

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/235901096>

Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s

ARTICLE *in* ENERGY & ENVIRONMENTAL SCIENCE · SEPTEMBER 2011

Impact Factor: 20.52 · DOI: 10.1039/C1ee01418h

CITATIONS

62

READS

255

8 AUTHORS, INCLUDING:



Smet Mario

University of Leuven

107 PUBLICATIONS 1,914 CITATIONS

SEE PROFILE



Wim Dehaen

University of Leuven

568 PUBLICATIONS 9,277 CITATIONS

SEE PROFILE



Jacobs Pierre

University of Leuven

838 PUBLICATIONS 26,413 CITATIONS

SEE PROFILE



Bert Sels

University of Leuven

97 PUBLICATIONS 1,871 CITATIONS

SEE PROFILE

Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s†

Stijn Van de Vyver,^a Joice Thomas,^b Jan Geboers,^a Stefaan Keyzer,^a Mario Smet,^{*b} Wim Dehaen,^b Pierre A. Jacobs^a and Bert F. Sels^{*a}

Received 5th April 2011, Accepted 7th July 2011

DOI: 10.1039/c1ee01418h

Innovative catalyst design holds the key to fundamental advances in the transformation of cellulose to chemicals and transportation fuels, both of which are vital to meet the challenge of increasing energy costs and the finite nature of fossil fuel reserves. Here we report on the functionalization, characterization and successful application of sulfonated hyperbranched poly(arylene oxindole)s for the direct catalytic conversion of cellulose to levulinic acid. The use of water-soluble hyperbranched polymers in combination with ultrafiltration is conceptually novel and opens new horizons in the aqueous-phase processing of cellulose substrates with various degrees of crystallinity. Compared to most conventional types of acid catalysts, these highly acidic polymers demonstrate superior catalytic performance in terms of both activity and selectivity. Additionally, this molecular approach can be successfully transferred to the acid-catalyzed degradation of other abundant biomass resources, including starch, inulin and xylan.

1. Introduction

The selective conversion of cellulosic biomass by mono- and bifunctional catalysts is of major industrial importance, and improving its efficiency and selectivity towards value-added products remains a prime objective.^{1–14} Examples are the reductive splitting of cellulose to sorbitol and mannitol,^{15–28} precursors in the production of plastics and pharmaceuticals, and saccharification of cellulose to glucose,^{29–38,119} which amongst others, offers a feedstock for bio-ethanol production. Likewise, ethylene glycol, obtainable from hydrogenolysis of cellulose,^{39–41} serves as an intermediate for the manufacture of polyester fibers and as anti-freeze agent. However, for incorporation in catalytic

^aCentre for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium. E-mail: bert.sels@biw.kuleuven.be; Fax: +32 1632 1998; Tel: +32 1632 1593

^bDepartment of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium. E-mail: mario.smet@chem.kuleuven.be; Fax: +32 1632 7990

† Electronic supplementary information (ESI) available: Additional experimental and analytical information; SEM images, XRD patterns, IR spectra and CP/MAS ¹³C NMR spectra of the cellulose samples; ¹H NMR characterization of the hyperbranched poly(arylene oxindole)s before and after sulfonation. See DOI: 10.1039/c1ee01418h

Broader context

Lignocellulosic biomass has the potential to supplement petroleum-derived hydrocarbons as a renewable feedstock for production of liquid transportation fuels and a range of industrially important platform chemicals. One of the key catalytic strategies in the biorefinery concept is the depolymerization of the lignocellulosic matrix in order to obtain smaller molecules that can be selectively transformed to functional intermediates with fewer oxygenated groups, thereby creating a chemical bridge to existing petrochemical processes. Current research breakthroughs focus on fuel platforms based on levulinic acid, such as methyltetrahydrofuran, alkyl valerate esters and liquid alkenes. Levulinic acid, identified by the US Department of Energy as one of the top 10 carbohydrate-derived target chemicals, can be produced from cellulose in aqueous reaction media *via* a Brønsted acid-catalyzed reaction sequence. However, when one considers the commercialized production of levulinic acid using dilute sulfuric acid, and reflects that this method has been hampered in large part by the complicated product isolation and purification, one can immediately see the incentive for catalytic chemists and engineers to advance the design of new recyclable catalysts. Herein, we present the application of a novel class of materials, the so-called sulfonated hyperbranched poly(arylene oxindole)s, which should extend the portfolio of acid catalysts for hydrolysis of biomass-derived carbohydrates.

processes compatible with the infrastructure of petrochemical industry plants, carbohydrates should be converted to compounds with fewer oxygenated groups.⁴² An important example is the catalytic conversion of lignocellulosic biomass to levulinic acid (LA, 4-oxopentanoic acid), which is a chemical intermediate used for production of δ -aminolevulinic acid herbicides (200–300 million lb per year),⁴³ acrylate polymers based on β -acetylacrylic acid (2.3 billion lb per year), and diphenolic acid,^{44–46} regarded as a structural analog and substitute for bisphenol A in the production of polycarbonate resins (4 billion lb per year).^{47,48}

LA has also been investigated as a feedstock for existing petrochemical processes, starting with the well-studied catalytic hydrogenation to γ -valerolactone (GVL).^{49–56} The subsequent removal of oxygen atoms to generate molecules more suitable for fuel application can be accomplished in two different approaches. Recent work by Bond *et al.* demonstrated a two-step process to decarboxylate a GVL feed over a silica/alumina catalyst, giving equimolar amounts of butene and carbon dioxide.⁵⁷ This gas stream is fed to an oligomerization reactor containing acid catalysts (*e.g.*, H-ZSM-5, Amberlyst-70) to couple butene monomers with formation of alkenes of sufficient molecular weight. Almost simultaneously, Lange *et al.* reported a strategy by which valeric acid (VA), produced from hydrogenation of GVL over a Pt-loaded SiO₂-bound H-ZSM-5, can be converted to a family of alkyl valerate esters suitable as gasoline-fuel or diesel-fuel additives.⁵⁰ Both strategies have been extensively reviewed and are therefore not described in detail here.^{1,10,58–60} However, we shall focus on the initial acid-catalyzed hydrolysis of cellulose to LA. Considering the feasibility of biofuel production scenarios, this key reaction still presents a major scientific challenge.⁴²

In this paper, we briefly review the mechanism and kinetics involved in the catalytic conversion of cellulose to LA, while addressing the performance of several homogeneous and heterogeneous catalysts. Without underestimating the contributions of other catalytic systems in ionic liquids,^{61–63} biphasic media,^{64–67} sub- and supercritical fluids,^{68,69} our primary focus is on the production of LA from aqueous mixtures of cellulose-derived carbohydrates. Secondly, we describe the synthetic approach and characterisation techniques employed for the synthesis of sulfonated hyperbranched poly(arylene oxindole)s. Based on this approach, powerful Brønsted acid catalysts can be obtained which are soluble in aqueous reaction media, thus overcoming previous constraints due to mass transfer limitations of the insoluble cellulose particles. Given the complexity of the involved reactions, the catalytic study starts by processing mono- and disaccharides, such as glucose, fructose, xylose, cellobiose and sucrose. Although focussing on cellulose as a model substrate, conclusions in this paper are extrapolated to other, less crystalline polysaccharides.

