Recent advances in production of γ-valerolactone from biomass-derived feedstock by heterogeneous catalytic transfer hydrogenation

Amin Osatiashtiani*, Adam F. Lee, Karen Wilson

European Bioenergy Research Institute, Aston University, Birmingham B4 7ET, UK.

* E-mail: a.osatiashtiani@aston.ac.uk, Tel: +44 121 204 5264

Abstract

γ-valerolactone (GVL) is an important intermediate chemical with a wide range of applications as fuel, fuel additive and as a green solvent which has received a great deal of attentions from both academia and industry. This review aims to summarise the advances in conversion of renewable feedstock into GVL through heterogeneous catalytic transfer hydrogenation (CTH) with a strong emphasis on discussing preparation, characterisation and performance of the catalysts in order to provide a better understanding of various catalytic systems and also to compare them in terms of catalytic performance.

Keywords: Heterogeneous catalysis, Supported Metal Catalysts and Supported Acid Catalysts, Biofuel, Catalytic processes, Hydrogenation/Hydrogenolysis

1 Introduction

Transition from fossil fuel based resources to renewable alternatives in order to meet the demands of rapidly rising global population is a significant challenge facing sustainable industrial development (1). The impact of CO_2 emission on climate change, and concerns over energy security and unpredictable oil pricing, have highlighted the need to reduce this societal dependency on fossil reserves (2). Biomass is the most abundant and readily available renewable source of carbon in the nature, providing a low cost solution for carbon-neutral transportation fuels (3) and the only pathway for production of bulk, fine and specialty chemicals (4) and polymers (5) from non-petroleum organic molecules. All of these products and power can be manufactured in an integrated process under the concept of biorefinery, similar to the today's petroleum refineries, thereby increasing the economic viability of bioderived processes (6). In this respect, lignocellulosic biomass offers great potential for sustainable production of fuels and chemicals (7).

One of the platform chemicals that can be derived from lignocellulosic materials is levulinic acid (LA). LA was accounted for on of the most promising building blocks according to a report released by the US Department of Energy in 2004 (8) which Bozell and Petersen confirmed in 2010

(9). LA can be produced from acid hydrolysis of cellulose, starch or C_6 sugars with formic acid (FA) as side product (10, 11) and 5-HMF as an intermediate compound (12-15). Also, it can be produced from hemicellulose in a 3 step process through furfural and furfuryl alcohol as intermediates (Figure 1) (16, 17). Additionally, furfuryl alcohol and LA can be esterified to produce levulinic acid ester (18-20). The ester and LA can then be hydrogenated to γ-valerolactone (GVL) (21-23). The fact that LA and GVL can be produced from both cellulose and hemicellulose is very important in terms of the economics of converting biomass and finding wider applications for these chemicals in a more efficient process (24).

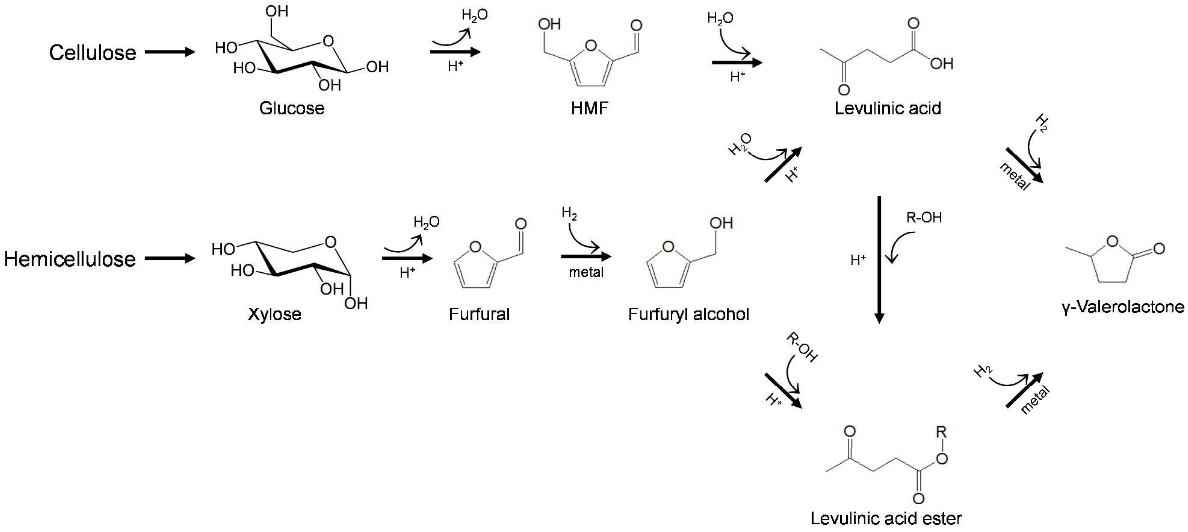

Figure 1. Reaction pathway from cellulose and hemicellulose to GVL.

The interest in GVL, as a renewable and versatile platform chemical has grown recently due to its application as a precursor for production of liquid alkanes and high value bio-polymers, chemicals and fuels, as a green solvent for biomass processing, as well as an approved fuel additive (25-35), resulting in a significant increase in the number of publications on GVL chemistry (Figure 2).

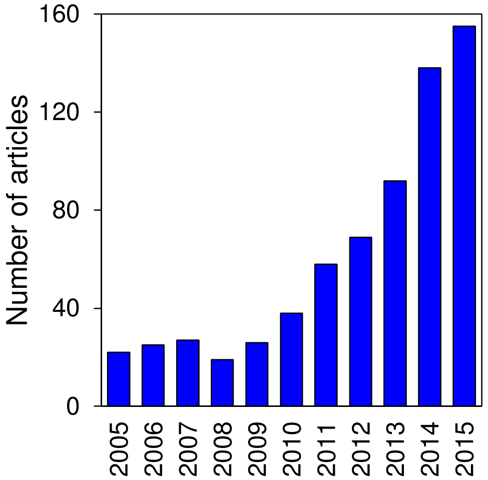

Figure 2. Number of published articles on "valerolactone" as registered by Web of Science.

2 Different routes for GVL synthesis

2. 1 LA hydrogenation using molecular H_2 and formic acid

Currently the process of GVL production from biomass-derived feedstock is based on a cascade process, starting with fractionation of lignocellulosic biomass and sugar productions and then acid catalysed transformation of sugars to LA, followed by noble-metal catalysed hydrogenation of LA to GVL using molecular H_2 (24, 34). However, this approach comes with some significant drawbacks such as the application of precious metal catalysts (e.g. Ru or Pt) for the LA hydrogenation step and also high pressure of H_2 (>30 bar) which can have a huge negative impact on the process economy (36-38). An alternative strategy could be using formic acid (FA) as hydrogen source instead of molecular H_2 in which H_2 in formed *in-situ* from dehydrogenation of FA. Although, this strategy do not require high H_2 pressure, it still depends heavily on noble metals and/or harsh reaction conditions (39, 40). Inexpensive supported transition metals such as Cu/A_2O_3 also have been tried in this reaction, however they suffer from deactivation by leaching and sintering over the course of reaction (41). And last but not least, the corrosive nature of formic acid is problematic in terms of maintenance. Therefore, for the large-scale production of GVL a process is required that do not depend on precious metals, high H_2 pressure, corrosive chemicals or an excessive number of unit operations.

