-P., Lee, A.F. & Wilson, K. 2012 *Heterogeneous catalysts for converting renewable feedstocks to fuels and chemicals*, Springer.
- [37] Cheng, K.K., Zhao, X.B., Zeng, J., Wu, R.C., Xu, Y.Z., Liu, D.H. & Zhang, J.A. 2012 Downstream processing of biotechnological produced succinic acid. *Appl. Microbiol. Biotechnol.* **95**, 841-850. (doi:10.1007/s00253-012-4214-x).
- [38] Huang, H.J., Ramaswamy, S., Tschirner, U.W. & Ramarao, B.V. 2008 A review of separation technologies in current and future biorefineries. *Sep. Purif. Technol.* **62**, 1-21. (doi:10.1016/j.seppur.2007.12.011).
- [39] Huh, Y.S., Jun, Y.S., Hong, Y.K., Song, H., Lee, S.Y. & Hong, W.H. 2006 Effective purification of succinic acid from fermentation broth produced by *Mannheimia succiniciproducens*. *Process Biochemistry* **41**, 1461-1465. (doi:10.1016/j.procbio.2006.01.020).
- [40] Corma, A., Renz, M. & Susarte, M. 2009 Transformation of Biomass Products into Fine Chemicals Catalyzed by Solid Lewis- and Bronsted-acids. *Topics in Catalysis* **52**, 1182-1189. (doi:10.1007/s11244-009-9266-5).
- [41] Corma, A., Iborra, S. & Velty, A. 2007 Chemical routes for the transformation of biomass into chemicals. *Chemical Reviews* **107**, 2411-2502. (doi:10.1021/cr050989d).
- [42] Climent, M.J., Corma, A. & Iborra, S. 2011 Converting carbohydrates to bulk chemicals and fine chemicals over heterogeneous catalysts. *Green Chemistry* **13**, 520-540. (doi:10.1039/c0gc00639d).
- [43] Fernando, S., Adhikari, S., Chandrapal, C. & Murali, N. 2006 Biorefineries: Current Status, Challenges, and Future Direction. *Energy & Fuels* **20**, 1727-1737. (doi:10.1021/ef060097w).
- [44] Clark, J.H. 2007 Green chemistry for the second generation biorefinery - sustainable chemical manufacturing based on biomass. *Journal of Chemical Technology and Biotechnology* **82**, 603-609. (doi:10.1002/jctb.1710).
- [45] Schlaf, M. 2006 Selective deoxygenation of sugar polyols to alpha,omega-diols and other oxygen content reduced materials - a new challenge to homogeneous ionic hydrogenation and hydrogenolysis catalysis. *Dalton T*, 4645-4653.
- [46] Catoire, L., Yahyaoui, M., Osmont, A. & Goekalp, I. 2008 Thermochemistry of Compounds Formed during Fast Pyrolysis of Lignocellulosic Biomass. *Energy & Fuels* **22**, 4265-4273. (doi:10.1021/ef800418z).
- [47] Ruppert, A.M., Weinberg, K. & Palkovits, R. 2012 Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals. *Angewandte Chemie-International Edition* **51**, 2564-2601. (doi:10.1002/anie.201105125).
- [48] Dacquin, J.P., Cross, H.E., Brown, D.R., Duren, T., Williams, J.J., Lee, A.F. & Wilson, K. 2010 Interdependent lateral interactions, hydrophobicity and acid strength and their influence on the catalytic activity of nanoporous sulfonic acid silicas. *Green Chemistry* **12**, 1383-1391. (doi:10.1039/c0gc00045k).
- [49] Li, W.C., Lu, A.H. & Schuth, F. 2005 Preparation of monolithic carbon aerogels and investigation of their pore interconnectivity by a nanocasting pathway. *Chemistry of Materials* **17**, 3620-3626. (doi:10.1021/cm050345m).
- [50] Climent, M.J., Corma, A. & Iborra, S. 2011 Heterogeneous Catalysts for the One-Pot Synthesis of Chemicals and Fine Chemicals. *Chemical Reviews* **111**, 1072-1133. (doi:10.1021/cr1002084).