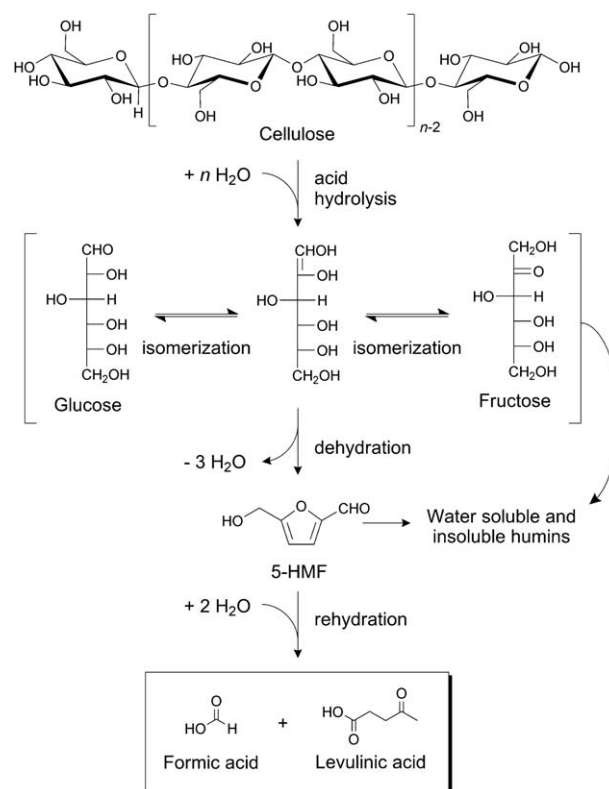
2. From cellulose to levulinic acid

2.1. Mechanism and kinetics

According to the generally accepted mechanism, acid-catalyzed hydrolysis of cellulose proceeds *via* protonation of the glycosidic oxygen in order to cleave the β -1,4-glycosidic bond into water-

soluble cello-oligomers and ultimately to glucose (Scheme 1). Because of its crystalline form and intense intra- and intermolecular hydrogen bonding, cellulose breakdown in aqueous reaction media is a very slow reaction, implying the need of elevated temperatures and acid catalysis. Subsequent formation of LA occurs through a series of acid-catalyzed reactions, including dehydration of the formed hexoses to 5-hydroxymethylfurfural (5-HMF), followed by rehydration-induced ring cleavage to yield LA along with an equivalent of formic acid. Enolization of D-glucose is identified as the key step in the formation of 5-HMF. Likewise, a similar mechanism allows rationalizing furfural formation in the acid-catalyzed decomposition of C5 sugars such as xylose or arabinose.

Since the first systematic kinetic study by Saeman in 1945,⁷⁰ the acid-catalyzed hydrolysis of cellulose has been studied extensively using a range of catalysts, temperatures and solvents. Neglecting issues associated with the changing physical and chemical properties of the insoluble substrate upon degradation, hydrolysis of cellulose is generally modeled by two consecutive first-order reactions.⁷¹ More recently, progress has been made by Girisuta *et al.* in obtaining kinetic information of all steps involved in the formation of LA and its byproducts from both monomeric sugars and cellulose.^{72–75} Using the power-law approach, they developed a novel kinetic model covering a broadly applicable range of process conditions for the cellulose to LA reaction, including side reactions to humins.⁷⁴ The highest yields of LA are shown to be generated at high sulfuric acid concentrations and relatively low operating temperatures (423–473 K). Noteworthy is that the model predicts the maximum



Scheme 1 Proposed reaction pathways for the acid-catalyzed hydrolysis of cellulose to levulinic acid.

obtainable yield in continuous-reactor configurations to be 76 mol% LA, which could be achieved when using continuous ideally stirred tank reactors with a large extent of backmixing. Humins were found to be mainly formed from glucose and 5-HMF with experimental activation energies of 164.7 vs. 111.3 kJ mol⁻¹, respectively.

In addition to the use of cellulose substrates, researchers have studied 5-HMF,⁷³ D-glucose,^{75–79} D-fructose,^{79–81} sucrose,^{82–84} and starch⁸⁵ as feedstocks for the production of LA. Furthermore, the viability of this chemistry was demonstrated in catalytic reactions with typical abundant biomass sources, such as low cost sorghum grain,⁸⁶ wheat straw,⁸⁷ bagasse and paddy straw,⁸⁸ and lignocellulosic material of various wood species.⁸⁹

2.2. State-of-the-art

Conversion of cellulose to LA can be catalyzed by a variety of mineral acids, such as H₂SO₄,^{50,59,74,75,86,89} HCl^{88,90,91} and HBr.^{85,92} In general, two catalytic strategies can be employed for the production of LA. The first strategy involves relatively high acid concentrations and low operating temperatures, which not only increases the operating cost of acid recovery but also implies the use of expensive corrosion-resistant materials for both the hydrolysis reactor and the acid recovery system.⁷⁴ On the other hand, the strategy most commonly used involves diluted acids at high operating temperatures. In particular, the engineering of LA production with dilute sulfuric acid has undergone significant progress by introduction of the Biofine Technology.^{48,93,94} In this process, hydrolysis of cellulose to intermediate 5-HMF is realized by first reacting the feedstock with sulfuric acid in a plug-flow reactor. A short residence time of 12 s in relatively harsh reaction conditions (483–493 K and a steam pressure of 2.5 MPa) allows minimization of byproduct formation. The final conversion of 5-HMF to LA is accomplished in a second reactor at 463–473 K and 1.4 MPa. Excellent yields of 0.5 kg LA per kg cellulose were obtained in a 1 ton per day pilot plant facility using diverse cellulose-containing waste materials, such as paper sludge, urban waste paper and agricultural residues.⁹⁴

However, downstream process applications of LA, such as the Ru/C catalyzed hydrogenation to GVL, are complicated by the need to isolate LA from sulfuric acid, mainly because trace amounts of sulfur are detrimental to the catalytic activity, and its removal currently necessitates energy-intensive procedures involving solvent extraction and distillation.^{59,95} Aiming at a solution to this problem, Gürbüz *et al.* recently proposed reactive extraction using butenes to produce hydrophobic esters of levulinic and formic acids.⁹⁶ They showed that the esters spontaneously separate from H₂SO₄, thereby eliminating the need for expensive separation steps in GVL production. Alternatively, in the case of LA production, the use of recyclable acid catalysts as replacements for mineral acid catalysts could potentially provide a way to improve the overall techno-economic efficiency of the production process and is usually preferable from an environmental point of view.

2.3. Design of new recyclable acid catalysts

Up to now, several solid catalysts have been reported for use in acid-catalyzed LA production, including sulfated TiO₂,⁹⁷ acidic

ion-exchange resins (Dowex, Amberlyst 15, Amberlyst IR-120 and Amberlyst 70),^{84,98,99} transition metal chlorides,¹⁰⁰ iron-pillared montmorillonites,¹⁰¹ MFI,⁷⁸ MCM-20, MCM-41,¹⁰² and Y-type zeolites with FAU topology.⁸⁰ Rataboul and Essayem also demonstrated the direct synthesis of methyl levulinate from cellulose in supercritical MeOH or MeOH-H₂O (90/10) mixtures using solid acid catalysts such as Cs_xH_{3–x}PW₁₂O₄₀ or sulfated zirconia.¹⁰³ Unfortunately, some of the aforementioned solid catalysts suffer from relatively low catalytic activity, acidities that are difficult to adjust, or a lack of stability.

The design of new recyclable catalysts for cellulose processing must be guided by two equally important principles: optimization of the effective density and strength of Brønsted acid sites in water as well as accessibility of catalytic sites to the large cellulose particles. The methods used to improve catalytic activity are diverse,^{1,120} ranging from functionalization of carbon materials for improved β-1,4 glucan adsorption^{29,38} to the use of bifunctional carbon nanofiber catalysts with sterically accessible sites.¹⁷ We recently reported the synthesis of a new kind of sulfonated silica/carbon nanocomposites which showed moderate catalytic activities in the hydrolysis of cellulose to glucose.²⁹ Although multiple other solid acid catalytic systems have been reported for the aqueous phase hydrolysis of cellulose, methods are scarce that circumvent the constraints of limited feedstock diffusivity and low accessibility of the catalytic sites, especially in micro- and mesoporous materials. However, functionalization of water-soluble polymeric supports in combination with suitable filtration methods for catalyst/product separation offers the attractive possibility to operate the catalyst under homogeneous reaction conditions,^{104–107} hence optimising accessibility of the acid sites, while reducing mass-transfer limitations and tackling issues associated with catalyst recovery and reuse.

3. Experimental section

3.1. Polymer synthesis and functionalization

The preparation of hyperbranched polymers was achieved by polycondensation of the A₂ monomer isatin and the B₃ monomer 1,3,5-tri-(4-phenoxybenzoyl)-benzene (Fig. 1). Synthesis of the latter monomer closely follows the reported procedure,¹⁰⁸ although the overall product yield could be further optimized up to 79%. To a round-bottom flask both the A₂ (0.11 g) and B₃ monomer (0.50 g) were added and mixed with an appropriate amount of methanesulfonic acid to obtain a concentration of 0.05 M. The polymerization was carried out at 308 K for 2 days under Ar atmosphere. After isolation by precipitation into water, the resulting white powder was filtered, extensively washed with water, again dissolved in CH₂Cl₂ and reprecipitated in large excess of methanol to remove any monomer or oligomer residues. The polymer (0.52 g) was then treated by sulfonation in oleum at 308 K for 2 days. After dialysis against water for 7–8 days (Spectra/Por CE dialysis membrane; molecular weight cutoff: 3500 Da) and removal of the solvent under reduced pressure, the sulfonated hyperbranched poly(arylene oxindole)s were obtained as brittle flakes (typical recovery 0.53 g), showing excellent solubility in water or methanol but poor solubility in common organic solvents such as THF or CH₂Cl₂.

