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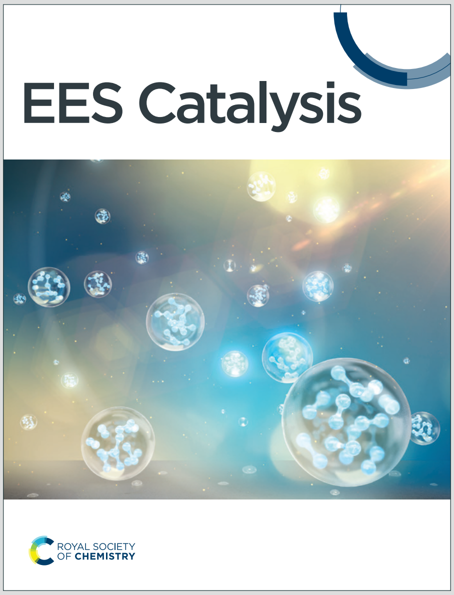

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Broader Context

Biomass is a renewable resource for the production of fuels and fine chemicals that can provide alternatives to petroleum commodities and therefore mitigate the energy and environmental issues. Catalytic fast pyrolysis can efficiently depolymerise macromolecular components of native biomass in seconds, releasing small-molecule oxygenates or aromatics that are highly concentrated in bio-oil and can be directly used in downstream manufacturing. Depending on the catalyst properties and heating temperature, catalytic fast pyrolysis offers a large variety of oxygenates, including anhydrosugars, furans and C2–C4 alcohols and aldehydes. This review summarises the recent discoveries on homogeneous and heterogeneous catalysts in fast pyrolysis of cellulose. Particular attention is focused on the reaction chemistry for secondary dehydration, cyclisation and benzylic arrangement over different catalysts, leading to three anhydrosugars with unique chiral structures. Opportunities and challenges behind catalyst site design, mechanism study and reactor engineering may provoke the development of precise and sustainable biorefineries based on catalytic fast pyrolysis.

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MINIREVIEW

Catalytic fast pyrolysis of cellulose to oxygenates: Roles of homogeneous and heterogeneous catalysts

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Yingchuan Zhang,*[ab] Zijing Li,[a] Tao Zhou[a] and Guangri Jia*[a]

Catalytic fast pyrolysis (CFP) of biomass is an efficient approach that can overcome the structural recalcitrance of solid biomass (e.g. crystalline cellulose) to produce sugar monomers and their derivatives in several seconds. The composition of the product mixture, accumulated in a liquid called bio-oil, is highly tuneable by the use of in-situ/ex-situ catalysts for downstream production of sustainable fuels and fine chemicals. This minireview summarises the recent advances in homogeneous and heterogeneous catalysts in CFP production of versatile oxygenates as fuel precursors or bulk chemicals. First, a brief overview of primary CFP pathways including cellulose-to-levoglucosan (LGA) conversion and production of three important derivative anhydrosugars is provided. Particular attention is paid to the roles of homogeneous and heterogeneous catalysts in promoting secondary reforming of LGA by dehydration, and alternative pathways via C3–C6 cyclisation or benzylic rearrangement over versatile catalysts (e.g. aqueous acids, zeolites, metal oxides) with Brønsted/Lewis acidity to produce a variety of oxygenates in bio-oil. This minireview may provoke more CFP technologies by clarifying opportunities and challenges behind the selective production of different reformed oxygenates, serving a complementary section for CFP-based production of aromatics from biomass.

1. Introduction

Fast pyrolysis is a promising technology for the conversion of solid biomass into bio-oil. This process involves direct loading of the solid biomass into a reactor, followed by anaerobic heating to temperatures ranging from 300–800 ºC at high rates of 100–300 ºC/s.[1] Compared to other conversion methods such as acid hydrolysis, fermentation and catalytic fraction, pyrolysis technology offers unique benefits in terms of process efficiency, feedstock feasibility and product selectivity.[2,3] During the rapid heating stage, the covalent-bonding network of the major components in biomass, including cellulose, hemicellulose and lignin, is disrupted, and these macromolecules are fractionised and depolymerised via reactive-end fragment intermediates to ultimately release small molecules, such as anhydrosugars, furans, alcohols, aldehydes, carbon monoxide, carbon oxide and hydrogen.[4] The liquid product of this process can be collected by one-pot or multiple cold trappers to yield bio-oil, which is a promising feedstock for the downstream production of fuels and fine chemicals. Fast pyrolysis enables high selectivity of desirable products in bio-oil due to the rapid transfer of heat energy from the reactor to the biomass feedstock without undergoing multiple transition states, making it an economically and environmentally viable technology (Fig. 1a).[5]

To further extend the product scope and improve product selectivity, versatile catalysts are loaded in-situ/ex-situ to promote desirable reaction pathways and/or reform initial pyrolysis products. This technology, namely catalytic fast pyrolysis (CFP), has been developed in the last decades with both benchtop and industrial applications.[6] Homogeneous catalysis using aqueous acids, ammonia hydroxide and ionic liquids, which are simply mixed with biomass feedstocks, is extensively employed in in-situ CFP to boost the production of levoglucosan (LGA) and its derivatives, such as levoglucosenone (LGO), 1,4:3,6-dianhydro-α-d-glucopyranose (DGP) and 1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one (LAC) (Fig. 1b). These compounds hold unique stereochemistry structures suitable for the synthesis of chiral pharmaceuticals and polymers, except for their direct use in fermentation towards bioalcohols.[7] Heterogeneous catalysis provides opportunities for recyclability and tuneability in CFP to promote in-situ depolymerisation and/or ex-situ secondary reforming in different reaction pathways.[8] There is a large amount of reports on zeolite-based CFP for the production of aromatics from cellulose with undergoing a cascade of depolymerisation, dehydration and hydrodeoxygenation (Fig. 1c).[9,10] In contrast, metal oxides in heterogeneous CFP can provide a variety of value-added oxygenates with high tuneability of the product scope and energy content but has rarely been summarised before.