- [51] Bechthold, I., Bretz, K., Kabasci, S., Kopitzky, R. & Springer, A. 2008 Succinic acid: A new platform chemical for biobased polymers from renewable resources. *Chemical Engineering & Technology* **31**, 647-654. (doi:10.1002/ceat.200800063).

- [52] Zhang, B., Ren, J., Liu, X., Guo, Y., Guo, Y., Lu, G. & Wang, Y. 2010 Novel sulfonated carbonaceous materials from p-toluenesulfonic acid/glucose as a high-performance solid-acid catalyst. *Catalysis Communications* **11**, 629-632. (doi:10.1016/j.catcom.2010.01.010).
- [53] Clark, J.H., Budarin, V., Dugmore, T., Luque, R., Macquarrie, D.J. & Strelko, V. 2008 Catalytic performance of carbonaceous materials in the esterification of succinic acid. *Catalysis Communications* **9**, 1709-1714. (doi:10.1016/j.catcom.2008.01.037).
- [54] Lin, C.S.K., Luque, R., Clark, J.H., Webb, C. & Du, C. 2012 Wheat-based biorefining strategy for fermentative production and chemical transformations of succinic acid. *Biofuels, Bioproducts and Biorefining* **6**, 88-104. (doi:10.1002/bbb.328).
- [55] Zhang, A.Y.-z., Sun, Z., Leung, C.C.J., Han, W., Lau, K.Y., Li, M. & Lin, C.S.K. 2013 Valorisation of bakery waste for succinic acid production. *Green chemistry* **15**, 690-695.
- [56] Choudhary, H., Nishimura, S. & Ebitani, K. 2012 Highly Efficient Aqueous Oxidation of Furfural to Succinic Acid Using Reusable Heterogeneous Acid Catalyst with Hydrogen Peroxide. *Chemistry Letters* **41**, 409-411. (doi:10.1246/cl.2012.409).
- [57] Guo, H. & Yin, G. 2011 Catalytic Aerobic Oxidation of Renewable Furfural with Phosphomolybdic Acid Catalyst: an Alternative Route to Maleic Acid. *The Journal of Physical Chemistry C* **115**, 17516-17522. (doi:10.1021/jp2054712).
- [58] Agirrezabal-Telleria, I., Gandarias, I. & Arias, P.L. 2014 Heterogeneous acid-catalysts for the production of furan-derived compounds (furfural and hydroxymethylfurfural) from renewable carbohydrates: A review. *Catalysis Today* **234**, 42-58. (doi:<http://dx.doi.org/10.1016/j.cattod.2013.11.027>).
- [59] Dashtban, M., Gilbert, A. & Fatehi, P. 2014 Recent advancements in the production of hydroxymethylfurfural. *RSC Advances* **4**, 2037-2050. (doi:10.1039/C3RA45396K).
- [60] van Putten, R.-J., van der Waal, J.C., de Jong, E., Rasrendra, C.B., Heeres, H.J. & de Vries, J.G. 2013 Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources. *Chemical Reviews* **113**, 1499-1597. (doi:10.1021/cr300182k).
- [61] Dutta, S., De, S. & Saha, B. 2012 A Brief Summary of the Synthesis of Polyester Building-Block Chemicals and Biofuels from 5-Hydroxymethylfurfural. *ChemPlusChem* **77**, 259-272. (doi:10.1002/cplu.201100035).
- [62] Hu, L., Zhao, G., Hao, W.W., Tang, X., Sun, Y., Lin, L. & Liu, S.J. 2012 Catalytic conversion of biomass-derived carbohydrates into fuels and chemicals via furanic aldehydes. *RSC Adv.* **2**, 11184-11206. (doi:10.1039/c2ra21811a).
- [63] Kuster, B.F.M. 1990 5-Hydroxymethylfurfural (Hmf) - a Review Focusing on Its Manufacture. *Starch-Starke* **42**, 314-321.
- [64] Roman-Leshkov, Y., Chheda, J.N. & Dumesic, J.A. 2006 Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* **312**, 1933-1937. (doi:10.1126/science.1126337).