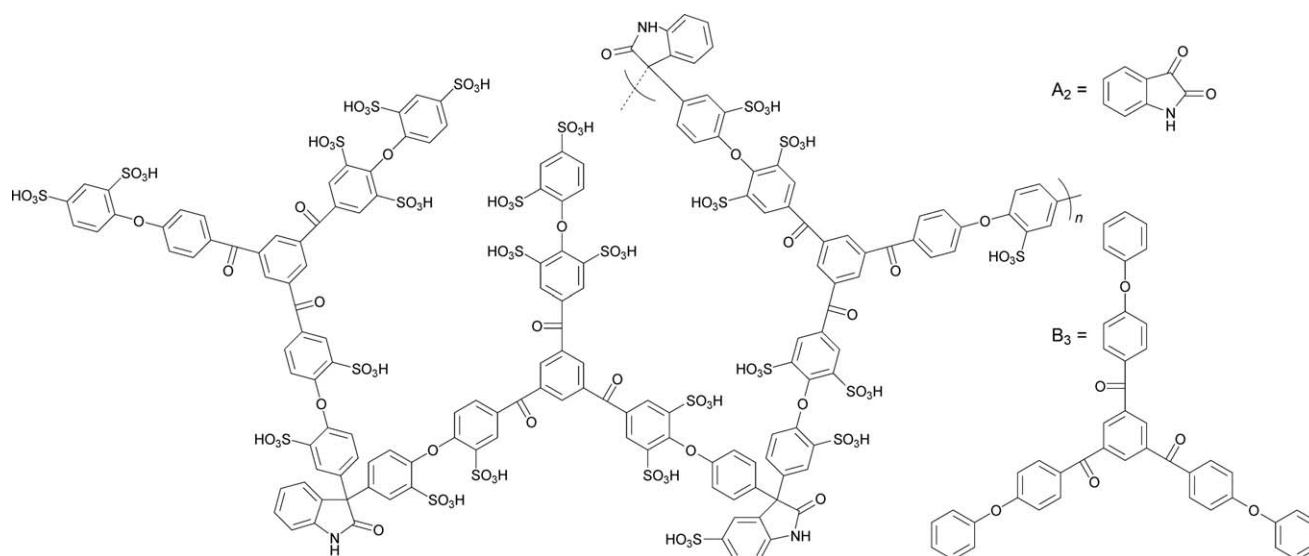


Fig. 1 Schematic representation of the sulfonated hyperbranched poly(arylene oxindole)s prepared by superelectrophilic arylation of isatin (A_2) and 1,3,5-tri-(4-phenoxybenzoyl)-benzene (B_3),¹⁰⁸ followed by controlled sulfonation in oleum at 308 K.

Polymer: ^1H NMR (DMSO): δ = 10.83 (br, H), 8.18 (br, 3H), 7.84 (br, 6H), 7.12–7.39 (br, 19H). ^{13}C NMR (DMSO): δ = 193.7, 178.8, 162.3, 162.0, 155.5, 154.7, 142.1, 139.1, 138.5, 134.0, 133.7, 133.5, 131.6, 131.4, 131.2, 130.8, 129.4, 126.8, 125.8, 123.0, 121.0, 120.8, 118.2, 117.9, 111.1, 61.9. \bar{M}_n = 9900, \bar{M}_w/\bar{M}_n = 1.89.

After sulfonation: ^1H NMR (H_2O): δ = 8.24 (d, 10H, 3J = 6 Hz), 7.99 (s, H), 7.75–7.86 (m, 6H), 7.63–7.76 (br, 5H), 7.37 (2H), 6.86–7.75 (br, 9H).

3.2. Characterization

Structures of the B_3 monomer and the hyperbranched poly(arylene oxindole)s, before and after sulfonation, were confirmed by NMR spectra (see ESI†), recorded on a Bruker AMX 400 (400 and 300 MHz). Gel permeation chromatography (GPC) was performed with a Shimadzu apparatus (UV and RI detection) with a PLgel D column (Polymer Laboratories) and THF as the eluent at 303 K calibrated with linear polystyrene standards. The acid site density of the sulfonated hyperbranched poly(arylene oxindole)s was determined by back titration with a 2 M NaCl and 0.001 M NaOH solution using a Metrohm 808 Titrando autotitrator & 801 stirrer. The titration experiments were performed in duplicate and the average number for the acid capacities reported. IR spectra on KBr pellets were recorded under vacuum on a Bruker IFS 66v/S instrument (see ESI†). UV/Vis spectra were recorded in a quartz cell using a Perkin-Elmer Lambda 12 spectrophotometer over the range 200 to 450 nm. Thermogravimetric analysis and mass spectrometry (TGA-MS) experiments were performed by heating the polymer under flowing oxygen on a TGA Q500 (TA Instruments, Brussels, Belgium). The flow rate was 20 mL min⁻¹. After 1 h dehydration at 373 K, about 10 mg of the sample was heated at 5 K min⁻¹ to 973 K. The released volatiles were transferred online to a quadrupole mass spectrometer (Pfeiffer Vacuum ThermoStar).

Structural information of the cellulose samples was obtained by scanning electron microscopy (SEM, Philips XL-30 FEG), powder X-ray diffraction (XRD), Fourier-transform infrared

(FT-IR) spectroscopy and ^{13}C cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR). XRD patterns of cellulose were recorded at room temperature with a STOE STADI P Combi diffractometer (see ESI†). The diffracted intensity of CuK α radiation (wavelength of 0.154 nm) was measured in a 2θ range between 0° and 75°. The ^{13}C CP MAS NMR spectra were recorded on a Bruker Avance DSX400 spectrometer (9.4 T). 4400 scans were accumulated with a recycle delay of 10 s. The contact time was 4 ms. The samples were packed in 4 mm rotors, and the spinning frequency of the rotor was 5000 Hz. Tetramethylsilane was used as shift reference. The crystallinity indices (CrI) presented in this manuscript are calculated after deconvolution of C4 regions (80 to 94 ppm) of the ^{13}C CP MAS NMR spectra into crystalline and amorphous peaks:¹⁰⁹

$$CrI = \frac{A_{\text{ordered}}}{A_{\text{ordered}} + A_{\text{disordered}}} \quad (1)$$

with A_{ordered} equal to the area of the crystalline peak and $A_{\text{disordered}}$ equal to the area of the amorphous peak (see ESI†). All ^{13}C CP MAS NMR spectra were fitted with the DMFit program,¹¹⁰ assuming Gaussian functions.

3.3. Catalytic experiments

The conversion of cellulose and other carbohydrates was carried out in a batch reactor, equipped with a thermocouple and a magnetic stirrer. Water content of the substrate samples was determined *via* thermogravimetric analysis (TGA). The acid catalysts tested were the sulfonated hyperbranched poly(arylene oxindole)s, sulfuric acid, Amberlyst® 15 (a polystyrene-based cation exchangeable resin bearing SO_3H , Sigma-Aldrich), Nafion® NR50 as well as Nafion® SAC-13 (perfluorosulfonated ionomers, Sigma-Aldrich), and a sulfonated silica-carbon nanocomposite ($\text{Si}_{33}\text{C}_{66}$ -673- SO_3H , see previous communication).²⁹ Within 15 minutes, the autoclave was heated to 438 or 443 K and kept there for the time specified in Tables 1 and 2. The reaction was stopped by rapidly cooling the reactor in an ice

Table 1 Acid density and catalytic activity in the conversion of cellulose to levulinic acid using the sulfonated hyperbranched polymers in comparison with commercial acid catalysts and literature precedents^a

Catalyst	Acid density/ mmol g ⁻¹	Cellulose conversion (%)	LA yield (%)
Sulfonated hyperbranched polymer	4.26	41.8	29.5
H ₂ SO ₄	—	64.1	39.1
Amberlyst® 15	2.26	49.8	13.1
Nafion® NR50	0.93	22.9	8.3
Nafion® SAC-13	0.16	43.5	8.6
Si ₃₃ C ₆₆ -673-SO ₃ H	0.57	61.8	0.9
No catalyst	—	20.9	1.2

^a Reaction conditions: Avicel® PH-101 cellulose pretreated by ball-milling 0.04 g, 0.17 mmol H⁺ in added catalyst, water 2 mL, reaction time 3 h, temperature 443 K.

bath. After each reaction, liquid samples were centrifuged, syringe filtered (0.45 µm PTFE membrane) and analyzed using HPLC analysis in an Agilent 1200 Series system equipped with isocratic pump and refractive index (RI) detector. Separation of the products was achieved with a Varian Metacarb 67H column (300 × 6.5 mm), using an aqueous solution of sulfuric acid (5 mM) at a flow rate of 0.8 mL min⁻¹ and a column temperature of 308 K. For some selected samples, the reaction products were identified by GC-MS using an Agilent 5973 Network Mass Selective Detector coupled to an Agilent 6890N GC with HP5MS capillary column (30 m × 0.25 mm).