2.2 Heterogeneous catalysis for GVL synthesis by CTH

Another approach for GVL production from LA or its esters is by catalytic transfer hydrogenation (CTH) through Meerwein–Ponndorf–Verley (MPV) reaction which doesn't necessarily requires precious metal catalysts or molecular H_2. This reaction is also known to be highly chemo-selective for the reduction of carbonyl groups under mild conditions and in the presence of other functional groups such as C=C double bond (21). In this review we focus on the studies that aimed for GVL production by CTH from a catalytic point of view. We refer the readers who are interested in mechanistic studies to a recent review paper by Gilkey and Xu (42).

2.2.1 Zirconium based catalysts

Chia and Dumesic for the first time reported CTH of LA and its esters to GVL (21). They used mixed metal oxides and metal oxides such as MgO/Al_2O_3, MgO/ZrO_2, $CeZrO_x$, γ-Al_2O_3 and ZrO_2 as catalyst and ethanol, 2-propanol, 1-butanol, 2-butanol and tetrahydropyran (THP) as H donor. Comparing the forth mentioned catalysts in a 5 wt% butyl levulinate (BL) in 2-butanol system using 42 wt% catalyst with respect to BL, 150 ℃ reaction temperature and about 20.7 bar pressure of He, ZrO_2 was by far the most active (>99.9 % conversion) and selective (85% GVL selectivity) catalyst.

Later on Tang *et al.* investigated the effect of calcination temperature of ZrO_2 on its performance in CTH of ethyl levulinate (EL) with ethanol in reaction temperature range of 180 to 260 ℃ (43). In this study, ZrO_2 was prepared by precipitation of $ZrOCl_2$ and it was found that amorphous ZrO_2, obtained by calcination at relatively low temperature of 300 ℃, is the most active catalyst with 96% EL conversion and 82% GVL yield. Pre-dominantly monoclinic 500 ℃ calcined ZrO_2 was less efficient in EL conversion and GVL formation and further increase in calcination temperature to 700 ℃ resulted in growth of m-ZrO_2 crystals, resulting in less catalytic activity. The superior performance of amorphous ZrO_2 was attributed to its better bifunctional acidic/basic properties. (Figure 3)

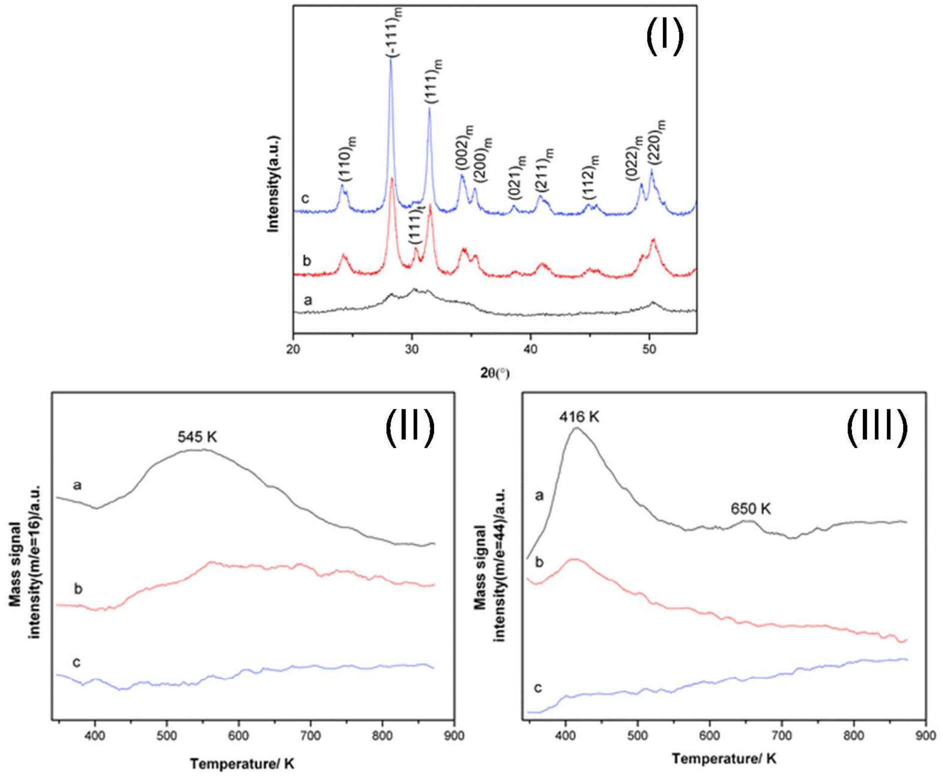

Figure 3. (I) XRD patterns, (II) NH_3-TPD and (II) CO_2-TPD for ZrO_2 calcined at a) 300, b) 500 and c) 700 °C adapted from reference (43) with permission of The Royal Society of Chemistry.

Performance of various metal hydroxides in CTH of EL with ethanol have been studied by Tang *et al.* (22). Among the various metal hydroxides (including $Cr(OH)_3$, $Sn(OH)_4$, $Ni(OH)_2$, $Fe(OH)_3$, $Mg(OH)_2$, $Al(OH)_3$, $La(OH)_3$, $Zr(OH)_4$, $Ca(OH)_2$, $Ba(OH)_2$ and NaOH, $Zr(OH)_4$ exhibited the highest activity (94% EL conversion) and excellent selectivity toward GVL (95%) after 1 h reaction at 200 °C. NaOH also showed great activity, however no GVL was yielded and instead considerable amount of coke was formed during the reaction. This phenomenon was explained by enhanced condensation of EL at the expense of GVL yield over strong basic sites. Therefore it was suggested moderate basicity is essential to ensure high GVL yield.

In another study, a series of Al_2O_3–ZrO_2 catalysts were prepared by He *et al.* and investigated for conversion of EL to GVL (44). Various reaction parameters, such as Al/Zr ratio, calcination temperature, reaction temperature and reaction time, catalyst dosage, and different alcohols as hydrogen donor, have been studied (Figure 4). Al_7Zr_3 calcined at 300 °C was found to exhibit the best catalytic performance, yielding 83% GVL with an excellent EL conversion of 95.5% when 2-propanol was used as hydrogen donor at 220 °C for 4 h. The enhanced performance of Al-Zr mixed oxide compared to pure ZrO_2 was explained by enlarged surface area as well as increased number of acid and base sites.