- [65] Zhang, Y., Wang, J., Ren, J., Liu, X., Li, X., Xia, Y., Lu, G. & Wang, Y. 2012 Mesoporous niobium phosphate: an excellent solid acid for the dehydration of fructose to 5-hydroxymethylfurfural in water. *Catalysis Science & Technology*. (doi:10.1039/C2CY20204B).
- [66] Wang, J., Xu, W., Ren, J., Liu, X., Lu, G. & Wang, Y. 2011 Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid. *Green Chemistry* **13**, 2678-2681. (doi:10.1039/c1gc15306d).
- [67] Cao, Q., Guo, X., Guan, J., Mu, X. & Zhang, D. 2011 A process for efficient conversion of fructose into 5-hydroxymethylfurfural in ammonium salts. *Applied Catalysis a-General* **403**, 98-103. (doi:10.1016/j.apcata.2011.06.018).
- [68] Zhao, Q., Wang, L., Zhao, S., Wang, X. & Wang, S. 2011 High selective production of 5-hydroxymethylfurfural from fructose by a solid heteropolyacid catalyst. *Fuel* **90**, 2289-2293. (doi:10.1016/j.fuel.2011.02.022).
- [69] Carlini, C., Patrono, P., Galletti, A.M.R. & Sbrana, G. 2004 Heterogeneous catalysts based on vanadyl phosphate for fructose dehydration to 5-hydroxymethyl-2-furaldehyde. *Applied Catalysis a-General* **275**, 111-118.
- [70] Crisci, A.J., Tucker, M.H., Dumesic, J.A. & Scott, S.L. 2010 Bifunctional Solid Catalysts for the Selective Conversion of Fructose to 5-Hydroxymethylfurfural. *Topics in Catalysis* **53**, 1185-1192.
- [71] Carniti, P., Gervasini, A. & Marzo, M. 2011 Absence of expected side-reactions in the dehydration reaction of fructose to HMF in water over niobic acid catalyst. *Catalysis Communications* **12**, 1122-1126. (doi:10.1016/j.catcom.2011.03.025).
- [72] Qi, X.H., Watanabe, M., Aida, T.M. & Smith, R.L. 2009 Sulfated zirconia as a solid acid catalyst for the dehydration of fructose to 5-hydroxymethylfurfural. *Catalysis Communications* **10**, 1771-1775.
- [73] Carniti, P., Gervasini, A., Biella, S. & Auroux, A. 2006 Niobic acid and niobium phosphate as highly acidic viable catalysts in aqueous medium: Fructose dehydration reaction. *Catalysis Today* **118**, 373-378. (doi:10.1016/j.cattod.2006.07.024).
- [74] Qi, X.H., Guo, H.X. & Li, L.Y. 2011 Efficient Conversion of Fructose to 5-Hydroxymethylfurfural Catalyzed by Sulfated Zirconia in Ionic Liquids. *Industrial & Engineering Chemistry Research* **50**, 7985-7989. (doi:10.1021/ie200488k).
- [75] Nakamura, Y. & Morikawa, S. 1980 The dehydration of d-fructose to 5-hydroxymethyl-2-furaldehyde. *Bulletin of the Chemical Society of Japan* **53**, 3705-3706. (doi:10.1246/bcsj.53.3705).
- [76] Moreau, C., Belgacem, M.N. & Gandini, A. 2004 Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers. *Topics in Catalysis* **27**, 11-30.

- [77] Amarasekara, A.S., Williams, L.D. & Ebede, C.C. 2008 Mechanism of the dehydration of d-fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150 °C: an NMR study. *Carbohydrate Research* **343**, 3021-3024. (doi:<http://dx.doi.org/10.1016/j.carres.2008.09.008>).
- [78] Zhao, H.B., Holladay, J.E., Brown, H. & Zhang, Z.C. 2007 Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science* **316**, 1597-1600.
- [79] Peterson, A.A., Vogel, F., Lachance, R.P., Froling, M., Antal, J.M.J. & Tester, J.W. 2008 Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy & Environmental Science* **1**, 32-65. (doi:10.1039/B810100K).
- [80] Stöcker, M. 2008 Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials. *Angewandte Chemie International Edition* **47**, 9200-9211. (doi:10.1002/anie.200801476).