3.4. Calculations

Quantification of each compound in the product mixture was based on calibration curves obtained by analyzing standard solutions with known concentrations. Conversions and molar yields are expressed relative to the initial molar amount of anhydroglucose units. Concerning evaluation of catalytic processing efficiency, previous studies by Palkovits *et al.* on hydrogenolysis of cellulose described carbon efficiency (E_C) based on the conversion of cellulose ($X_{\text{Cellulose}}$) and the yield of desired products in the liquid phase ($Yield_{\text{Liquid}}$):²²

$$E_C = \frac{Yield_{\text{Liquid}}}{X_{\text{Cellulose}}} \quad (2)$$

Importantly, we only consider intermediate and end products in the formation of LA as desirable, *i.e.* glucose, fructose and 5-HMF. Since HPLC analysis indicated consistently equimolar amounts of LA and formic acid, the yield of the latter compound is only mentioned when discussing the kinetic profiles.

4. Results and discussion

4.1. Catalyst characterisation

The hyperbranched poly(arylene oxindole)s were synthesized according to the procedure reported by Smet *et al.*,¹⁰⁸ applying superelectrophilic arylation of isatin within an A₂ + B₃ polymerization (Fig. 1). Although the present note is not meant to divulge synthetic details, it has been shown that in a superacidic environment, the A₂ monomer isatin becomes doubly protonated

and condenses readily with aromatic hydrocarbons, such as B₃ partner 1,3,5-tri-(4-phenoxybenzoyl)-benzene, to give 3,3-diaryl-oxindoles in high yields. The ¹H NMR spectrum of the resulting polymer shows an absence of resonance signals for isatin, indicating complete integration of the A₂ units in the macromolecular structure (see ESI†). Via GPC analysis, a relatively high molecular weight (\bar{M}_n) of 9900 was found with a polydispersity index (\bar{M}_w/\bar{M}_n) of 1.89.

Although the hyperbranched poly(arylene oxindole)s contain more branching defects compared to dendrimers, their one step synthesis proceeds remarkably easier and allows further functionalization at the free *ortho*- and *para* positions (with respect to the ether group) and even at the reactive position on the oxindole group. Here, a new type of acid catalyst is obtained by controlled sulfonation of the polymer in oleum (30% SO₃), resulting in hyperbranched structures with an unprecedented high density of sulfonic acid groups (Fig. 1). Typically, the shift of the characteristic ¹H NMR signals for the aromatic ether moieties is evidence for this successful functionalization (see ESI†). Moreover, the efficiency of the sulfonation treatment is clearly seen in the FT-IR spectra in Fig. 2. Indeed, the occurrence of intense bands around 1029 and 1087 cm⁻¹ is assigned to asymmetric and symmetric SO₃⁻ stretching vibrations. Elemental analysis of the polymer shows an approximate sulfur content of 20% (by mass), implying the presence of *ca.* 1.2 sulfonyl groups per aromatic group. Along with this result, acid–base titrations of the sulfonated polymer confirmed its high acid density of 4.3 mmol H⁺ g⁻¹ on a wet basis (Table 1).

To test the thermal stability of the sulfonated hyperbranched polymer, thermogravimetric analysis (TGA) coupled with mass spectrometry was carried out after dehydrating the sample at 373 K for 1 hour. Concerning this pretreatment, it should be noted that the highly hydrophilic catalyst contains about 23% physisorbed water at room temperature. Fig. 3 reveals a marginal weight loss of 4% over a temperature range of 373–548 K due to the loss of a small amount of remaining water. The TGA results further indicate a rapid decomposition of the sulfonated polymer upon heating above 573 K, a temperature at which both CO₂ (M_r = 44 Da) and SO₂ (M_r = 64 Da) begin to evolve.

4.2. Catalytic conversion of cellulose to LA

Our initial experiments investigated the catalytic hydrolysis of ball-mill pretreated cellulose using the sulfonated hyperbranched poly(arylene oxindole)s as the acid catalyst. Whereas under relatively mild conditions (423 K, 24 h) and low catalyst concentrations (≤1 wt%), cellulose could be hydrolyzed into D-glucose with 28% yield and 72% selectivity, only 5% of the target product LA and 1% of 5-HMF were detected. While carefully investigating the influence of reaction parameters, we discovered that, at more elevated temperatures (443 K) and higher catalyst concentrations (2 wt%), cellulose is directly transformed to LA in yields amounting to 30%. Besides the products and intermediates anticipated in Scheme 1, small amounts of furfural, levoglucosan (1,6-anhydro-β-D-glucopyranose) and formaldehyde were detected in the liquid phase. Within the frame of undesired decomposition reactions, the formation of byproduct formaldehyde was ascribed earlier to the conversion of 5-HMF into furfural.^{61,111}

Table 2 Conversion, carbon efficiency and product yields in the catalytic hydrolysis of cellulose and other biomass-derived carbohydrates over sulfonated hyperbranched poly(arylene oxindole)s^a

Entry	Substrate	Time/h	Conv. (%)	E_C (%)	Yield (%)					
					LA	D-Glucose	D-Fructose	5-HMF	Furfural	Levoglucosan
<i>Decomposition of reaction products</i>										
1	Levulinic acid	1	0.0	0.0	—	0.0	0.0	0.0	0.0	0.0
2	D-Glucose	1	97.0	40.5	29.0	—	0.0	4.4	2.2	0.0
3	D-Fructose	1	99.7	71.3	69.6	0.9	—	0.2	1.4	0.2
4	5-Hydroxymethylfurfural	1	99.4	76.7	75.9	0.1	0.2	—	0.1	0.0
5	Xylose	1	99.7	42.1 ^b	0.0	0.0	0.0	0.0	41.9	0.0
<i>Processing of oligo- and polysaccharide feedstocks</i>										
6	Sucrose	5	39.7	80.2	31.1	0.2	0.2	0.3	1.7	0.7
7	Cellobiose	5	47.5	73.5	32.6	0.7	0.3	1.4	2.2	1.8
8	Cellohexaose	5	51.0	59.3	28.4	0.6	0.5	0.8	3.6	0.0
9	Ball-milled cellulose (4.1) ^c	5	43.8	66.4	27.1	0.5	0.3	1.2	2.3	0.0
10	α -Cellulose (25.4) ^c	5	21.6	41.0	8.0	0.3	0.2	0.3	7.1	0.4
11	Sigmacell Type 20 (36.1) ^c	5	42.7	67.1	26.9	0.3	0.6	1.0	0.5	1.4
12	Sigmacell Type 50 (38.9) ^c	5	33.9	63.5	19.3	0.7	0.8	0.6	0.4	1.8
13	Avicel® PH-101 (46.2) ^c	5	15.1	70.7	9.6	0.6	0.2	0.3	1.7	0.0
14	Starch	5	51.1	62.5	31.1	0.2	0.2	0.5	1.3	0.5
15	Inulin	5	68.9	93.1	63.2	0.1	0.4	0.3	0.4	0.4
16	Xylan	5	40.9	59.0 ^b	0.0	0.0	0.0	0.0	24.1	0.0

^a Reaction conditions: substrate 0.04 g, catalyst 0.04 g, water 2 mL, temperature 438 K. ^b Carbon efficiencies calculated by dividing the yields of furfural and xylose by the conversion of the respective substrate. ^c Cellulose crystallinity indices (%) estimated from ¹³C CP MAS NMR shown in parentheses.