Despite recent similar work on reaction engineering towards the production of common oxygenates and aromatics, to the best of our knowledge, the catalyst design and underlying chemistry for the production of specific anhydrosugars (LGO, DGP, LAC) via cellulose CFP, have rarely been summarised before.[11] In this Minireview, recent discoveries on oxygenate

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[a] Department of Chemistry, The University of Hong Kong, Hong Kong SAR, China. E-mail: jiagr23@hku.hk
[b] Department of Chemical and Biological Engineering, University of Wisconsin–Madison, WI 53706, United States. E-mail: zhang2985@wisc.edu

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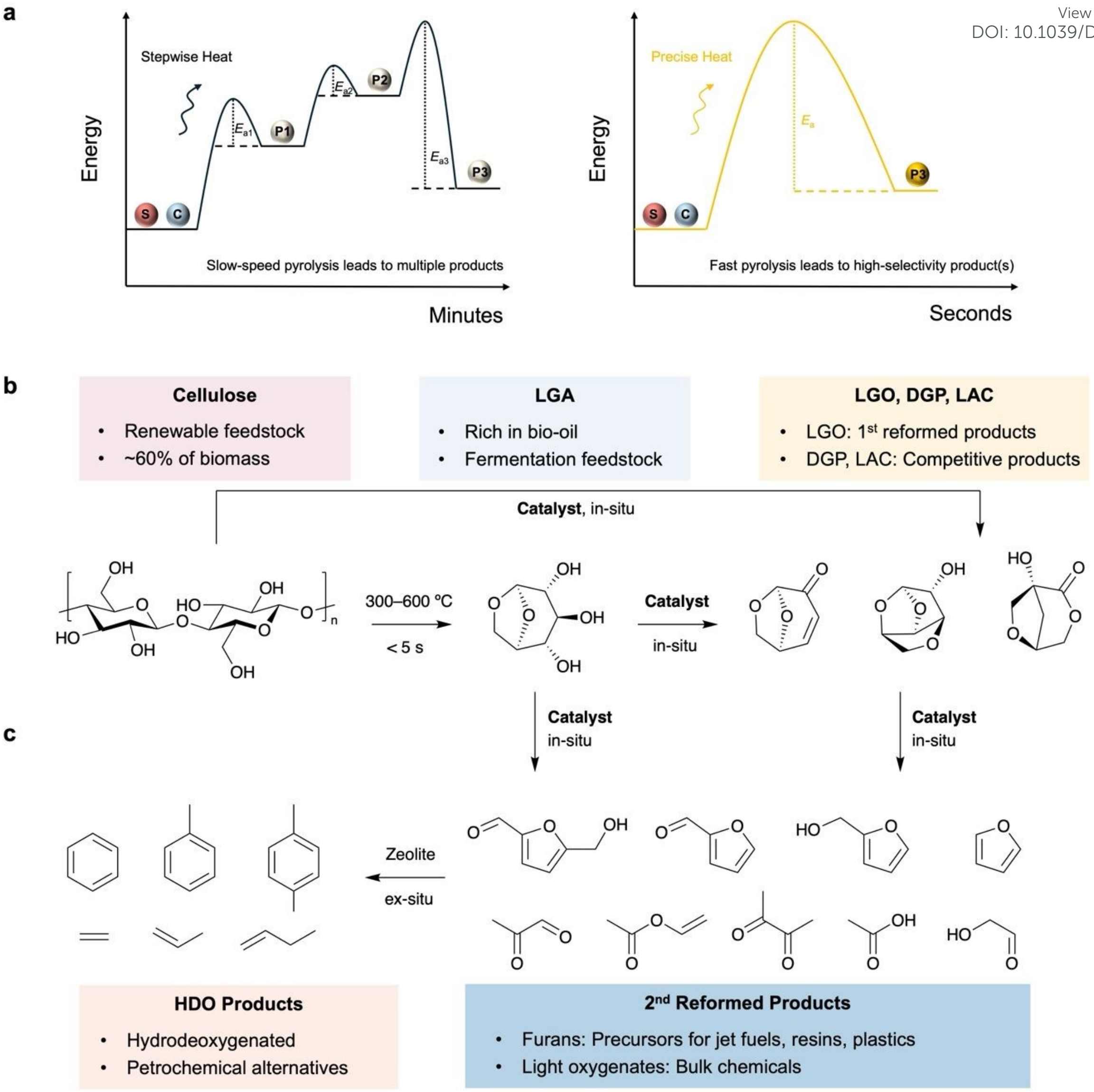

Fig. 1 (a) Schematic illustration of reaction progresses in slow-speed pyrolysis and fast pyrolysis. Reaction scheme of cellulose CFP to produce (b) anhydrous sugars and (c) furans, light oxygenates and aromatics in CFP (catalysts to be discussed are in bold font).

production via CFP are summarised by comparing the roles of homogeneous and heterogeneous catalysts in 1) tuning the competitive pathways in initial depolymerisation of cellulose; and 2) promoting secondary reforming reactions including dehydration, isomerisation, cyclisation, retro-aldol condensation and hydrodeoxygenation. Challenges and future perspectives are further discussed in terms of catalyst design, in-situ/operando catalyst characterisations and reaction engineering.