- [81] Serrano-Ruiz, J.C., Luque, R. & Sepulveda-Escribano, A. 2011 Transformations of biomass-derived platform molecules: from high added-value chemicals to fuels via aqueous-phase processing. *Chemical Society Reviews* **40**, 5266-5281. (doi:10.1039/C1CS15131B).
- [82] McNeff, C.V., Nowlan, D.T., McNeff, L.C., Yan, B.W. & Fedie, R.L. 2010 Continuous production of 5-hydroxymethylfurfural from simple and complex carbohydrates. *Applied Catalysis a-General* **384**, 65-69. (doi:10.1016/j.apcata.2010.06.008).
- [83] Chheda, J.N., Roman-Leshkov, Y. & Dumesic, J.A. 2007 Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chemistry* **9**, 342-350. (doi:10.1039/B611568C).
- [84] Pagan-Torres, Y.J., Wang, T., Gallo, J.M.R., Shanks, B.H. & Dumesic, J.A. 2012 Production of 5-Hydroxymethylfurfural from Glucose Using a Combination of Lewis and Bronsted Acid Catalysts in Water in a Biphasic Reactor with an Alkylphenol Solvent. *ACS Catalysis* **2**, 930-934. (doi:10.1021/cs300192z).
- [85] Ordonsky, V.V., van der Schaaf, J., Schouten, J.C. & Nijhuis, T.A. 2012 The effect of solvent addition on fructose dehydration to 5-hydroxymethylfurfural in biphasic system over zeolites. *Journal of Catalysis* **287**, 68-75. (doi:10.1016/j.jcat.2011.12.002).
- [86] Moreau, C., Durand, R., Razigade, S., Duhamet, J., Faugeras, P., Rivalier, P., Ros, P. & Avignon, G. 1996 Dehydration of fructose to 5-hydroxymethylfurfural over H-mordenites. *Applied Catalysis a-General* **145**, 211-224.
- [87] Rivalier, P., Duhamet, J., Moreau, C. & Durand, R. 1995 Development of a Continuous Catalytic Heterogeneous Column Reactor with Simultaneous Extraction of an Intermediate Product by an Organic-Solvent Circulating in Countercurrent Manner with the Aqueous-Phase. *Catalysis Today* **24**, 165-171.
- [88] Pagan-Torres, Y.J., Wang, T.F., Gallo, J.M.R., Shanks, B.H. & Dumesic, J.A. 2012 Production of 5-Hydroxymethylfurfural from Glucose Using a Combination of Lewis and Bronsted Acid Catalysts in Water in a Biphasic Reactor with an Alkylphenol Solvent. *ACS Catalysis* **2**, 930-934.
- [89] Choudhary, V., Mushrif, S.H., Ho, C., Anderko, A., Nikolakis, V., Marinkovic, N.S., Frenkel, A.I., Sandler, S.I. & Vlachos, D.G. 2013 Insights into the Interplay of Lewis and Brønsted Acid Catalysts in Glucose and Fructose Conversion to 5-(Hydroxymethyl)furfural and Levulinic Acid in Aqueous Media. *Journal of the American Chemical Society* **135**, 3997-4006. (doi:10.1021/ja3122763).
- [90] Rasrendra, C.B., Makertihartha, I.G.B.N., Adisasmito, S. & Heeres, H.J. 2010 Green Chemicals from d-glucose: Systematic Studies on Catalytic Effects of Inorganic Salts on the Chemo-Selectivity and Yield in Aqueous Solutions. *Topics in Catalysis* **53**, 1241-1247. (doi:10.1007/s11244-010-9570-0).
- [91] Wang, T.F., Pagan-Torres, Y.J., Combs, E.J., Dumesic, J.A. & Shanks, B.H. 2012 Water-Compatible Lewis Acid-Catalyzed Conversion of Carbohydrates to 5-Hydroxymethylfurfural in a Biphasic Solvent System. *Topics in Catalysis* **55**, 657-662.