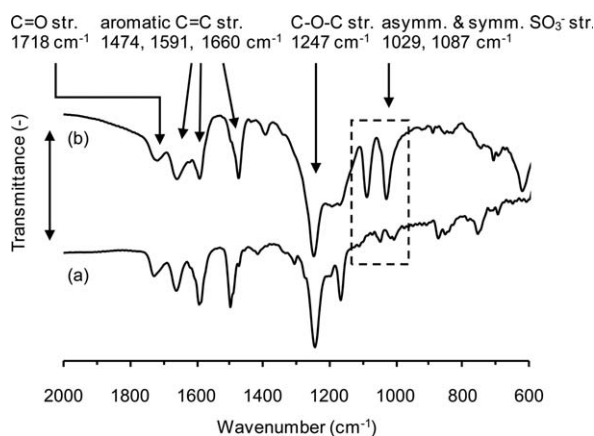
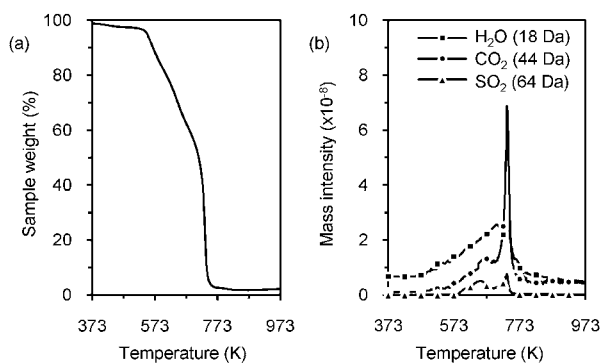
**Fig. 2** Comparison of FT-IR spectra of the hyperbranched poly(arylene oxindole)s before (a) and after sulfonation (b).**Fig. 3** (a) TGA of the sulfonated hyperbranched poly(arylene oxindole)s; (b) MS signal of the evolved gas stream. The sulfonated polymer sample was preheated at 373 K for 1 hour prior to TGA-MS analysis.

Table 1 shows the acid density, cellulose conversion and LA yield on the new catalyst. For comparison, we also included the catalytic results with dilute sulfuric acid, commercial ion-exchange resins (Amberlyst® 15, Nafion® NR50 and Nafion® SAC-13) and a sulfonated silica-carbon nanocomposite catalyst (Si₃₃C₆₆-673-SO₃H), prepared according to our previous paper.²⁹ When compared on an equivalent acid basis (0.17 mmol H⁺), the sulfonated hyperbranched polymers exhibit a remarkably high catalytic efficiency for the formation of LA, its yield being much higher than with conventional solid acids and comparable to that of dilute sulfuric acid. In the case of sulfonated silica/carbon nanocomposites, only negligible yields of LA can be observed. Interestingly, for this reaction D-glucose (47%) and D-fructose (4%) remain among the main products. In the reactions catalyzed by Amberlyst® 15 and Nafion® SAC-13, the combined yields of glucose and fructose are 27 and 25%, respectively. Concerning the influence of acid concentration on LA production, no clear trend can be observed in Table 1, although the results clearly point out the need for high acid densities of the catalyst. With regard to the high LA yield for the sulfonated hyperbranched polymer, it is questionable whether this enhanced hydrolytic activity can be adequately explained in terms of acid density alone. A better understanding of the factors that control cellulose hydrolysis was sought by investigating the adsorption of the sulfonated polymer on cellulose and by correlating the results with recent similar experiments.¹¹² In our study, 40 mg of the polymer was added for 1 h to a 2 mL stirred suspension containing 40 mg cellulose at room temperature (*i.e.*, identical concentrations to those used in the catalytic reactions). After centrifugation of the cellulose particles, a part of the solution was withdrawn, the concentration of the polymer was followed by UV/Vis spectroscopy and the formation of hydrolysis products was checked by HPLC analysis. In this way it was determined that

approximately 60% of the polymer was reversibly adsorbed on the cellulose particles, thus strongly suggesting a high affinity of the catalyst for the polar substrate. Notably, when heating the mixture to 373 K, still 42% of the polymer remained adsorbed.

In Fig. 4, the product distribution is plotted against reaction time for hydrolysis of cellulose over the sulfonated hyperbranched poly(arylene oxindole)s at 438 K. All products arising from the generally accepted literature mechanism could be observed (Scheme 1). Moreover, the plot in Fig. 4b clearly identifies glucose as the primary reaction product, whereas 5-HMF and fructose are secondary products that appear at a later reaction stage. The reason for the slightly higher yields for formic acid than for LA in Fig. 4a can be attributed to the undesired formation of humins by reaction of LA with intermediate compounds. Under conditions of acid hydrolysis, LA is thought to be partly protonated at the ketone oxygen with formation of carbocations, which then react with the functional groups and free positions of the furan ring of 5-HMF.¹¹³

Subsequently, after 5 h reaction, the polymer catalyst could be readily separated from the reaction solution containing dissolved saccharides by means of ultrafiltration (*vide infra*). Therein, the visual appearance of a dark-brown solid residue indicated a substantial formation of insoluble humins during the catalytic conversion of cellulose. This supports the hypothesis that humin formation indeed limits selective LA production. According to the SEM micrograph in Fig. 5, the spherical, agglomerated humin particles look fairly similar to those reported earlier by Girisuta *et al.* for the sulfuric acid catalyzed hydrolysis of 5-HMF^{73,75} and cellulose⁷⁴ to LA.

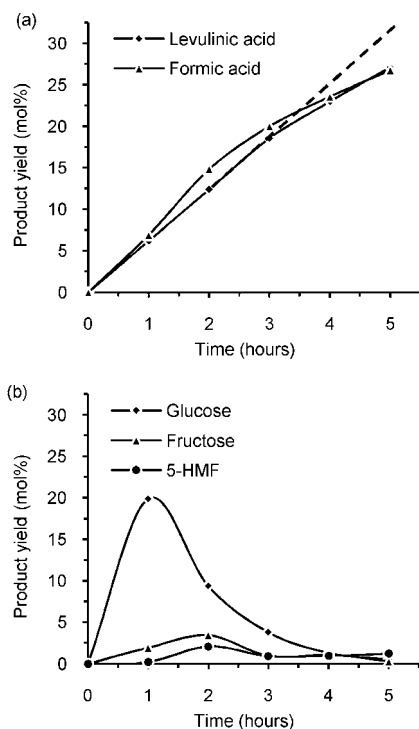


Fig. 4 Product distribution against time in the hydrolysis of cellulose over sulfonated hyperbranched poly(arylene oxindole)s at 438 K.

4.3. Decomposition of reaction products

In a further set of experiments, the catalytic conversion of a series of reaction products was explored, including glucose, fructose, 5-HMF, and LA itself (Table 2, entries 1 to 4). The experimental conditions were chosen to enable comparative assessment of the reactivity of these substrates in the presence of the sulfonated polymer. First, to determine the stability of the product LA, we measured the extent to which it was degraded by the catalyst in 1 h at 438 K (entry 1). Apparently, an aqueous solution of pure LA is stable at the reaction conditions applied in this study and is not a source of byproducts, since after reaction, only LA was detected in the solution. Table 2 further illustrates that both selectivity for LA production and carbon efficiency, E_C , improve in the order: glucose < fructose < 5-HMF. Importantly, while it is possible to isomerize aldohexoses to ketohexoses and *vice versa*, the results in Table 2 reveal a much higher LA yield for hydrolysis starting from fructose than from glucose. With our non-optimized polymer-based system, yields of 70% LA can be achieved from fructose (entry 3), which is higher than previous reports with zeolite Y-catalyzed dehydration.⁸⁰ A reasonable explanation for the distinct behavior of both hexoses stems from the more stable ring structure of glucose, resulting in a much lower relative abundance of acyclic glucose compared to acyclic fructose.^{79,114} At this point, it was assumed that enolization of hexoses (*via* an open chain mechanism) constitutes the rate-determining step in the formation of 5-HMF,⁶⁶ thereby leading to a much faster dehydration of fructose. Another plausible explanation for the difference in LA selectivity can be found in the undesired formation of reversion products by self-condensation of two aldose or ketose molecules.¹¹⁵ Indeed, glucose is known to form oligosaccharides functionalized with reactive reducing groups, enabling cross-polymerization reactions with reactive intermediates such as 5-HMF. Fructose, on the other hand, can form di-fructose dianhydrides (DFAs), wherein the most reactive groups for cross-polymerization are internally blocked.