2. Reaction pathways of cellulose pyrolysis

Fast pyrolysis enables both fractionation of lignin-carbohydrate complexes and depolymerisation of three components in biomass.[12] Compared to cellulose and hemicellulose, lignin depolymerisation requires higher energy and may undergoes re-condensation after cracking of C–C and C–O bonds.[13] Cellulose depolymerisation, on the other hand, starts from the middle or end of the chains, where the β-1,4-glycosidic bond undergoes homolytic cleavage involving radical intermediates to form a LGA or LGA-end anhydro-oligosaccharide) and a glucose-end anhydro-oligosaccharide, along with the release of a water molecule (Fig. 2a).[4] The glucose-end anhydro-oligosaccharide rapidly undergoes further dehydration to form another LGA end, ultimately releasing LGA. Overall, anhydro-oligosaccharides predominantly release LGA as a dehydrated product at C1–O and O–C4, leading to up to 80% selectivity in bio-oil.[14,15]

While LGA can be directly utilised in fermentation to produce bioethanol, CFP provides opportunities to in-situ reform nascent LGA or promote its competitive pathways towards other anhydrosugars, including LGO, DGP and LAC, with unique stereochemistry.[16] LGO maintains the intramolecular ester bond but loses two hydroxyl groups to

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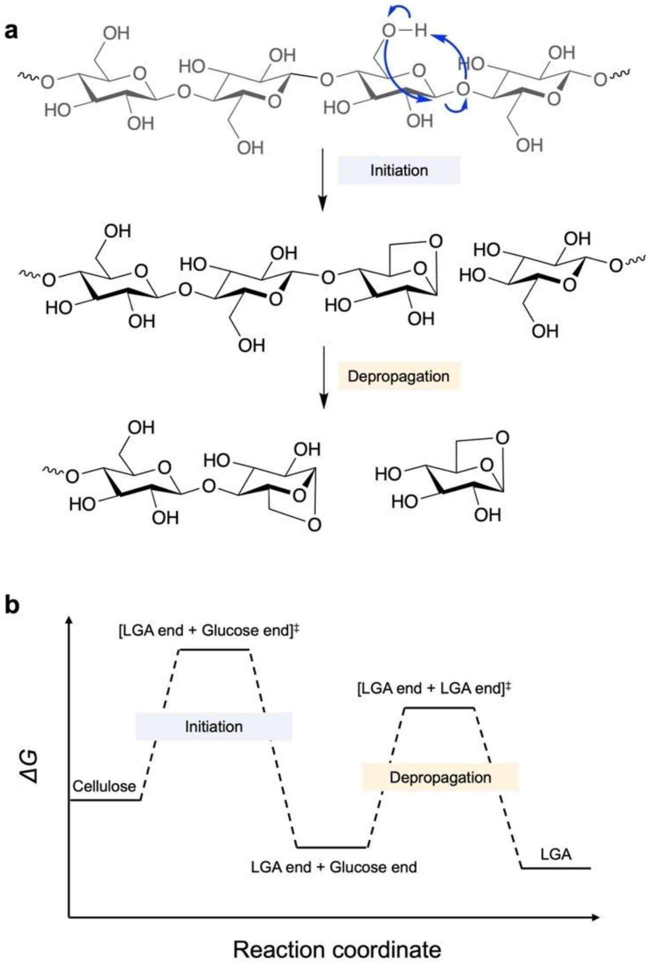

Fig. 2 (a) Reaction scheme of cellulose depolymerisation to release LGA in pyrolysis. (b) Free energy change of key steps in cellulose depolymerization.[15]

endow an unsaturated bond and an aldehyde group, serving as an important platform for the stereoselective synthesis of chiral compounds used as anticancer drugs (e.g. RAS inhibitors) and antibiotic (e.g. chloriolide).[17] Its hydrogenated product, Cyrene, is considered the next-generation green aprotic solvent. Moreover, a cascade of reduction and hydrogenolysis enable the production of tetrahydrofurandimethanol (THFDM) and further to 1,6-hexanediol (HDO) for the green synthesis of chiral polymer, coatings and adhesives with potential stereoselectivity.[18] DGP and LAC are deoxygenated products of LGA with multi-cyclic chiral structures that are in higher energy content and can be used to synthesize complicated non-natural compounds.[19] Moreover, these anhydrosugars can further undergo isomerisation, acetal and decarboxylation, to produce furan compounds including 5-hydroxymethylfurfural (HMF), furfural, furfuryl alcohol and furan, or retro-aldol reaction to generate light oxygenate (C2–C4) such as glycolaldehyde and 3-heptanol.[20]