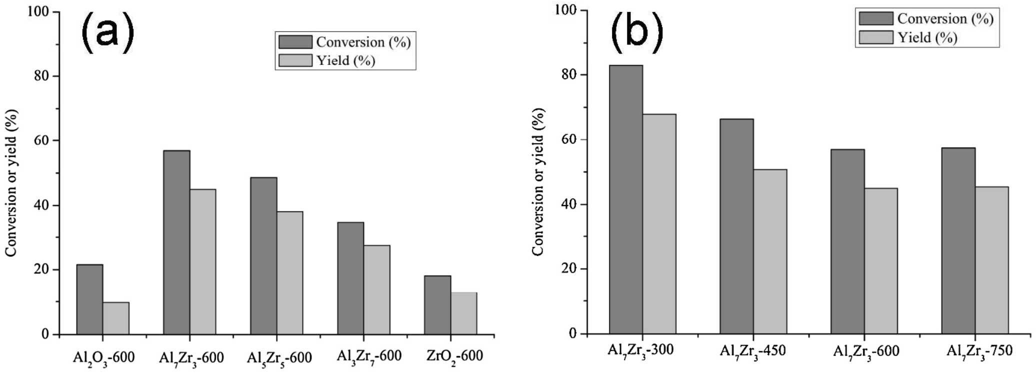

Figure 4. a) Effect of different ratios of aluminium to zirconium mixed oxides calcined at 600 ℃ and b) effect of calcination temperature on Al_7Zr_3 in the catalytic conversion of EL into GVL. Reprinted from reference (44), Copyright 2016 with permission from Elsevier. (Reaction conditions: 1 mmol EL, 5 mL 2-propanol, 0.072 g catalyst, T= 180 ℃, t= 6 h)

Song *et al.* prepared a porous zirconium based catalyst consisted of carboxylate and phenate groups using 4-hydroxybenzoic acid dipotassium salt and $ZrOCl_2$ in order to obtain a catalyst with improved basic properties, however the basic sites of the catalyst were not characterised. The Zr-HBA catalyst (Figure 5) completely outperformed ZrO_2 in CTH of EL with 2-propanol. The catalyst also showed excellent reusability after 5 runs of 4 h reaction at 150 ℃ (45).

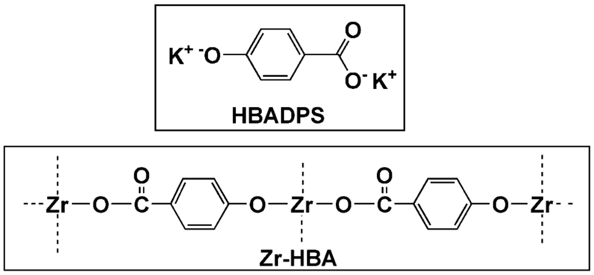

Figure 5. The structure of HBADPS and Zr-HBA reproduced from reference (45) with permission of The Royal Society of Chemistry.

The application of *in-situ* generated transition metal hydroxides/HCl for conversion of LA to GVL using 2-butanol as hydrogen donor has also been reported (46). Various precursor salts including chloride salts of Ba, Mg, Cu, Mn, Cr, Al, Sn and Zr as well as zirconium nitrate and zirconium sulfate were tested and the best catalytic performance was observed from $ZrOCl_2.8H_2O$ with 99.9% LA conversion and 85% GVL yield after 1 h reaction at 240 ℃ using a 5 wt% LA in 2-butanol solution and 5 mol% salt precursor relative to LA. It was also tried to optimise the process for reaction temperature and H donor and was found that the difference in GVL yield using 2-propanol and 2-butanol is only 2% at 240 ℃. Although high conversion and yield are obtained using this technique, the co-formation of homogeneous HCl catalyst and relatively high reaction temperature are undesirable.

Another zirconium based catalyst that was tested for LA and its ester conversion to GVL is zirconium phosphonate (Zr-PhyA). Song *et al.* synthesised an organic-inorganic hybrid catalyst by using natural phytic acid as building block and $ZrCl_4$ as Zr source to obtain a mesoporous material with pore sizes centred around 8.5 nm. (Figure 6) (47). As shown in Table 1, the Zr-PhyA catalyst is extremely active and selective in LA and EL transformation into GVL at relatively low temperature of 130 °C which the authors attribute this great catalytic performance to good acidic and basic properties of the material.

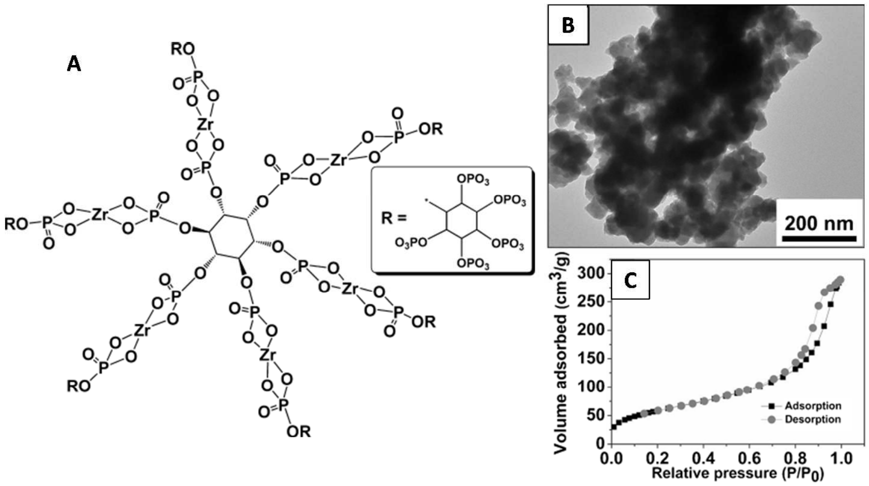

Figure 6. a) The most plausible connectivity pattern between PhyA and Zr^{4+}, b) TEM image and c) N_2 porosimetry isotherm of Zr-PhyA catalyst. Adapted from reference (47), Copyright 2015, with permission from Wiley.

The performance of highly dispersed Zr on silica supports have also explored by many scientists (48-50). Iglesias *et al.* prepared a high surface area (553 m^2 g^{-1}) mesoporous Zr-SBA-15 material with 8.3 wt% Zr loading and employed it in CTH of EL with 2-propanol at 110 °C resulting in 42% GVL yield (48). Kuwahara and co-workers synthesised a series of SBA-15 supported ZrO_2 catalysts with ZrO_2 loading ranging from 10 to 60 wt% and tested them in CTH of methyl levulinate (ML) to GVL at 150 °C and 10 bar Ar pressure (49). For the same mass of ZrO_2, the catalytic performance in terms of ML conversion and GVL yield improved with decreasing ZrO_2 loading of the catalysts. The authors correlated GVL production rate to dispersion of Zr atoms on silica rather than other textural properties and more specifically, and the highly-dispersed Zr^{4+} oxide species with low-coordination geometry was suggested as the dominant active species (Figure 7a). Moreover, the reusability tests demonstrated that the highly dispersed ZrO_2/SBA-15 catalyst is much more stable than bulk ZrO_2 (Figure 7b). The observed difference in the catalyst reusability between ZrO_2/SBA-15 and bulk ZrO_2 catalysts was attributed to the different chemical environment of Zr species, *i.e.* the highly-dispersed Zr species stabilised on high surface area SBA-15 may suppress over-accumulation of organic species owing to the site separation effect, leaving spaces where the reactants can access, whereas bulk ZrO_2 with low surface area causes an easy accumulation of organic species due to the proximity of each active site. Although no characterisation was conducted on spent bulk ZrO_2 to verify the claims.