- [92] Nikolla, E., Roman-Leshkov, Y., Moliner, M. & Davis, M.E. 2011 "One-Pot" Synthesis of 5-(Hydroxymethyl)furfural from Carbohydrates using Tin-Beta Zeolite. *ACS Catalysis* **1**, 408-410. (doi:10.1021/cs2000544).
- [93] Takagaki, A., Ohara, M., Nishimura, S. & Ebitani, K. 2009 A one-pot reaction for biorefinery: combination of solid acid and base catalysts for direct production of 5-hydroxymethylfurfural from saccharides. *Chemical Communications*, 6276-6278.
- [94] Aramendía, M.A., Boráu, V., Jiménez, C., Marinas, J.M., Marinas, A., Porras, A. & Urbano, F.J. 1999 Synthesis and Characterization of ZrO₂ as Acid-Basic Catalysts: Reactivity of 2-Methyl-3-butyn-2-ol. *Journal of Catalysis* **183**, 240-250. (doi:<http://dx.doi.org/10.1006/jcat.1999.2418>).
- [95] Tanabe, K. & Yamaguchi, T. 1994 Acid-base bifunctional catalysis by ZrO₂ and its mixed oxides. *Catalysis Today* **20**, 185-197. (doi:[http://dx.doi.org/10.1016/0920-5861\(94\)80002-2](http://dx.doi.org/10.1016/0920-5861(94)80002-2)).
- [96] Qi, X., Watanabe, M., Aida, T.M. & Smith, R.L., Jr. 2008 Catalytic conversion of fructose and glucose into 5-hydroxymethylfurfural in hot compressed water by microwave heating. *Catalysis Communications* **9**, 2244-2249. (doi:10.1016/j.catcom.2008.04.025).
- [97] Dijs, I.J., Geus, J.W. & Jenneken, L.W. 2003 Effect of Size and Extent of Sulfation of Bulk and Silica-Supported ZrO₂ on Catalytic Activity in Gas- and Liquid-Phase Reactions. *The Journal of Physical Chemistry B* **107**, 13403-13413. (doi:10.1021/jp030436b).

- [98] Das, S.K., Bhunia, M.K., Sinha, A.K. & Bhaumik, A. 2009 Self-Assembled Mesoporous Zirconia and Sulfated Zirconia Nanoparticles Synthesized by Triblock Copolymer as Template. *The Journal of Physical Chemistry C* **113**, 8918-8923. (doi:10.1021/jp9014096).
- [99] Krishnan, C.K., Hayashi, T. & Ogura, M. 2008 A New Method for Post-Synthesis Coating of Zirconia on the Mesopore Walls of SBA-15 Without Pore Blocking. *Advanced Materials* **20**, 2131-2136. (doi:10.1002/adma.200702822).
- [100] Ecomier, M.A., Lee, A.F. & Wilson, K. 2005 High activity, templated mesoporous SO₄/ZrO₂/HMS catalysts with controlled acid site density for α -pinene isomerisation. *Microporous and Mesoporous Materials* **80**, 301-310. (doi:<http://dx.doi.org/10.1016/j.micromeso.2005.01.007>).
- [101] Zhu, Y., Jaenicke, S. & Chuah, G.K. 2003 Supported zirconium propoxide—a versatile heterogeneous catalyst for the Meerwein–Ponndorf–Verley reduction. *Journal of Catalysis* **218**, 396-404. (doi:[http://dx.doi.org/10.1016/S0021-9517\(03\)00160-X](http://dx.doi.org/10.1016/S0021-9517(03)00160-X)).
- [102] Katryniok, B., Paul, S., Capron, M., Royer, S., Lancelot, C., Jalowiecki-Duhamel, L., Belliere-Baca, V., Rey, P. & Dumeignil, F. 2011 Synthesis and characterization of zirconia-grafted SBA-15 nanocomposites. *Journal of Materials Chemistry* **21**, 8159-8168. (doi:10.1039/C0JM04588H).
- [103] Gutiérrez, O.Y., Fuentes, G.A., Salcedo, C. & Klimova, T. 2006 SBA-15 supports modified by Ti and Zr grafting for NiMo hydrodesulfurization catalysts. *Catalysis Today* **116**, 485-497. (doi:<http://dx.doi.org/10.1016/j.cattod.2006.06.035>).