As seen in entry 4, decomposition of 5-HMF gives a LA yield of 76% at full conversion, which is consistent with the behavior of fructose when assuming a loss in selectivity during dehydration (Scheme 1). Next, the improved selectivities observed in the conversion of fructose led us to study the reactivity of inulin, *i.e.*, a non-digestible fructose

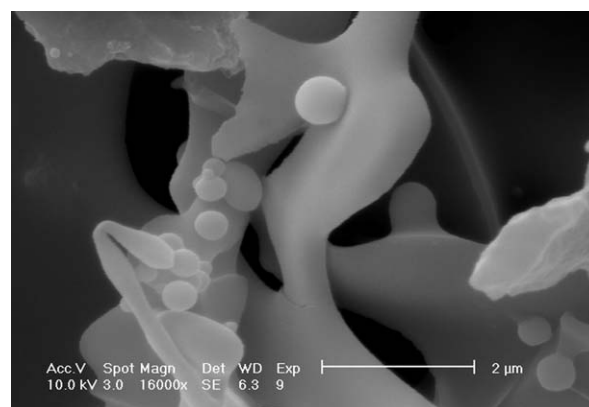


Fig. 5 SEM micrograph of humins formed during the acid-catalyzed conversion of cellulose using sulfonated hyperbranched polymers.

oligosaccharide available in large quantities in the roots of chicory. The direct conversion of inulin gave a yield of 63% LA at 69% conversion (Table 2, entry 15), thus demonstrating the capability of the sulfonated polymers to produce LA from diverse biomass-derived polysaccharides with good selectivities. The good performance of the acid catalyst for inulin hydrolysis is not only reflected in a high LA yield, but additionally in a carbon efficiency of 93%.

4.4. Effect of cellulose crystallinity

Entries 9 to 13 in Table 2 show the effect of cellulose crystallinity on the selectivity for LA production using sulfonated hyperbranched poly(arylene oxindole)s as the acid catalyst. The crystallinity indices for ball-milled cellulose, α -cellulose, Sigmacell Type 20, Sigmacell Type 50 and Avicel® PH-101 cellulose were estimated by performing solid-state ^{13}C NMR (see ESI†) and by deconvoluting C4 regions of the spectra into crystalline and amorphous peaks.¹⁰⁹ In agreement with previous studies,⁹³ our results indicate the reaction rates of cellulose hydrolysis to be strongly dependent on the degree of crystallinity. Since the cleavage of the β -1,4-glycosidic bonds is considered to be rate-determining, hydrolysis of ball-milled cellulose gave the highest conversion, carbon efficiency and selectivity among the five cellulose fractions, with a LA yield higher than 27% (Table 2, entry 9). Interestingly, the observed LA yield corresponds well to the results for cellobiose, cellohexaose and even starch (Table 2, entries 7, 8 and 14). The latter observation should be explained based on the low crystallinity index of 4.1% for ball-milled cellulose when compared to the substantially higher crystallinities for commercial cellulose substrates. Generally, a limited accessibility of the β -1,4-glycosidic linkages of cellulose is likely responsible for slower hydrolysis rates at higher crystallinity. Nevertheless, we note that the carbon efficiency of the catalytic process remains high even for the most crystalline celluloses.

Although the low LA yield for α -cellulose initially appears anomalous, it probably originates from (i) the significantly higher degree of polymerization of α -cellulose compared to microcrystalline cellulose,¹¹⁶ and/or (ii) the presence of 10% hemicellulose in this sample.²² The latter is supported by the relatively high amounts of furfural observed in the reaction solution. To further elaborate on this finding, xylan (a xylose polysaccharide) was used as a representative to investigate the potential of acid-catalyzed hemicellulose conversion. Therein, 24% furfural yield with 59% carbon efficiency could be achieved at 41% xylan conversion (Table 2, entry 16).

4.5. Catalyst separation, recovery and recycling

The recyclability of the sulfonated hyperbranched poly(arylene oxindole)s was examined by using ball-milled cellulose as the model substrate. Upon completion of the reaction after 5 h, the reaction solution was placed in the upper chamber of a Microsep 3K Omega centrifuge filtering tube (Pall Corp., East Hills, NY) containing a semipermeable membrane with a molecular weight cutoff of 3000 Da. The filtering tube was centrifuged at 12 000 rpm for 2 h, which forced the aqueous solution of levulinic acid into the lower reservoir. After

centrifugation, the retentate containing the polymer ($M_w \geq 3500$ Da) was collected in the upper sample reservoir and washed with hot distilled water. After replenishment of an appropriate amount of fresh cellulose, the recovered catalyst was reused in the hydrolysis reaction with full retention of catalytic activity and selectivity. When the same reaction was conducted with the aqueous filtrate obtained from the first reaction, no significant product formation was observed. Based on inductively coupled plasma (ICP) spectroscopy, we estimated that less than 2.8% of the initial sulfonic acid groups had leached into the filtrate solution throughout the reaction. The leaching gradually decreased to 2.0% after the second and 1.8% after the third cycle.

Carrying out such recycling experiments by means of ultrafiltration is, however, cumbersome. The additional handling steps not only make the process considerably more complex, but also render it less cost and energy efficient. A possible solution to this problem might lie in the use of biphasic water/organic reactor systems where the levulinic acid produced in the aqueous phase can be selectively extracted by the organic phase, thus minimizing humin formation. The results of several analogue studies have already demonstrated the potential of biphasic catalytic processes for the selective production of 5-HMF and furfural by dehydration of mono- and polysaccharides.^{64–67} In the case of the sulfonated hyperbranched polymers, we further argue that the plausible formation of 5-HMF should not be regarded as a limitation, considering the high yields of levulinic acid obtainable from reaction with 5-HMF (Table 2, entry 4).

5. Conclusions and outlook

This study demonstrates the successful application of sulfonated hyperbranched poly(arylene oxindole)s as a new class of water-soluble acid catalysts, found to be very effective in the hydrolytic degradation of cellulose to LA in aqueous reaction media, while catalyst/product separation being performed by ultrafiltration. With the synthetic conditions described, it is possible to obtain an acid density of $4.3 \text{ mmol H}^+ \text{ g}^{-1}$ for the sulfonated polymer, resulting in yields of approximately 30 mol% LA from cellulose after reaction for 3 h at 443 K or 5 h at 438 K.

The knowledge of its catalytic behavior in the conversion of other polysaccharides, such as sucrose, starch, inulin and xylan, provides some insight into the factors responsible for the control of this reaction and possibly in further optimization of this important process. We note that in order to have a practical impact on future biorefinery approaches, the long-term stability of the polymer catalyst will need to be demonstrated and the residual leaching of trace amounts of sulfur will need to be addressed. The necessity to achieve quantitative catalyst recovery is most stringent when considering the integration of this process with transition metal-catalyzed hydrogenation of LA to GVL. In parallel, attempts will be made to improve the yields of levulinic acid, perhaps by initial isomerization of glucose into more reactive fructose before acid-catalyzed hydrolysis. In this respect, Sn-beta zeolites have recently been reported to catalyze isomerization of glucose in aqueous reaction media with high activity and selectivity.^{117,118} Work along these lines is currently in progress in our group.

Acknowledgements

This work was performed within the framework of IAP (Belspo), IDECAT and Methusalem (CASAS, long-term structural funding by the Flemish Government) projects. S.V.d.V. is an aspirant of the FWO (Fonds Wetenschappelijk Onderzoek—Vlaanderen). J.G. thanks IWT (Institute for the Promotion of Innovation by Science and Technology in Flanders) for a doctoral fellowship. We gratefully acknowledge Kristof Houthoofd for help with ^{13}C NMR spectroscopy, Walter Verman del for TGA-MS analysis, Dirk Henot for CHN elemental analysis and Rudy De Vos (Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven) for SEM measurements.