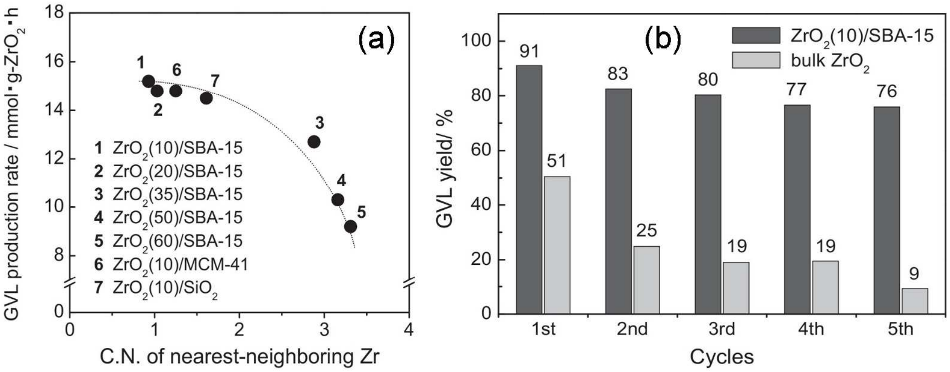

Figure 7. a) Relationship between coordination numbers (C.N.) of nearest-neighbouring Zr atoms and catalytic activities in the CTH reaction of ML with 2-propanol over silica-supported ZrO_2 catalysts and b) Catalyst reusability tests of ZrO_2(10)/SBA-15 and bulk ZrO_2 catalysts (150 °C, Ar 1.0 MPa, 3 h). Reprinted from reference (49), Copyright 2016, with permission from Elsevier.

Recently, the application of ZrO_2/SBA-15 catalyst was reported for continuous flow vapour phase transformation of LA to GVL using 2-propanol (50). In this study, SBA-15 was functionalised with 10 to 30 wt% ZrO_2 and then used in a fixed bed flow reactor at 250 °C and 1 atm N_2 pressure. In these conditions, LA was fully converted regardless of catalyst ZrO_2 loading. Even 100% LA conversion was obtained using pure SBA-15. However, the selectivity towards GVL was enhanced with increased ZrO_2 loading, exhibiting a maximum of ~90% over 25% ZrO_2/SBA-15 sample. Furthermore, the stability of the best catalyst was examined by extending the reaction time and about 10% decrease in GVL selectivity was observed over 20 h reaction, although the catalyst regained its good performance after regeneration by calcining in air to remove carbonaceous deposits. NH_3 TPD on the spent ZrO_2/SBA-15 catalyst revealed that the decrease in the acidity is due to the depletion of weak and moderate acidic sites, probably because of poisoning by carbonaceous deposits (Figure 8).

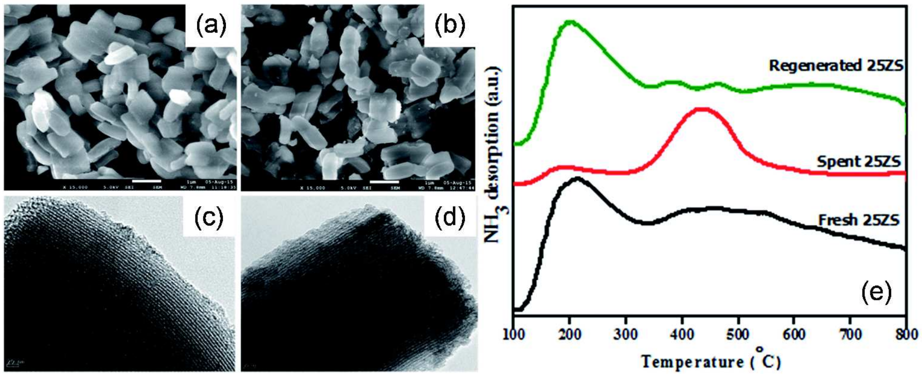

Figure 8. SEM images of (a) parent SBA-15 and (b) 25ZS, TEM images of (c) parent SBA-15 and (d) 25ZS and (e) NH3 TPD of fresh, spent and regenerated 25ZS adapted from reference (50) with permission of The Royal Society of Chemistry.

Ni or Fe containing magnetic catalysts offer a facile catalyst separation process, therefore they have attracted a great deal of attentions. Li *et al.* developed acid–base bifunctional superparamagnetic FeZrOx nanoparticles (Figure 9) for GVL production from EL using ethanol and 2-propanol as H donor and solvent, showing the introduction of Fe_3O_4 cores into ZrO_2 improves physicochemical properties of ZrO_2, such as smaller particle diameters (<20 nm), larger pore sizes (>6.9 nm), almost constant Lewis acidity, and provides strong paramagnetism for catalyst separation, however decreases Lewis base contents (51). Also the authors claim that Lewis acid and base sites play a synergic role in MPV reduction in combination with subsequent lactonisation to boost the production of GVL from EL.

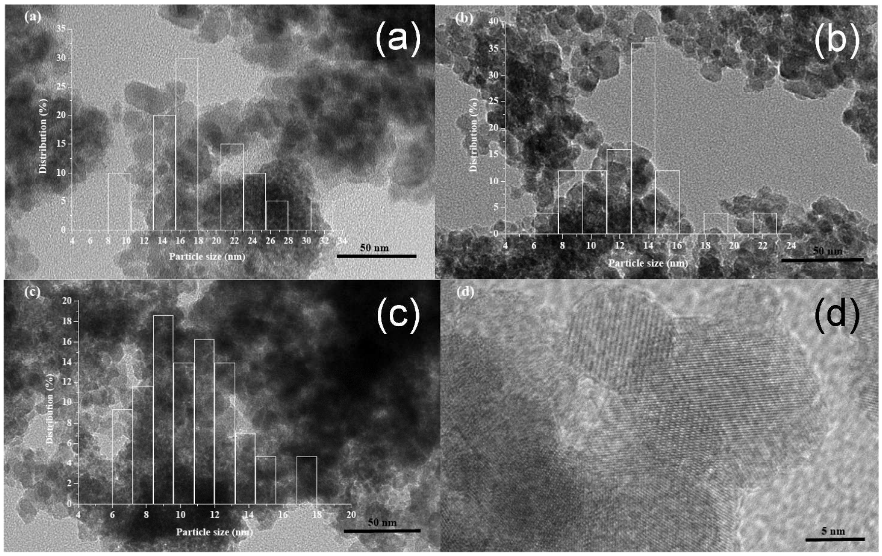

Figure 9. TEM images and particle size distributions of (a) ZrFeO(1:1)-300, (b) ZrFeO(1:3)-300, and (c) ZrFeO(1:9)-300, as well as (d) HRTEM image of ZrFeO(1:3)-300. Reprinted with permission from reference (51). Copyright 2016 American Chemical Society.

Another example of magnetic Zr-based catalyst for GVL production is H_2 reduced Ni/Zr mixed metal oxide. Li and co-workers tested several metal oxides (including Cu, Zn, Al, Fe and Ni) mixed with ZrO_2 in EL conversion to GVL via CTH reduction (50). Among the tested material reduced Ni/Zr not only offered easy magnetic separation but also the highest GVL productivity with a small margin compared to other candidates (Figure 10). This small difference makes it difficult to believe whether there is a genuine difference between these materials, especially without exploring the porous structure and other physicochemical properties of these materials. Moreover, by deliberate poisoning of Lewis acid and Lewis basic sites with tetraethoxysilane and benzoic acid respectively, it was shown that Lewis acid and base sites have a synergic effect on GVL formation. A summary of Zr-based heterogeneous catalysts for GVL production through CTH is given in Table 1.