- [104] Zhang, J., Ma, Z., Jiao, J., Yin, H., Yan, W., Hagaman, E.W., Yu, J. & Dai, S. 2010 Surface functionalization of mesoporous silica SBA-15 by liquid-phase grafting of zirconium phosphate. *Microporous and Mesoporous Materials* **129**, 200-209. (doi:<http://dx.doi.org/10.1016/j.micromeso.2009.09.016>).
- [105] Thitsartarn, W. & Kawi, S. 2011 Transesterification of Oil by Sulfated Zr-Supported Mesoporous Silica. *Industrial & Engineering Chemistry Research* **50**, 7857-7865. (doi:10.1021/ie1022817).
- [106] Reyes-Carmona, Á., Moreno-Tost, R., Mérida-Robles, J., Santamaría-González, J., Maireles-Torres, P., Jiménez-López, A., Moretti, E., Lenarda, M. & Rodríguez-Castellón, E. 2011 Preparation, characterization and catalytic applications of ZrO₂ supported on low cost SBA-15. *Adsorption* **17**, 527-538. (doi:10.1007/s10450-010-9315-1).
- [107] Lanzafame, P., Temi, D.M., Perathoner, S., Spadaro, A.N. & Centi, G. 2012 Direct conversion of cellulose to glucose and valuable intermediates in mild reaction conditions over solid acid catalysts. *Catalysis Today* **179**, 178-184. (doi:<http://dx.doi.org/10.1016/j.cattod.2011.07.018>).
- [108] Chang, B., Fu, J., Tian, Y. & Dong, X. 2012 Mesoporous solid acid catalysts of sulfated zirconia/SBA-15 derived from a vapor-induced hydrolysis route. *Applied Catalysis A: General* **437–438**, 149-154. (doi:<http://dx.doi.org/10.1016/j.apcata.2012.06.031>).
- [109] Morales, G., Osatiashtiani, A., Hernandez, B., Iglesias, J., Melero, J.A., Paniagua, M., Robert Brown, D., Granollers, M., Lee, A.F. & Wilson, K. 2014 Conformal sulfated zirconia monolayer catalysts for the one-pot synthesis of ethyl levulinate from glucose. *Chemical Communications* **50**, 11742-11745. (doi:10.1039/C4CC04594G).
- [110] Osatiashtiani, A., Lee, A.F., Granollers, M., Brown, D.R., Olivi, L., Morales, G., Melero, J.A. & Wilson, K. 2015 Hydrothermally stable, conformal sulfated zirconia monolayer catalysts for glucose conversion to 5-HMF. *ACS Catalysis*. (doi:10.1021/acscatal.5b00965).
- [111] Wilson, K., Rénon, A. & Clark, J.H. 1999 Novel heterogeneous zinc triflate catalysts for the rearrangement of α -pinene oxide. *Catal Lett* **61**, 51-55. (doi:10.1023/A:1019000317198).
- [112] Margolese, D., Melero, J.A., Christiansen, S.C., Chmelka, B.F. & Stucky, G.D. 2000 Direct Syntheses of Ordered SBA-15 Mesoporous Silica Containing Sulfonic Acid Groups. *Chemistry of Materials* **12**, 2448-2459. (doi:10.1021/cm0010304).
- [113] Díaz, I., Márquez-Alvarez, C., Mohino, F., Pérez-Pariente, J.n. & Sastre, E. 2000 Combined Alkyl and Sulfonic Acid Functionalization of MCM-41-Type Silica: Part 1. Synthesis and Characterization. *Journal of Catalysis* **193**, 283-294. (doi:<http://dx.doi.org/10.1006/jcat.2000.2898>).
- [114] Dhainaut, J., Dacquin, J.-P., Lee, A.F. & Wilson, K. 2010 Hierarchical macroporous-mesoporous SBA-15 sulfonic acid catalysts for biodiesel synthesis. *Green Chemistry* **12**, 296-303. (doi:10.1039/b919341c).