Notes and references

- 1 S. Van de Vyver, J. Geboers, P. A. Jacobs and B. F. Sels, *ChemCatChem*, 2011, **3**, 82–94.
- 2 J. A. Geboers, S. Van de Vyver, R. Ooms, B. Op de Beeck, P. A. Jacobs and B. F. Sels, *Catal. Sci. Technol.*, 2011, **1**, 714–726.
- 3 M. Rose and R. Palkovits, *Macromol. Rapid Commun.*, 2011, DOI: 10.1002/marc.201100230.
- 4 R. Palkovits, *Chemie Ingenieur Technik*, 2011, **83**, 411–419.
- 5 J. C. Serrano-Ruiz and J. A. Dumesic, *Energy Environ. Sci.*, 2011, **4**, 83–99.
- 6 P. F. Yang, H. Kobayashi and A. Fukuoka, *Chin. J. Catal.*, 2011, **32**, 716–722.
- 7 E. Taarning, C. M. Osmundsen, X. Yang, B. Voss, S. I. Andersen and C. H. Christensen, *Energy Environ. Sci.*, 2011, **4**, 793–804.
- 8 M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2011, **13**, 520–540.
- 9 M. Hara, *Energy Environ. Sci.*, 2010, **3**, 601–607.
- 10 D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.
- 11 R. Rinaldi and F. Schuth, *Energy Environ. Sci.*, 2009, **2**, 610–626.
- 12 R. Rinaldi and F. Schuth, *ChemSusChem*, 2009, **2**, 1096–1107.
- 13 P. L. Dhepe and A. Fukuoka, *ChemSusChem*, 2008, **1**, 969–975.
- 14 J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164–7183.
- 15 J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs and B. Sels, *Green Chem.*, 2011, **13**, 2167–2174.
- 16 J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs and B. Sels, *Chem. Commun.*, 2011, **47**, 5590–5592.
- 17 S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Vosch, L. A. Zhang, G. Van Tendeloo, P. A. Jacobs and B. F. Sels, *ChemSusChem*, 2010, **3**, 698–701.
- 18 J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blohouse, P. Jacobs and B. Sels, *Chem. Commun.*, 2010, **46**, 3577–3579.
- 19 R. Palkovits, K. Tajvidi, A. M. Ruppert and J. Procelewska, *Chem. Commun.*, 2011, **47**, 576–578.
- 20 H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara and A. Fukuoka, *Green Chem.*, 2011, **13**, 326–333.
- 21 H. Kobayashi, H. Matsubashi, T. Komanoya, K. Hara and A. Fukuoka, *Chem. Commun.*, 2011, **47**, 2366–2368.
- 22 R. Palkovits, K. Tajvidi, J. Procelewska, R. Rinaldi and A. Ruppert, *Green Chem.*, 2010, **12**, 972–978.
- 23 L.-N. Ding, A.-Q. Wang, M.-Y. Zheng and T. Zhang, *ChemSusChem*, 2010, **3**, 818–821.
- 24 W. Deng, X. Tan, W. Fang, Q. Zhang and Y. Wang, *Catal. Lett.*, 2009, **133**, 167–174.
- 25 V. Jollet, F. Chambon, F. Rataboul, A. Cabioc, C. Pinel, E. Guillon and N. Essayem, *Green Chem.*, 2009, **11**, 2052–2060.
- 26 C. Luo, S. Wang and H. Liu, *Angew. Chem., Int. Ed.*, 2007, **46**, 7636–7639.
- 27 P. Dhepe and A. Fukuoka, *Catal. Surv. Asia*, 2007, **11**, 186–191.
- 28 A. Fukuoka and P. L. Dhepe, *Angew. Chem., Int. Ed.*, 2006, **45**, 5161–5163.
- 29 S. Van de Vyver, L. Peng, J. Geboers, H. Schepers, F. de Clippel, C. J. Gommès, B. Goderis, P. A. Jacobs and B. F. Sels, *Green Chem.*, 2010, **12**, 1560–1563.
- 30 K. i. Matsumoto, H. Kobayashi, K. Ikeda, T. Komanoya, A. Fukuoka and S. Taguchi, *Bioresour. Technol.*, 2011, **102**, 3564–3567.
- 31 D.-m. Lai, L. Deng, J. Li, B. Liao, Q.-x. Guo and Y. Fu, *ChemSusChem*, 2011, **4**, 55–58.
- 32 Y. Ogasawara, S. Itagaki, K. Yamaguchi and N. Mizuno, *ChemSusChem*, 2011, **4**, 519–525.
- 33 J. Pang, A. Wang, M. Zheng and T. Zhang, *Chem. Commun.*, 2010, **46**, 6935–6937.
- 34 H. Kobayashi, T. Komanoya, K. Hara and A. Fukuoka, *ChemSusChem*, 2010, **3**, 440–443.
- 35 C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J. N. Kondo, K. Ebitani, T. Tatsumi and K. Domen, *Chem. Mater.*, 2010, **22**, 3072–3078.
- 36 A. Takagaki, C. Tagusagawa and K. Domen, *Chem. Commun.*, 2008, 5363–5365.
- 37 S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2008, **130**, 12787–12793.
- 38 A. Onda, T. Ochi and K. Yanagisawa, *Green Chem.*, 2008, **10**, 1033–1037.
- 39 M. Y. Zheng, A. Q. Wang, N. Ji, J. F. Pang, X. D. Wang and T. Zhang, *ChemSusChem*, 2010, **3**, 63–66.
- 40 N. Ji, T. Zhang, M. Y. Zheng, A. Q. Wang, H. Wang, X. D. Wang, Y. Y. Shu, A. L. Stottlemeyer and J. G. G. Chen, *Catal. Today*, 2009, **147**, 77–85.
- 41 N. Ji, T. Zhang, M. Y. Zheng, A. Q. Wang, H. Wang, X. D. Wang and J. G. G. Chen, *Angew. Chem., Int. Ed.*, 2008, **47**, 8510–8513.
- 42 J. Bozell, *Science*, 2010, **329**, 522–523.
- 43 M. Mascal and S. Dutta, *Green Chem.*, 2011, **13**, 40–41.
- 44 X. D. Yu, Y. H. Guo, K. X. Li, X. Yang, L. L. Xu, Y. N. Guo and J. L. Hu, *J. Mol. Catal. A: Chem.*, 2008, **290**, 44–53.
- 45 Y. H. Guo, K. X. Li, X. D. Yu and J. H. Clark, *Appl. Catal., B*, 2008, **81**, 182–191.
- 46 K. Li, J. Hu, W. Li, F. Ma, L. Xu and Y. Guo, *J. Mater. Chem.*, 2009, **19**, 8628–8638.
- 47 T. Werpy and G. Petersen, in *Top Value Added Chemicals from Biomass, Vol. 1—Results of Screening for Potential Candidates from Sugars and Synthesis Gas*, US Dep. Energy, Off. Sci. Tech. Inf., 2004, <http://www.nrel.gov/docs/fy04osti/35523.pdf>, accessed July 2011.
- 48 J. J. Bozell, L. Moens, D. C. Elliott, Y. Wang, G. G. Neuenschwander, S. W. Fitzpatrick, R. J. Bilski and J. L. Jarnefeld, *Resour., Conserv. Recycl.*, 2000, **28**, 227–239.
- 49 D. J. Braden, C. A. Henao, J. Heltzel, C. C. Maravelias and J. A. Dumesic, *Green Chem.*, 2011, **13**, 1755–1765.
- 50 J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke and H. Gosselink, *Angew. Chem., Int. Ed.*, 2010, **49**, 4479–4483.
- 51 L. Deng, Y. Zhao, J. A. Li, Y. Fu, B. Liao and Q. X. Guo, *ChemSusChem*, 2010, **3**, 1172–1175.
- 52 D. Kopetzki and M. Antonietti, *Green Chem.*, 2010, **12**, 656–660.
- 53 J. C. Serrano-Ruiz, D. Wang and J. A. Dumesic, *Green Chem.*, 2010, **12**, 574–577.
- 54 Z. P. Yan, L. Lin and S. J. Liu, *Energy Fuels*, 2009, **23**, 3853–3858.
- 55 H. Heeres, R. Handana, D. Chunai, C. B. Rasrendra, B. Girisuta and H. J. Heeres, *Green Chem.*, 2009, **11**, 1247–1255.
- 56 L. E. Manzer, *Appl. Catal., A*, 2004, **272**, 249–256.
- 57 J. Q. Bond, D. M. Alonso, R. M. West and J. A. Dumesic, *Langmuir*, 2010, **26**, 16291–16298.
- 58 R. Palkovits, *Angew. Chem., Int. Ed.*, 2010, **49**, 4336–4338.
- 59 J. C. Serrano-Ruiz, D. J. Braden, R. M. West and J. A. Dumesic, *Appl. Catal., B*, 2010, **100**, 184–189.
- 60 D. W. Rackemann and W. O. S. Doherty, *Biofuels, Bioprod. Biorefin.*, 2011, **5**, 198–214.
- 61 F. R. Tao, H. L. Song and L. J. Chou, *ChemSusChem*, 2010, **3**, 1298–1303.
- 62 M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Energy Fuels*, 2010, **24**, 737–745.
- 63 I. T. Horvath, *Green Chem.*, 2008, **10**, 1024–1028.
- 64 A. I. Torres, P. Daoutidis and M. Tsapatsis, *Energy Environ. Sci.*, 2010, **3**, 1560–1572.
- 65 Y. Román-Leshkov and J. Dumesic, *Top. Catal.*, 2009, **52**, 297–303.
- 66 J. N. Chheda, Y. Roman-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342–350.