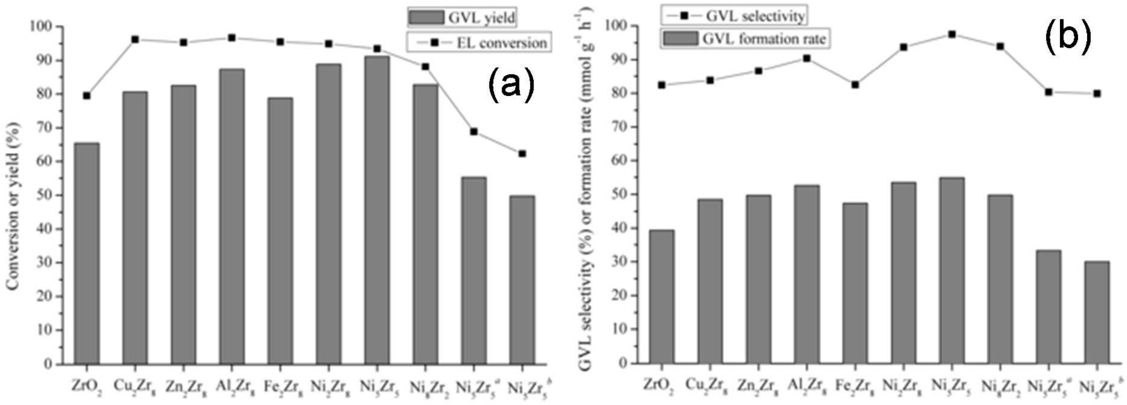

Figure 10. Catalytic conversion of EL into GVL in 2-propanol over mixed metal oxides (EL (0.65 g, 5.5 wt %), 2-propanol (11.8 g), catalyst (0.15 g), at 230 ℃ and 0.5 h). a) Ni_5Zr_5 was treated with tetraethoxysilane (0.1 g) to cover the Lewis acid sites; b) Ni_5Zr_5 was titrated with benzoic acid (0.1 g) to poison the Lewis base sites. Adapted from reference (50), Copyright 2015, with permission from Wiley.

Table 1. Overview of Zr-based catalysts used in GVL production using alcohols as H donor.

Reactant	H donor	Catalyst	Catalyst:Reactant	Reaction temp. / °C	Conv. / %	GVL yield / %	Productivity / $mmol_{GVL}\ h^{-1}\ g_{cat}^{-1}$	Ref
BL[a] (5wt%)	2-butanol	ZrO_2	42 wt%	150	>99	85	0.7	(21)
LA[b] (5 wt%)	2-butanol	ZrO_2	50 wt%	150	52	22	0.2	(21)
EL[c] (5 wt%)	Ethanol	Amorphous ZrO_2	50 wt%	250	82	63	8.7	(43)
EL (5 wt%)	Ethanol	m-ZrO_2	50 wt%	250	32	29	4.0	(43)
EL (5 wt%)	Ethanol	$Zr(OH)_4$	50 wt%	200	51	43	6.0	(22)
EL (3.5 wt%)	2-propanol	Al_2O_3–ZrO_2	50 wt%	220	96	83	2.9	(44)
EL (2.3 wt%)	2-propanol	ZrO_2	139 wt%	150	25	21	0.3	(45)
EL (2.3 wt%)	2-propanol	Zr-HBA	139 wt%	150	>99	94	1.2	(45)
EL (1.9 wt%)	2-butanol	Zr-HBA	139 wt%	150	>99	96	1.2	(45)
LA (5 wt%)	2-propanol	HCl/$ZrO(OH)_2$	5 mol%	240	>99	83	117.9	(46)
LA (5 wt%)	2-butanol	HCl/$ZrO(OH)_2$	5 mol%	240	>99	85	119.8	(46)
EL (4.4 wt%)	2-propanol	Zr-PhyA	139 wt%	130	99	95	0.6	(47)
EL (4.4 wt%)	2-propanol	ZrO_2	139 wt%	130	11	8	0.05	(47)
LA (3.6 wt%)	2-propanol	Zr-PhyA	139 wt%	130	>99	99	2.5	(47)
EL (7.4 wt%)	2-propanol	Zr/SBA-15	63 wt%	110	-	42	0.8	(48)
ML[d] (3.2 wt%)	2-propanol	ZrO_2 (10 wt%)/SBA-15	150 wt%	150	>99	91	1.5	(49)
ML (3.2 wt%)	2-propanol	ZrO_2	15 wt%	150	55	53	8.8	(49)
LA (12.5 mol%)	2-propanol	ZrO_2/SBA-15	Continuous flow	250	>99	90	-	(50)
EL (5.5 wt%)	Ethanol	ZrFeO	31 wt%	230	59	49	22.0	(51)
EL (5.5 wt%)	2-propanol	ZrFeO	31 wt%	230	94	87	39.1	(51)
EL (5.5 wt%)	2-propanol	Ni_5Zr_5	23 wt%	200	96	94	9.4	(50)

[a] Butyl levulinate, [b] Levulinic acid, [c] Ethyl levulinate, [d] Methyl levulinate

2.2.2 Zeolites

It has been reported that pure-silica zeolites containing a small amount of tetravalent heteroatoms with open coordination sites (*e.g.*, Zr or Sn) as solid Lewis acids can promote CTH reactions (52). A research led by Román-Leshkov explored the performance of some Lewis acidic zeolites such as Zr-Beta, Sn-Beta, Al-Beta and Ti-Beta in GVL production from ML using 2-butanol as H donor at 120 °C (52). The best result was obtained over Zr-Beta with 97% ML conversion and >99% GVL selectivity after 5 h reaction, outperforming all other above-mentioned catalysts by far. It's also worth mentioning that they found pure ZrO_2 inactive at this reaction condition. Furthermore, Zr-Beta (Figure 11) was tested for LA conversion, leading to 98% conversion with >99% selectivity towards GVL, however this was achieved by running the reaction for 11 h.

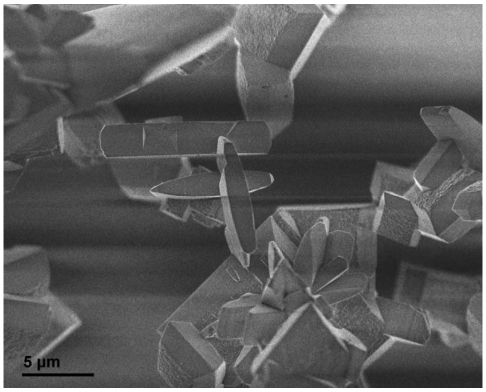

Figure 11. SEM of Zr-Beta zeolite calcined at 700 °C. Reproduced from reference (52), Copyright 2013, with permission from Wiley.