- [115] Schumacher, C., Gonzalez, J., Wright, P.A. & Seaton, N.A. 2005 Generation of Atomistic Models of Periodic Mesoporous Silica by Kinetic Monte Carlo Simulation of the Synthesis of the Material. *The Journal of Physical Chemistry B* **110**, 319-333. (doi:10.1021/jp0551871).
- [116] Dacquin, J.-P., Cross, H.E., Brown, D.R., Duren, T., Williams, J.J., Lee, A.F. & Wilson, K. 2010 Interdependent lateral interactions, hydrophobicity and acid strength and their influence on the catalytic activity of nanoporous sulfonic acid silicas. *Green Chemistry* **12**, 1383-1391. (doi:10.1039/c0gc00045k).
- [117] Luque, R., Herrero-Davila, L., Campelo, J.M., Clark, J.H., Hidalgo, J.M., Luna, D., Marinas, J.M. & Romero, A.A. 2008 Biofuels: a technological perspective. *Energy & Environmental Science* **1**, 542-564. (doi:10.1039/B807094F).
- [118] Lin, C.S.K., Pfaltzgraff, L.A., Herrero-Davila, L., Mubofu, E.B., Abderrahim, S., Clark, J.H., Koutinas, A.A., Kopsahelis, N., Stamatelatos, K., Dickson, F., et al. 2013 Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective. *Energy & Environmental Science* **6**, 426-464. (doi:10.1039/C2EE23440H).

- [119] Demirbas, A. 2007 Importance of biodiesel as transportation fuel. *Energy Policy* **35**, 4661-4670. (doi:<http://dx.doi.org/10.1016/j.enpol.2007.04.003>).
- [120] Shah, P., Ramaswamy, A.V., Lazar, K. & Ramaswamy, V. 2004 Synthesis and characterization of tin oxide-modified mesoporous SBA-15 molecular sieves and catalytic activity in trans-esterification reaction. *Applied Catalysis a-General* **273**, 239-248. (doi:10.1016/j.apcata.2004.06.039).
- [121] Gaudino, M.C., Valentin, R., Brunel, D., Fajula, F., Quignard, F. & Riondel, A. 2005 Titanium-based solid catalysts for transesterification of methyl-methacrylate by catalysis 1-butanol: the homogeneous contribution. *Applied Catalysis a-General* **280**, 157-164. (doi:10.1016/j.apcata.2004.10.007).
- [122] Ying, J.Y., Mehnert, C.P. & Wong, M.S. 1999 Synthesis and Applications of Supramolecular-Templated Mesoporous Materials. *Angewandte Chemie International Edition* **38**, 56-77. (doi:10.1002/(SICI)1521-3773(19990115)38:1/2<56::AID-ANIE56>3.0.CO;2-E).
- [123] Lu, Y. 2006 Surfactant-Templated Mesoporous Materials: From Inorganic to Hybrid to Organic. *Angewandte Chemie International Edition* **45**, 7664-7667. (doi:10.1002/anie.200602489).
- [124] Mbaraka, I.K., Radu, D.R., Lin, V.S.Y. & Shanks, B.H. 2003 Organosulfonic acid-functionalized mesoporous silicas for the esterification of fatty acid. *Journal of Catalysis* **219**, 329-336. (doi:[http://dx.doi.org/10.1016/S0021-9517\(03\)00193-3](http://dx.doi.org/10.1016/S0021-9517(03)00193-3)).
- [125] Melero, J.A., Bautista, L.F., Morales, G., Iglesias, J. & Briones, D. 2008 Biodiesel Production with Heterogeneous Sulfonic Acid-Functionalized Mesostructured Catalysts. *Energy & Fuels* **23**, 539-547. (doi:10.1021/ef8005756).
- [126] Garg, S., Soni, K., Kumaran, G.M., Bal, R., Gora-Marek, K., Gupta, J.K., Sharma, L.D. & Dhar, G.M. 2009 Acidity and catalytic activities of sulfated zirconia inside SBA-15. *Catalysis Today* **141**, 125-129. (doi:<http://dx.doi.org/10.1016/j.cattod.2008.03.021>).