3. Roles of catalysts in cellulose CFP

3.1 Strong Brønsted acid driven dehydration of LGA to LGO

In the presence of Brønsted acids, LGA can undergo in-situ dehydration to form a C=C bond between C3 and C4 and a ketone group at C5 in LGO.[6,21] The reactive ketone group makes it a promising platform for subsequent transformations, such as coupling, amination, halogenation and ring-opening.[22] If the CFP catalysts have additional Lewis acid sites, LGO will be isomerised to HMF and further undergo retro-aldol condensation to form C2–C4 light oxygenates (e.g. levulinic acid and acetaldehyde).[23] Until recently, highly selective production of LGO has only been achieved in milligram pyroprobe systems. Although Huber et al. report large-scale production of LGO from cellulose by solvolysis (in a mixture of polar aprotic solvent and water) under harsh conditions (230 ºC, catalysed by aqueous H_2SO_4 or propylsulfonic acid functionalised silica as a solid acid), the evitable production of HMF with ~30% yield make it difficult for separation, and the large amount of waste increases the environmental impact.[17,24,25] In comparison, if the previously developed CFP catalysts can be compatible well in large-scale pyrolysis reactors, the CFP-based production of high-purity LGO should be more efficient and cost-effective compared to solvolysis.

Within several seconds, LGO can be produced in CFP with both homogeneous and heterogeneous catalysts at temperature of 300–500 ºC. As shown in Fig. 3b, a variety of aqueous acids (H_3PO_4, HCl, H_2SO_4) can catalyse cellulose depolymerisation and LGA dehydration to afford high-yield LGO as the major product in bio-oil, with a maximum selectivity of 50%.[21,26,27] In these cases, biomass solids are impregnated with 3–10 wt% acids prior to pyrolysis, which inevitably induce reactor corrosion and increase environment impact. As green alternatives, sulfonated ionic liquids (ILs) [bmmim][CF3SO3] (50 wt%, bmmim = 1-butyl-2,3-dimethylimidazol-3-ium) and deep eutectic solvents (DESs) containing *p*-toluenesulfonic acid (*p*-TSA) as a hydrogen bond donor have been employed in cellulose pyrolysis (5 ºC/min), which is comparatively effective in the cleavage of β-1,4-glycosidic bond by protonating the bridging O atom.[28–30] Despite numerous effects in this series of homogeneous catalysts such as increasing the thermal stability towards recyclable use, the poor recovery rate and reactor corrosion make these approaches less beneficial to industrial applications. Nevertheless, these studies suggest that CFP production of LGO can effectively surpass the production of side products such as HMF, char and retro-aldol condensation compounds, and provide a higher selectivity of LGO than that from solvolysis, in alignment with the purpose of directly using bio-oil as a sustainable feedstock.

The application of heterogeneous catalysts in CFP holds great promise due to their durability and recyclability. Until recently, only solid acids, all of which are modified with acidic groups, have been developed in CFP for LGO production. Metal oxides, zeolites and activated carbon (AC) are used as the supports. For example, TiO_2 itself shows a very limited effect on LGO production. By sol–gel mixing of $Ti(OH)_4$/Ferric hydrates and sulfuric acid, solid acids SO_4^{2-}/TiO_2 and $SO_4^{2-}/TiO_2–Fe_3O_4$ (further endowed with magnetism for recyclable collection) are developed and exhibit higher LGO yields from cellulose than that of sulfuric acid.[31] $SO_4^{2-}/TiO_2–Fe_3O_4$ further exhibits its potential in CFP of native biomass, since it shows a LGO yield of

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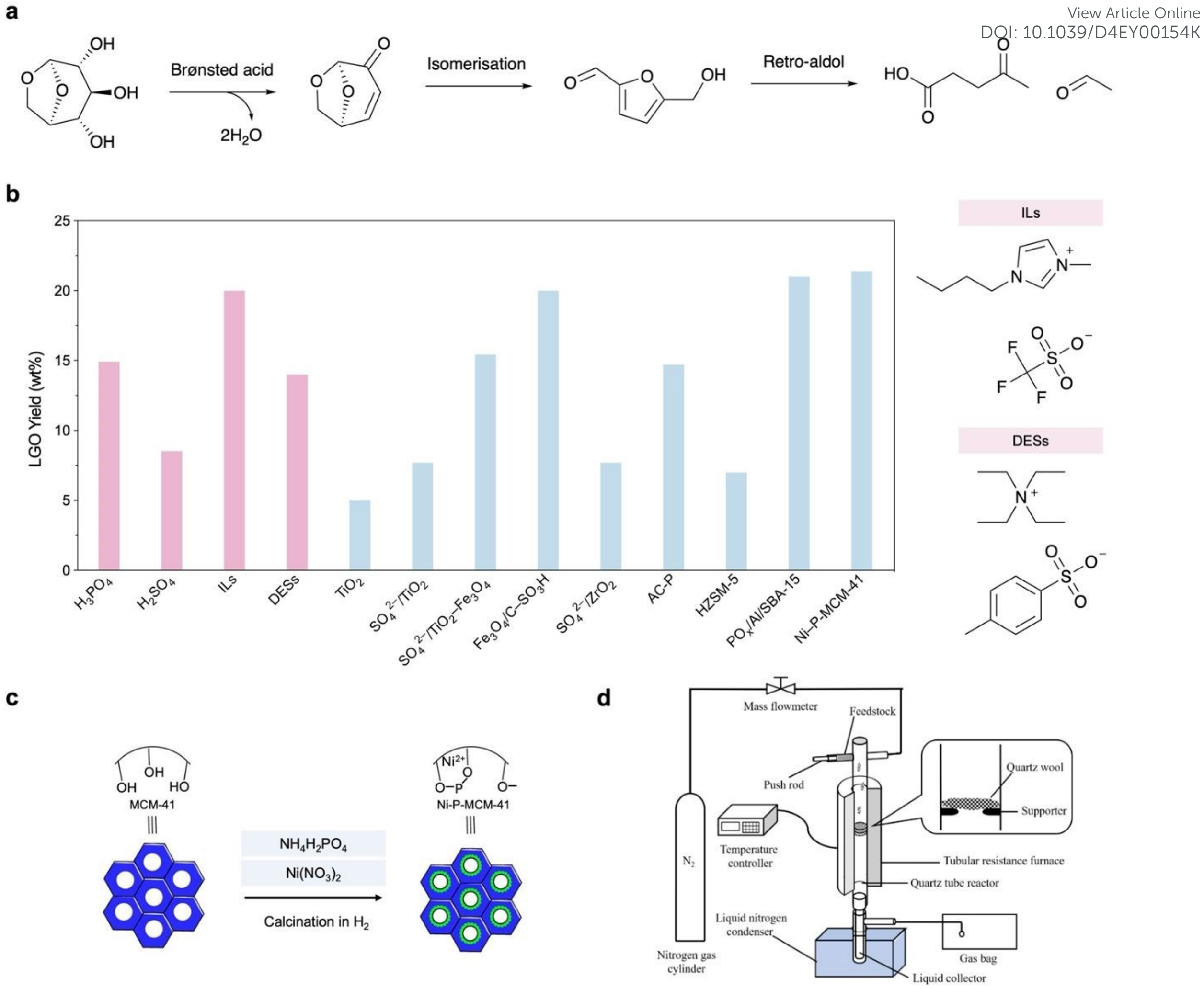