Lou and co-workers tried to understand the reason behind superior performance of Zr-Beta compared to other zeolite-Beta catalysts by performing kinetic studies and measuring the rate constant and activation energy for catalytic transfer hydrogenation of ML using 2-butanol as H source and solvent (53). It was shown that Hf-Beta is even more active than Zr-Beta, converting ML to GVL in BuOH with high selectivity and with a rate constant that is twice larger than that of Zr-Beta and seven times larger compared to Sn-Beta at 150 °C. Despite of different rate constants, the calculated apparent activation energies were very close to each other (52.5 kJ mol^{-1} for Hf-, 51.8 kJ mol^{-1} for Zr- and 51.7 kJ mol^{-1} for Sn- Beta), indicating that the E_a of the hydride shift and the adsorption enthalpy of ML are either very similar for Sn-, Zr-, and Hf-Beta or that the differences in E_a and adsorption enthalpies for each catalyst exactly offset to give the same apparent energies. (Figure 12) The observed differences in initial rates that exist for catalysts possessing similar activation barriers could also be a result of different proportions of catalytically active sites with respect to total metal content.

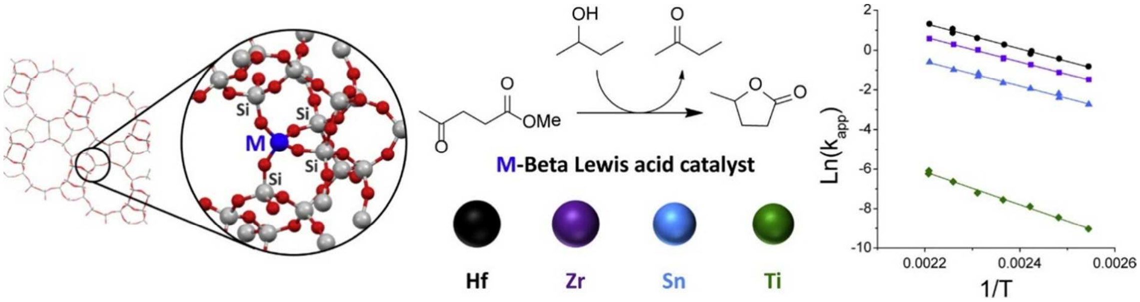

Figure 12. M-Beta zeolite catalysed MPV reaction for GVL production. Reprinted from reference (53), Copyright 2014, with permission from Elsevier.

Later on Wang *et al.* investigated the effect of Si:Zr ratio of Zr-Beta zeolite in LA hydrogenation using 2-pentanol as H donor, revealing Si:Zr = 100 being the optimum ratio with high activity and selectivity for the GVL production with 0.48 $mmol_{GVL}$ g_{cat}^{-1} h^{-1} productivity (54). The better catalytic performance of Zr-Beta-100 was attributed to the presence of Lewis acid sites with moderate strength and also availability of a small number of basic sites. A summary of some studies on zeolite catalysts for GVL production via CTH is given in Table 2.

Table 2. Overview of zeolite catalysts used in GVL production using alcohols as H donor.

Reactant	H donor	Catalyst	Catalyst:Reactant	Reaction temp. / ℃	Conv. / %	GVL yield / %	Productivity / $mmol_{GVL}$ h^{-1} g_{cat}^{-1}	Ref
ML (6.7 wt%)	2-butanol	Zr-Beta	56.5 wt%	120	97	97	2.6	(52)
LA (6.7 wt%)	2-butanol	Zr-Beta	63.3 wt%	120	98	98	1.2	(52)
LA (5.4 wt%)	2-butanol	Zr-Beta	43.1 wt%	150	>99	92	3.1	(54)
LA (2.8 wt%)	2-pentanol	Zr-Beta	172.2%	118	>99	96	0.48	(54)

2.2.3 Other metal-based catalysts

Metal catalysts and in particular noble metals are known to be effective in hydrogenation and hydrogenolysis reactions due to their capability in activating H−H, C=O, C−O, and C−H bonds (42). Metal catalysts are usually supported, either on a chemically inert material such as activated carbon (55-57) or on an acidic or basic support such as Al_2O_3 (55, 58), zeolites (59, 60), or other porous metal oxides (61). Many researchers has investigated the possibility of employing metal-based catalysts in CHT of LA and its esters for GVL production.

Lv *et al.* prepared several supported Ni catalysts using SiO_2, Al_2O_3, TiO_2, ZrO_2, ZnO and MgO by means of deposition–precipitation (DP) method (62). The optimal catalyst was obtained by using $[Ni(NO_3)_2]$ as a precursor salt and $[(NH_4)_2CO_3]$ as a precipitant. As a result, 44 wt% Ni on MgO provided the relatively high productivity of 320 $mmol_{GVL}$ g_{metal}^{-1} h^{-1} at 150 ℃. The superior performance of Ni/MgO compared to other supported Ni catalysts was explained by the basic properties of MgO promoting esterification of 2-propanol with LA. But, a comprehensive characterisation of the catalysts is lacking in this study, making it difficult to explore the rationale behind this. Moreover, the catalyst durability is reported to be far from satisfaction. Again without characterising the fresh and spent catalysts, it's hard to find out the origin of catalysts instability. But one reason could be neutralisation of MgO's basic site with LA and/or sintering of Ni particles.

Unsupported porous metal catalysts such as Raney® Ni produced from the alkali corrosion of Ni−Al alloy has shown promise for valorisation of alkyl levulinates (63). Yang *et al.* compared the performance of Ni catalysts supported on TiO_2, SiO_2, CeO_2, C with Raney® Ni in GVL synthesis from EL using secondary alcohols under Ar atmosphere (64). Interestingly, Raney® Ni yielded ~99% GVL at 80 ℃ using 2-propanol as H donor and even decreasing the reaction temperature to room temperature didn't affect the catalytic performance of Raney® Ni. In comparison, there was almost no GVL formed over the other Ni supported catalysts. A comparison was also made between Raney® Ni and precious metal catalysts supported on C and among them only Ru/C could come close to Raney® by 93% GVL yield at 80 ℃, however at room temperature it could only yield 27% GVL. Despite the exceptional catalytic performance under inert atmosphere, Raney® Ni was sensitive to air and quickly lost its catalytic activity during the reaction under air.

Precious metal catalysts have been widely studied in CTH for GVL production. For example, Kuwahara and co-workers prepared a series of $Ru(OH)_X$ catalysts with different supports such as TiO_2, ZrO_2, Al_2O_2, CeO_2, MgO and hydrotalcite and tested them in methyl levulinate CTH with 2-propanol (65). The highest GVL yield was obtained over ruthenium hydroxide supported on two types of TiO_2, one pure anatase and the other a mixture of anatase and rutile (P25). (Figure 13) The better catalytic performance of anatase TiO_2 was attributed to the presence of larger amount of basic sites on anatase TiO_2 compared to rutile TiO_2 crystals which can promote the intramolecular dealcoholation step. Furthermore, the effect of Ru loading was explored, revealing that highest Ru containing sample (4 wt%) on pure anatase TiO_2 is the best catalyst. Then the best catalyst was used for EL and LA transformation to GVL, showing a drop in productivity compared to ML conversion. Also, authors proposed that GVL production route involves sequential two reaction steps; (i) a CTH reaction to reduce ML to 4-HPM by $Ru(OH)_X$ catalyst and (ii) the following intramolecular dealcoholation reaction of 4-HPM to produce GVL by basic sites, where the latter step dominates the GVL production rates. In this respect, the effect of addition of solid base to the reaction was explored, revealing that a physical mixture of MgO or hydrotalcite with 4 wt% Ru on anatase TiO_2 can fully convert ML to GVL after 24 h under Ar at mild temperature of 90 ℃.