- [127] Chen, D., Li, Z., Wan, Y., Tu, X., Shi, Y., Chen, Z., Shen, W., Yu, C., Tu, B. & Zhao, D. 2006 Anionic surfactant induced mesophase transformation to synthesize highly ordered large-pore mesoporous silica structures. *Journal of Materials Chemistry* **16**, 1511-1519. (doi:10.1039/B517975K).
- [128] Cao, L., Man, T. & Kruk, M. 2009 Synthesis of Ultra-Large-Pore SBA-15 Silica with Two-Dimensional Hexagonal Structure Using Triisopropylbenzene As Micelle Expander. *Chemistry of Materials* **21**, 1144-1153. (doi:10.1021/cm8012733).
- [129] Dacquin, J.P., Lee, A.F., Pirez, C. & Wilson, K. 2012 Pore-expanded SBA-15 sulfonic acid silicas for biodiesel synthesis. *Chemical Communications* **48**, 212-214. (doi:10.1039/c1cc14563k).
- [130] Pirez, C., Caderon, J.-M., Dacquin, J.-P., Lee, A.F. & Wilson, K. 2012 Tunable KIT-6 Mesoporous Sulfonic Acid Catalysts for Fatty Acid Esterification. *ACS Catalysis* **2**, 1607-1614. (doi:10.1021/cs300161a).
- [131] Gheorghiu, S. & Coppens, M.-O. 2004 Optimal bimodal pore networks for heterogeneous catalysis. *AIChE Journal* **50**, 812-820. (doi:10.1002/aic.10076).
- [132] Zhang, X., Zhang, F. & Chan, K.-Y. 2004 The synthesis of large mesopores alumina by microemulsion templating, their characterization and properties as catalyst support. *Materials Letters* **58**, 2872-2877. (doi:<http://dx.doi.org/10.1016/j.matlet.2004.05.008>).
- [133] Sun, J.-H., Shan, Z., Maschmeyer, T. & Coppens, M.-O. 2003 Synthesis of Bimodal Nanostructured Silicas with Independently Controlled Small and Large Mesopore Sizes. *Langmuir* **19**, 8395-8402. (doi:10.1021/la0351156).
- [134] Dacquin, J.-P., Dhainaut, J.r.m., Duprez, D., Royer, S.b., Lee, A.F. & Wilson, K. 2009 An Efficient Route to Highly Organized, Tunable Macroporous-Mesoporous Alumina. *Journal of the American Chemical Society* **131**, 12896-12897. (doi:10.1021/ja9056486).
- [135] Pinzi, S., Garcia, I.L., Lopez-Gimenez, F.J., Luque de Castro, M.D., Dorado, G. & Dorado, M.P. 2009 The Ideal Vegetable Oil-based Biodiesel Composition: A Review of Social, Economical and Technical Implications. *Energy & Fuels* **23**, 2325-2341. (doi:10.1021/ef801098a).
- [136] Azadi, P., Inderwildi, O.R., Farnood, R. & King, D.A. 2013 Liquid fuels, hydrogen and chemicals from lignin: A critical review. *Renewable and Sustainable Energy Reviews* **21**, 506-523. (doi:<http://dx.doi.org/10.1016/j.rser.2012.12.022>).
- [137] Huber, G.W. & Corma, A. 2007 Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass. *Angewandte Chemie International Edition* **46**, 7184-7201. (doi:10.1002/anie.200604504).
- [138] Vennestrøm, P.N.R., Osmundsen, C.M., Christensen, C.H. & Taarning, E. 2011 Beyond Petrochemicals: The Renewable Chemicals Industry. *Angewandte Chemie International Edition* **50**, 10502-10509. (doi:10.1002/anie.201102117).
- [139] Hick, S.M., Griebel, C., Restrepo, D.T., Truitt, J.H., Buker, E.J., Bylda, C. & Blair, R.G. 2010 Mechanocatalysis for biomass-derived chemicals and fuels. *Green Chemistry* **12**, 468-474. (doi:10.1039/b923079c).
- [140] Dornath, P., Cho, H.J., Paulsen, A., Dauenhauer, P. & Fan, W. 2015 Efficient mechano-catalytic depolymerization of crystalline cellulose by formation of branched glucan chains. *Green Chemistry* **17**, 769-775. (doi:10.1039/C4GC02187H).