Fig. 3 (a) Reaction scheme of LGA-to-LGO process and production of side-products. (b) Performance comparison of previously reported catalysts for LGO production in cellulose pyrolysis and molecular structures of ILs and DESs as representative of homogeneous catalysts (selected from the highest yield achieved under ambient conditions).[21] (c) Modification of MCM-41 for cellulose CFP.[39] (d) Reaction set-up for cellulose CFP to produce LGO.[38]

7 wt% when poplar wood is used as the feedstock. A similar magnetic solid acid, Fe_3O_4/C–SO_3H, exhibits 20 wt% LGO yield with enhanced pyrolysis kinetics, which enables a lowered activation energy (from 187.4 to 168.1 kJ/mol) and a smaller deviation factor representing concentrated heating in TG analysis.[32] SO_4^{2-}/ZrO_2 exhibits long-span LGO production with a yield of 8 wt% in a continuous reactor.[33] H_3PO_4-inpreganted activated carbon (P-AC) also shows a LGO yield of 18 wt%.[34] However, the recyclability of all the sulfonated/phosphated catalysts is within 5 cycles due to a loss in the acidic groups. Therefore, the development of alternative Brønsted acid sites with higher durability is of great significance for CFP-based LGO production in the future.

Zeolites are ideal Brønsted/Lewis acid catalysts but can endowed with stronger acid properties by bridging O–H groups with adsorbed water or further decorated with acidic groups in a porous Al/Si/O framework, which hold a variety applications for biomass upgrading reactions such as dehydration, decarbonylation and decarboxylation.[35] Lewis acid HZSM-5 shows a limited LGO yield, suggesting the key role of Brønsted acid sites in LGA dehydration.[36] To improve the catalytic performance in CFP towards LGO production, SBA-15 and MCM-41 are modified with phosphate groups and grafted with Al^{3+} ad Ni^{2+} species in the framework, respectively (Fig. 3c).[37,38] The resulting PO_x/Al/SBA-15 and Ni–P-MCM-41 exhibit LGO yields of 21 wt% and 10 wt%, and more importantly, comparative yields in CFP of native biomass. It is found that the loaded Al^{3+} ad Ni^{2+} species can accelerate the water deprotonation and increase the overall Brønsted acidity. Notably, XPS/XRD analysis suggest that they maintain structural durability even after 300 ºC in a fixed bad, demonstrating the feasibility of acidic group modified zeolites with cooperation of Lewis and Brønsted acid sites for large-scale LGO production.

Despite the achievements of these heterogeneous CFP processes, acidic groups (sulfonate and phosphate) are still the crucial species to promote the LGA dehydration with inevitable loss after each cycle. Moreover, when the acidity is too high, the nascent LGO will further undergo undesirable reactions such as isomerisation to HMF, re-condensation to coke, and/or retro-aldol to light oxygenates and ultimately to CO_2.[21] Nevertheless,