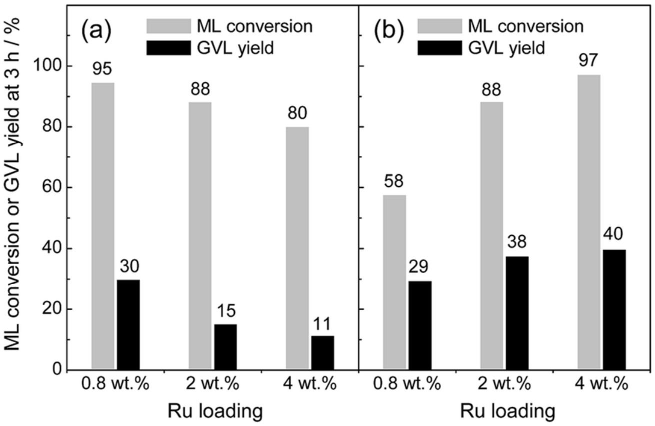

Figure 13. Comparison of methyl levulinate (ML) conversion and GVL yield at 3 h of reaction on (a) $Ru(OH)_x/TiO_2$(AR) and (b) $Ru(OH)_x/TiO_2$(A) with different Ru loadings. Reaction conditions: catalyst (Ru 0.8 mol%), ML (1 mmol), 2-PrOH (5 mL), 90 ℃, 3 h, Ar. Reproduced from reference (65) with permission of The Royal Society of Chemistry.

Some researchers have tried using microwave heating instead of conventional heating methods using carbon supported noble metal catalysts. Amarasekara and Hasan used a commercial 5% Pd on activated carbon in combination with KOH to convert LA to GVL with a 920W microwave yielding 86% GVL only after 50 s (66). However when no homogeneous base was used, no GVL was formed. Also, Palkovits's group explored application of microwave heating in GVL production with MPV reduction using Ru/C catalyst (67). A 300 W microwave was applied using a temperature-control program, *i.e.* the power of irradiation changed in order to keep temperature of the reaction mixture constant. Significant improvement in reaction rate was observed when microwave heating was used. The difference in reaction kinetics was attributed to improved heat transfer for microwave-induced heating compared to conventional heating. Table 3 summarises the metal-based catalysts performance in CTH for GVL synthesis.

Table 3. Overview of metal-based catalysts used in GVL production using alcohols as H donor.

Reactant	**H donor**	**Catalyst**	**Metal loading**	**Reaction temp.** / ℃	**Conv.** / %	**GVL yield** / %	**Productivity** / $mmol_{GVL}$ h^{-1} g_{metal}^{-1}	**Ref**
EL (1.8 wt%)	2-propanol	Raney® Ni	21 wt%	25	>99	>99	3.7	(64)
ML (3.2 wt%)	2-propanol	$Ru(OH)_X/TiO_2$	4 wt%	90	>99	89	46.4	(65)
EL (3.5 wt%)	2-propanol	$Ru(OH)_X/TiO_2$	4 wt%	90	>99	71	37.0	(65)
LA (2.9 wt%)	2-propanol	$Ru(OH)_X/TiO_2$	4 wt%	90	80	64	6.7	(65)
ML (3.2 wt%)	2-propanol	$Ru(OH)_X/TiO_2$ + MgO or HT	4 wt%	90	>99	>99	52.1	(65)
LA (7.4 wt%)	Ethanol	Pd/C + KOH (4 mmol)	4.3 wt%	920W for 50 s	-	86	123840	(66)
LA (6 wt%)	2-propanol	Ru/C	5 wt%	160	>99	>99	8268	(67)

2. 2. 4 Direct conversion of sugars to GVL

As explained above, most of studies so far have focused on using levulinic acid or its esters as reactant and there are fewer publications about direct conversion of lignocellulosic feedstock or sugars due to complexity and lower reactivity of these materials compared to platform chemicals. However, direct conversion of lignocellulose or sugars to GVL would be desirable since it can lower the process cost and facilitate the commercialisation and large scale production of GVL.

As mentioned in the previous section, Raney® Ni is a great catalyst for EL conversion to GVL, however when furfuryl alcohol, HMF or fructose were used as starting material, it requires a co-catalyst to do the acid catalysed alcoholysis step (to form EL). Even when an acid catalyst such as Amberlyst-15 was used to catalyse the first step, Raney® Ni was essentially inactive, probably poisoned by the humins formed during the alcoholysis process (64).

Le *et al.* also tried their acid–base bifunctional FeZrOx nanocatalysts in direct conversion of fructose, sucrose and glucose in ethanol (51). Starting with fructose, only 7% GVL was yielded after 6 h due to lack of strong acid sites for upstream synthesis of EL. Therefore, HY2.6 zeolite was used in conjunction with FeZrOx resulting in significant productivity enhancement. Interestingly, when the catalysts were added sequentially, the enhancement was greater (45% GVL yield) compared to when they were added simultaneously (37% GVL yield).

Zhu *et al.* proposed an integrated two-step process to convert carbohydrates and biomass to GVL in which first xylose or hemicellulose is converted to furfural over ZSM-5 in presence of a small amount of bio-derived γ-butyrolactone (GBL) and then furfural undergo tandem conversion to produce GVL over Au/ZrO_2 and ZSM-5 hybrid catalysts (68). The reason for addition of GBL is to solubilise robust humins, restrain furfural degradation reactions, and improve furfural yields (69, 70). 2-propanol was used as solvent for both steps, however the reaction temperature for the two steps were different; 160 ℃ for alcoholysis and 120 ℃ for MPV reaction. Using this method, it was managed to obtain a total GVL yield of 55% and 62% starting with xylose and hemicellulose respectively.

NiZr nanocatalysts have also shown promise for conversion of sugars and hydrocarbons to GVL when they were used in parallel with acidic HY6 catalyst. Using ethanol as solvent and H donor, after 5 h reaction at 200 ℃ with fructose, glucose, cellobiose and carboxymethyl cellulose, 43, 42, 36 and 30% GVL yield was obtained respectively (50).

3 Conclusions and future perspective

In this review, the importance of GVL production by catalytic transfer hydrogenation was highlighted and advances in terms of development of heterogeneous catalysts for this process was systematically summarised on the basis of different classes of catalysts and key features affecting the performance of the existing catalysts were critically reviewed.

In general, most studies are focused on GVL production from levulinic acid or its esters which are more facile compared to direct conversion of lignocellulose or sugars to GVL. A wide range of catalysts have been used for GVL production via CTH using various primary and secondary alcohols including transition metal oxides, zeolites and other noble and non-noble-metal catalysts. It has been shown that Lewis acidic, moderate basic or metal catalysts such as Ni are effective in GVL production from LA esters. However, starting from LA, sugars or biomass requires the presence of Brønsted acid sites as well, hence development of a bifunctional catalysts and or a dual-bed continuous flow reactor would be desired.