- 67 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.
- 68 M. Bicker, J. Hirth and H. Vogel, *Green Chem.*, 2003, **5**, 280–284.
- 69 F. Jin and H. Enomoto, *Energy Environ. Sci.*, 2011, **4**, 382–397.
- 70 J. F. Saeman, *Ind. Eng. Chem.*, 1945, **37**, 43.
- 71 N. S. Mosier, C. M. Ladisch and M. R. Ladisch, *Biotechnol. Bioeng.*, 2002, **79**, 610–618.
- 72 B. Girisuta, L. Janssen and H. J. Heeres, *Chem. Eng. Res. Des.*, 2006, **84**, 339–349.
- 73 B. Girisuta, L. Janssen and H. J. Heeres, *Green Chem.*, 2006, **8**, 701–709.
- 74 B. Girisuta, L. Janssen and H. J. Heeres, *Ind. Eng. Chem. Res.*, 2007, **46**, 1696–1708.
- 75 B. Girisuta, PhD thesis, University of Groningen, The Netherlands, 2007.
- 76 S. W. McKibbins, J. F. Harris, J. F. Saeman and W. Neill, *For. Prod. J.*, 1962, **17**.
- 77 J. Hegner, K. C. Pereira, B. DeBoef and B. L. Lucht, *Tetrahedron Lett.*, 2010, **51**, 2356–2358.
- 78 W. Zeng, D. G. Cheng, H. H. Zhang, F. Q. Chen and X. L. Zhan, *React. Kinet., Mech. Catal.*, 2010, **100**, 377–384.
- 79 H. E. Vandam, A. P. G. Kieboom and H. Vanbekkum, *Starch/Staerke*, 1986, **38**, 95–101.
- 80 J. Jow, G. L. Rorrer, M. C. Hawley and D. T. A. Lampert, *Biomass*, 1987, **14**, 185–194.
- 81 F. S. Asghari and H. Yoshida, *Ind. Eng. Chem. Res.*, 2007, **46**, 7703–7710.
- 82 H. Mehdi, V. Fabos, R. Tuba, A. Bodor, L. T. Mika and I. T. Horvath, *Top. Catal.*, 2008, **48**, 49–54.
- 83 V. E. Tarabanko, M. Y. Chernyak, S. V. Aralova and B. N. Kuznetsov, *React. Kinet. Catal. Lett.*, 2002, **75**, 117–126.
- 84 R. A. Schraufnagel and H. F. Rase, *Ind. Eng. Chem. Prod. Res. Dev.*, 1975, **14**, 40–44.
- 85 J. Y. Cha and M. A. Hanna, *Ind. Crops Prod.*, 2002, **16**, 109–118.
- 86 Q. Fang and M. A. Hanna, *Bioresour. Technol.*, 2002, **81**, 187–192.
- 87 C. Chang, P. L. Cen and X. J. Ma, *Bioresour. Technol.*, 2007, **98**, 1448–1453.
- 88 L. F. Yan, N. K. Yang, H. Pang and B. Liao, *Clean: Soil, Air, Water*, 2008, **36**, 158–163.
- 89 A. A. Efremov, G. G. Pervyshina and B. N. Kuznetsov, *Chem. Nat. Compd.*, 1998, **34**, 182–185.
- 90 J. Horvat, B. Klaic, B. Metelko and V. Sunjic, *Tetrahedron Lett.*, 1985, **26**, 2111–2114.
- 91 B. F. McKenzie, *Org. Synth.*, 1929, **9**, 50–51.
- 92 I. F. Wiggins, *Advances in Carbohydrate Chemistry*, 1950, vol. 4, pp. 306–314.
- 93 D. J. Hayes, S. Fitzpatrick, M. H. B. Hayes and J. R. H. Ross, in *Biorefineries: Industrial Processes and Products*, ed. B. Kamm, P. R. Gruber and M. Kamm, Wiley-VCH, Weinheim, 2006, vol. 1, pp. 139–164.
- 94 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.
- 95 H. Uslu, S. İsmail Kırbaslar and K. L. Wasewar, *J. Chem. Eng. Data*, 2009, **54**, 712–718.
- 96 E. I. Gürbüz, D. M. Alonso, J. Q. Bond and J. A. Dumesic, *ChemSusChem*, 2011, **4**, 357–361.
- 97 P. Wang, S. H. Zhan and H. B. Yu, *Advance in Ecological Environment Functional Materials and Ion Industry*, 2010, vol. 96, pp. 183–187.
- 98 B. C. Redmond, *US pat.*, 2738367, 1956.
- 99 X. Hu and C.-Z. Li, *Green Chem.*, 2011, **13**, 1676–1679.
- 100 L. C. Peng, L. Lin, J. H. Zhang, J. P. Zhuang, B. X. Zhang and Y. Gong, *Molecules*, 2010, **15**, 5258–5272.
- 101 K. Lourvanij and G. L. Rorrer, *Appl. Catal., A*, 1994, **109**, 147–165.
- 102 K. Lourvanij and G. L. Rorrer, *J. Chem. Technol. Biotechnol.*, 1997, **69**, 35–44.
- 103 F. Rataboul and N. Essayem, *Ind. Eng. Chem. Res.*, 2010, **50**, 799–805.
- 104 M. Janssen, C. Muller and D. Vogt, *Green Chem.*, 2011, DOI: 10.1039/c1gc15264e.
- 105 M. Janssen, C. Muller and D. Vogt, *Dalton Trans.*, 2010, **39**, 8403–8411.
- 106 C. Müller, M. G. Nijkamp and D. Vogt, *Eur. J. Inorg. Chem.*, 2005, 4011–4021.
- 107 D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702–1706.
- 108 M. Smet, K. Fu, X. Zhang, E. H. Schacht and W. Dehaen, *Macromol. Rapid Commun.*, 2005, **26**, 1458–1463.
- 109 S. Park, D. Johnson, C. Ishizawa, P. Parilla and M. Davis, *Cellulose*, 2009, **16**, 641–647.
- 110 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.*, 2002, **40**, 70–76.
- 111 T. M. Aida, Y. Sato, M. Watanabe, K. Tajima, T. Nonaka, H. Hattori and K. Arai, *J. Supercrit. Fluids*, 2007, **40**, 381–388.
- 112 M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi and M. Hara, *Langmuir*, 2009, **25**, 5068–5075.
- 113 I. V. Sumerskii, S. M. Krutov and M. Y. Zarubin, *Russ. J. Appl. Chem.*, 2010, **83**, 320–327.
- 114 F. S. Asghari and H. Yoshida, *Ind. Eng. Chem. Res.*, 2006, **45**, 2163–2173.
- 115 B. F. M. Kuster, *Starch/Staerke*, 1990, **42**, 314–321.
- 116 R. Rinaldi, R. Palkovits and F. Schüth, *Angew. Chem., Int. Ed.*, 2008, **47**, 8047–8050.
- 117 M. Moliner, Y. Roman-Leshkov and M. E. Davis, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 6164–6168.
- 118 Y. Román-Leshkov, M. Moliner, J. A. Labinger and M. E. Davis, *Angew. Chem., Int. Ed.*, 2010, **49**, 8954–8957.
- 119 D.-m. Lai, L. Deng, Q.-x. Guo and Y. Fu, *Energy Environ. Sci.*, 2011, DOI: 10.1039/c1ee01526e.
- 120 K.-i. Shimizu and A. Satsuma, *Energy Environ. Sci.*, 2011, DOI: 10.1039/c1ee01458g.