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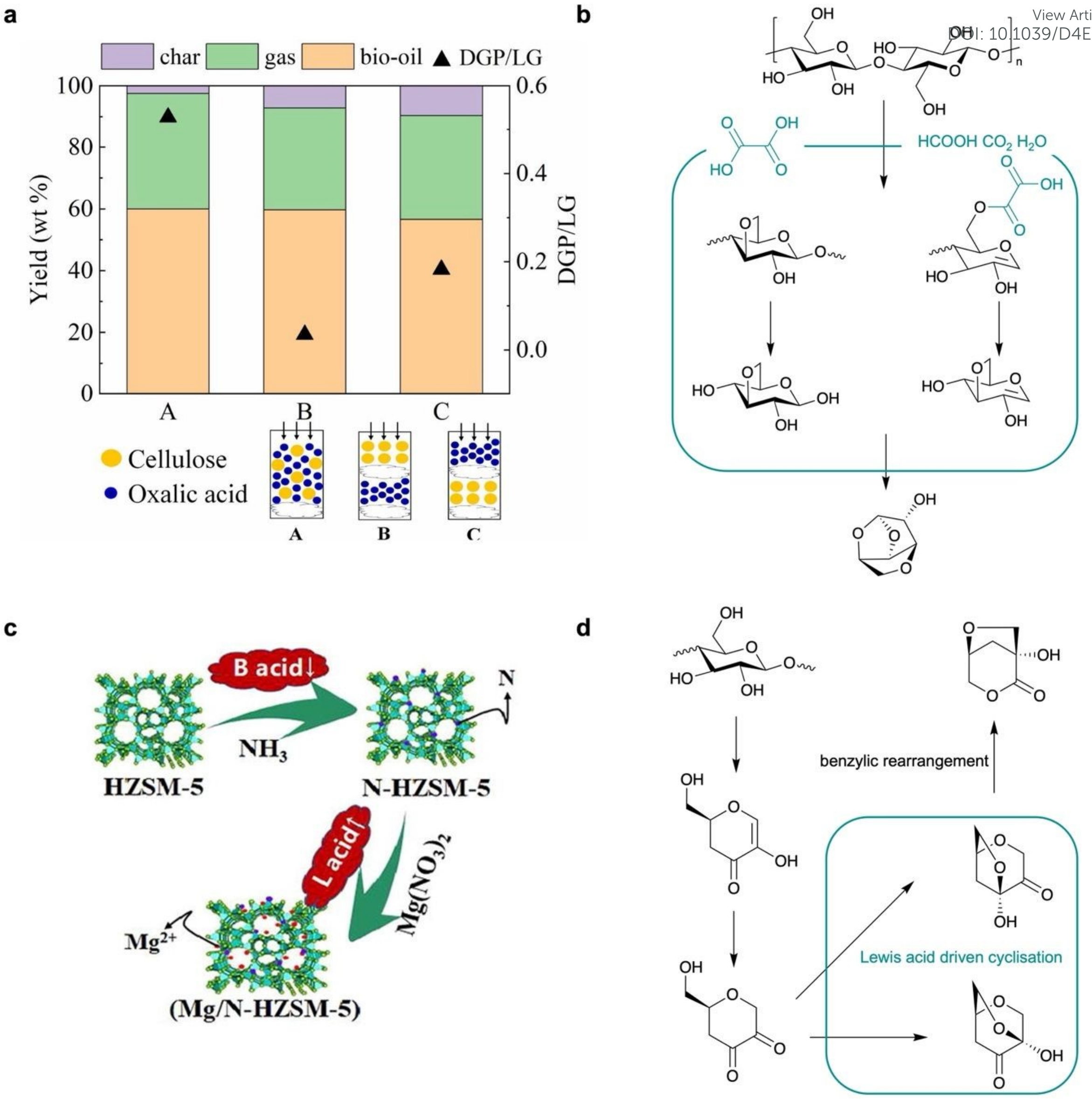

Fig. 4 (a) Performance comparison of cellulose CFP with oxalic acid to produce DGP in different loading set-up.[18] (b) Reaction pathway of cellulose CFP to produce DGP. (c) Modification of HZSM-5 for cellulose CFP.[40] (d) Reaction pathway of cellulose CFP to produce LAC.

heterogeneous CFP is the most promising approach for LGO production, provided that an alternative Brønsted acid without sulfonate and phosphate groups in a tuneable acidity.

3.2 Oxalic acid mediated C3–C6 cyclisation to produce DGP

In comparison, it is rarely reported that CFP of cellulose produce DGP, a promising chiral planform with a rigid and multi-cyclic structure but without C=O and C=C bonds. DGP is commonly a by-product in acid-based CFP for LGO production, with a selectivity less than 10%. Until recently, only Lu et al. report an oxalic acid catalysed approach to producing DGP in a 14 wt% yield with in-situ loading (oxalic acid: cellulose = 9: 1) (Fig. 4a).[19] Compared to aqueous acid such as H_3PO_4 and H_2SO_4, the moderate acidity of oxalic acid without introduction of water plays a key role in promoting competitive reactions against LGA formation, leading to the alternative production of DGP. This process starts from the formation of an unsaturated C=C bond is preferably formed between C1 and C2 of a glucose unit, followed by the esterification of the hydroxyls at C3 and C6, resulting in a 3,6-acetal ring in DGP instead of a ring between C1 and C6 of LGA. A higher temperature (400–450 ºC) is required than that of LGO production due to higher energy barriers, but lowered by oxalic acid that is directly involved in transition states instead of decomposition into formic acid for protonation (Fig. 4b). For the first time, this work suggests that a specific structure enabling hydrogen-bond-based transition state formation can promote the alternative pathway in cellulose CFP. However, oxalic acid plays a “catalyst-like” role rather than heterogeneous catalysts in DGP production, with comparative consumption into formic acid and CO_2. It is of great significance to develop alternative heterogeneous catalysts with capacity of inducing similar interactions to stabilise transition state before intermediate cyclisation, so as to produce this valuable but less exploited chiral platform in sustainable CFP approaches.

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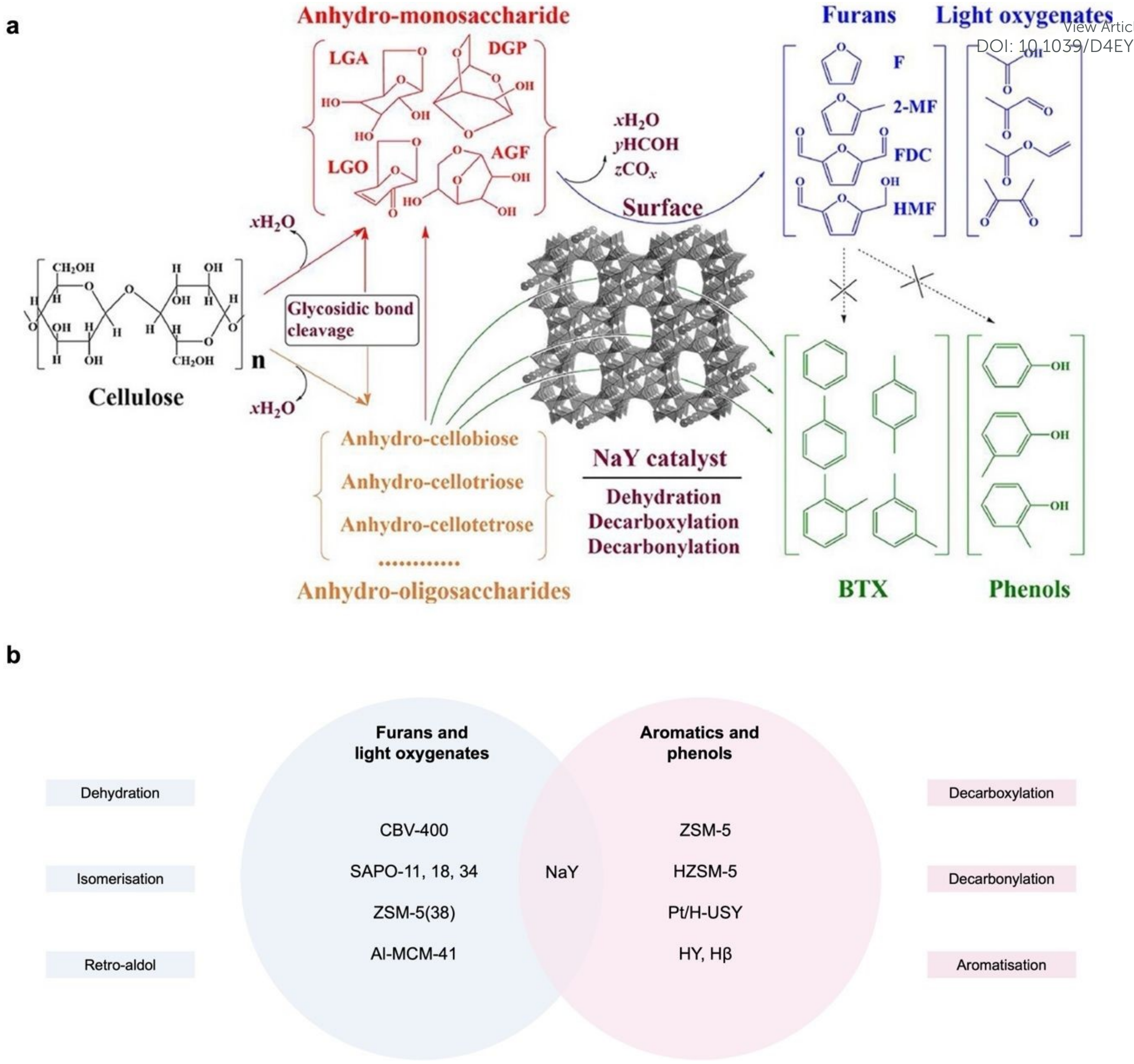

Fig. 5 (a) Product scope of cellulose CFP on the surface or in the pores of NaY. (b) Reaction types of cellulose pyrolysis over zeolites to produce furan/light oxygenates or aromatics/phenols.

3.3 Lewis acid assisted benzylic rearrangement to produce LAC

In the presence of Lewis acid sites, cellulose CFP over metal oxides or metal-loaded zeolites can produce LAC with co-production of LGA or LGO. Fabbri et al. first report a Al–Ti nanopowder catalysed slow pyrolysis of cellulose to produce LAC in a 6% yield, where the separation and upgrading approaches to chiral amines further support the usefulness of LAC in green synthesis of bioproduct.[40] It is found that high temperatures (~500 ºC) can supress the generation of LGO to less than 1% in the bio-oil, and Lewis acid sites in Al–Ti nanopowder can effectively coordinate with glucopyranosides intermediates to promote its benzylic rearrangement towards LAC, instead of Brønsted acid driven dehydration to produce LGP. Moreover, Lu et al. report a CFP of cellulose to produce LAC in 33% selectivity using Mg modified nitride HZSM-5.[41] To mitigate the deoxygenation capacity of HZSM-5, it is first nitridated by calcination in a NH_3 atmosphere to block the Brønsted acid sites (Fig. 4c).[4] Mg^{2+} species are further loaded into the mesoporous structure, and achieved a higher LAC yield that those of Fe, Co, Cu, Ni and Zn loaded N-HZSM-5. The authors further develop a Ni–Sn layered double oxide (Ni–Ti LDO) with a 9% yield in cellulose CFP at lowered temperatures (320 ºC).[42] The LDO synthesized from layered double hydroxide (LDH) exhibits a special crystal structure of $NiSnO_3$ phase, providing enriched and active Lewis acid sites for cyclization, isomerization and benzyl rearrangement reactions towards LAC production (Fig. 4d). These work suggest the switching of catalysts from Brønsted acid to Lewis acid in CFP can alternatively produce LAC as the main product instead of LGO or DGP, demonstrating the compatibility of versatile acid catalysts with CFP towards anhydrosugar production.

3.4 Zeolite mediated bond cleavage to produce furans, light oxygenates and aromatics

With longer durations and/or ex-situ catalyst loading, CFP can alternatively produce furans/light oxygenates or aromatics, in a complicated composition. In the presence of moderate

Brønsted acid sites, all the initial products including LGA and LGO from cellulose depolymerisation will further undergo isomerisation and/or decarboxylation to produce furan compounds, or retro-aldol condensation to generate C2–C4 light oxygenates.[20] Depending on the type of zeolites, the composition of bio-oil is tuneable, yet in a mixture of these volatile compounds. Interestingly, Wang et al. demonstrate that in the different phase of NaY zeolite, cellulose pyrolysis will lead to different product scope.[43] Furans are the dominant products on the surface of NaY with a small amount of light oxygenates from enhanced dehydration, acetal reaction and cyclisation of LGA. Anhydrous intermediates diffusing into the NaY pores will undergo hydrodeoxygenation (including decarbonylation and decarboxylation) to produce aromatics and phenols as the main products, likely due to enriched and stronger acid sites. Most of zeolites in cellulose CFP promote secondary hydrodeoxygenation to produce aromatics or hydrocarbons, but NaY, H-form zeolite (CBV 400) and SAPO-series zeolites can alternatively produce furans.[44,45] However, the underlying chemistry related to porosity, channel distance and/or acidity is still unclear. In general, a higher temperature (500–600 ºC) is required for compared to CFP for anhydrosugar production (300–400 ºC), as C–C/C–O bond cleavage has a higher activation energy than those of dehydration, cyclisation and rearrangement.[46]

4. Conclusion and future perspectives

Cellulose CFP is a highly efficient approach to directly converting native biomass into versatile precursors of fuels and fine chemicals. The ultrafast heating provide precise energy to specifically activate macromolecules in biomass, thereby enabling high selectivity of desirable products in the bio-oil. By employing different catalysts (Brønsted acid, Lewis acid, catalyst-like activator, metal active site) in-situ or ex-situ, cellulose can undertake depolymerisation and further, a series of programmable reactions including dehydration, alternative cyclisation, rearrangement, isomerisation and retro-aldol condensation, to produce LGA, LGO, DGP, LAC, furans, and C2–C4 light oxygenates several seconds. Notably, LGO, DGP, and LAC are promising building blocks for chiral pharmaceuticals, antibacterial and polymers, and can be produced in high-concentrated bio-oils with facile separation and cost effectiveness. The utilisation of heterogeneous catalysts with post-modifications (e.g. sulfonation, phosphorylation, metal loading, amination) further expands the reaction chemistry and process sustainability of CFP towards bio-based circular economy, by elucidating the role of these catalysts in the complicated pyrolysis process. In CFP, homogeneous and heterogeneous catalysts hold their unique strengths and weaknesses in terms of catalyst recyclability, product scope, reactor maintenance and mass/energy transfer (Fig. 6).

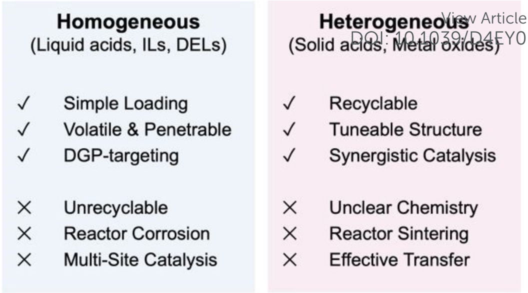

Fig. 6 Strengths and weaknesses of homogeneous and heterogeneous catalysts in CFP.

However, they are still many uncertain things in terms of the reaction pathway, mass/species transfer and reactor engineering. The toolbox of studying biomass pyrolysis consisting of multiple reactions is of lack, since most of the previous work only focuses on reaction produce and such as thermogravimetric analysis (TGA) and pyrolysis-GC/MS.[47] In-situ spectroscopy, especially the recently emerging photoelectron photoion coincidence spectroscopy (PEPICO), can directly detect intermediate species and facilitate a deeper understanding of activation and transformation of functional groups in biomass molecules, to confirm the existing mechanism from theoretical calculations.[48–50] Moreover, Operando characterisations of catalyst surface and structure, such as microscopy, X-ray diffraction (XRD) and synchrony techniques, can effectively elucidate the role of active sites in CFP.[51] In association with the previously developed thermodynamics and kinetics tools, molecular dynamics (MD) can facilitate the understanding of mass and species transfer after their activation on catalyst surface, as there is a dynamic network derived from covalent/noncovalent interactions within different components in biomass.[52] Since most of volatile oxygenates produced in CFP are highly reactive, the rational construction of efficient reactors integrating cooler, condenser and phase separator is necessary for scalable CFP processes.[53] Overall, combining catalyst design, thermochemistry and reaction engineering, there is a still long journey towards net-zero CFP biorefineries.

Conflicts of interest

There are no conflicts to declare.

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Data Availability

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