In conclusion, CTH of biomass-derived feedstock eliminates the need for precious metal catalysts, resulting in reduced process cost. Also, replacement of H_2 gas with organic H donors such as alcohols further decreases process cost since it does not require high pressure reactors and also improves process sustainability by cutting the dependence on non-renewable natural gas-derived hydrogen, reducing the carbon footprint and enhancing the sustainability of the process. However, the price of the external alcohol will be an important factor, playing a key role in determining whether the process can compete with conventional H_2 based hydrogenation. Therefore, developing an efficient heterogeneous catalytic system in which relatively cheap primary alcohols are used as H donor (rather than expensive secondary alcohols) and sugars or hemi/cellulose as feedstock would be highly desirable as working with corrosive LA is problematic.

Acknowledgements

We thank the EPSRC (EP/K014676/1) for financial support.

Reference

1. Jakob M, Hilaire J. Climate science: Unburnable fossil-fuel reserves. Nature. 2015;517(7533):150-2.

2. Tapia Reche M, Osatiashtiani A, Durndell LJ, Isaacs MA, Silva A, Lee AF, et al. Niobic acid nanoparticle catalysts for the aqueous phase transformation of glucose and fructose to 5-hydroxymethylfurfural. Catalysis Science & Technology. 2016;6(19):7334-41.

3. Huber GW, Iborra S, Corma A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. Chemical Reviews. 2006;106(9):4044-98.
4. Kamm B. Production of Platform Chemicals and Synthesis Gas from Biomass. Angewandte Chemie International Edition. 2007;46(27):5056-8.
5. Coombs J, Hall K. Renewable Energy Energy Efficiency, Policy and the EnvironmentChemicals and polymers from biomass. Renewable Energy. 1998;15(1):54-9.
6. Fatih Demirbas M. Biorefineries for biofuel upgrading: A critical review. Applied Energy. 2009;86, Supplement 1:S151-S61.
7. Tuck CO, Pérez E, Horváth IT, Sheldon RA, Poliakoff M. Valorization of Biomass: Deriving More Value from Waste. Science. 2012;337(6095):695-9.
8. Werpy T, Petersen G, Aden A, Bozell J, Holladay J, White J, et al. Top value added chemicals from biomass. Volume 1-Results of screening for potential candidates from sugars and synthesis gas. DTIC Document, 2004.
9. Bozell JJ, Petersen GR. Technology development for the production of biobased products from biorefinery carbohydrates-the US Department of Energy's "Top 10" revisited. Green Chemistry. 2010;12(4):539-54.
10. Van de Vyver S, Thomas J, Geboers J, Keyzer S, Smet M, Dehaen W, et al. Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s. Energy & Environmental Science. 2011;4(9):3601-10.
11. Weingarten R, Conner WC, Huber GW. Production of levulinic acid from cellulose by hydrothermal decomposition combined with aqueous phase dehydration with a solid acid catalyst. Energy & Environmental Science. 2012;5(6):7559-74.
12. Girisuta B, L. P. B. M. Janssen, H. J. Heeres. Green Chemicals: A Kinetic Study on the Conversion of Glucose to Levulinic Acid. Chemical Engineering Research and Design. 2006;84(5):339-49.
13. Girisuta B, Janssen LPBM, Heeres HJ. A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid. Green Chemistry. 2006;8(8):701-9.
14. Girisuta B, L. P. B. M. Janssen, H. J. Heeres. Kinetic Study on the Acid-Catalyzed Hydrolysis of Cellulose to Levulinic Acid. Industrial & Engineering Chemistry Research. 2007;46(6):1696-708.
15. Weingarten R, Cho J, Xing R, Conner WC, Huber GW. Kinetics and Reaction Engineering of Levulinic Acid Production from Aqueous Glucose Solutions. ChemSusChem. 2012;5(7):1280-90.
16. Lange J-P, van der Heide E, van Buijtenen J, Price R. Furfural—A Promising Platform for Lignocellulosic Biofuels. ChemSusChem. 2012;5(1):150-66.
17. Maldonado GMG, Assary RS, Dumesic J, Curtiss LA. Experimental and theoretical studies of the acid-catalyzed conversion of furfuryl alcohol to levulinic acid in aqueous solution. Energy & Environmental Science. 2012;5(5):6981-9.
18. Maldonado GMG, Assary RS, Dumesic JA, Curtiss LA. Acid-catalyzed conversion of furfuryl alcohol to ethyl levulinate in liquid ethanol. Energy & environmental science. 2012;5(10):8990-7.
19. Bozell JJ, Patel MK. Feedstocks for the Future: Renewables for the Production of Chemicals and Materials: ACS Publications; 2006.
20. Lange J-P, van de Graaf WD, Haan RJ. Conversion of Furfuryl Alcohol into Ethyl Levulinate using Solid Acid Catalysts. ChemSusChem. 2009;2(5):437-41.
21. Chia M, Dumesic JA. Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to [gamma]-valerolactone over metal oxide catalysts. Chemical Communications. 2011;47(44):12233-5.
22. Tang X, Chen H, Hu L, Hao W, Sun Y, Zeng X, et al. Conversion of biomass to γ-valerolactone by catalytic transfer hydrogenation of ethyl levulinate over metal hydroxides. Applied Catalysis B: Environmental. 2014;147:827-34.
23. Yan Z-p, Lin L, Liu S. Synthesis of γ-Valerolactone by Hydrogenation of Biomass-derived Levulinic Acid over Ru/C Catalyst. Energy & Fuels. 2009;23(8):3853-8.

24. Alonso DM, Wettstein SG, Dumesic JA. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. Green Chemistry. 2013;15(3):584-95.
25. Bond JQ, Alonso DM, Wang D, West RM, Dumesic JA. Integrated catalytic conversion of γ-valerolactone to liquid alkenes for transportation fuels. Science. 2010;327(5969):1110-4.
26. Bozell JJ. Connecting biomass and petroleum processing with a chemical bridge. Science. 2010;329(5991):522-3.
27. Lange J-P, Price R, Ayoub PM, Louis J, Petrus L, Clarke L, et al. Valeric Biofuels: A Platform of Cellulosic Transportation Fuels. Angewandte Chemie. 2010;122(26):4581-5.
28. Horvath IT, Mehdi H, Fabos V, Boda L, Mika LT. [gamma]-Valerolactone-a sustainable liquid for energy and carbon-based chemicals. Green Chemistry. 2008;10(2):238-42.
29. Lange J-P, Vestering JZ, Haan RJ. Towards 'bio-based' Nylon: conversion of [gamma]-valerolactone to methyl pentenoate under catalytic distillation conditions. Chemical Communications. 2007(33):3488-90.
30. Van de Vyver S, Roman-Leshkov Y. Emerging catalytic processes for the production of adipic acid. Catalysis Science & Technology. 2013;3(6):1465-79.
31. Yao K, Tang C. Controlled Polymerization of Next-Generation Renewable Monomers and Beyond. Macromolecules. 2013;46(5):1689-712.
32. Fegyverneki D, Orha L, Láng G, Horváth IT. Gamma-valerolactone-based solvents. Tetrahedron. 2010;66(5):1078-81.
33. Alonso DM, Bond JQ, Dumesic JA. Catalytic conversion of biomass to biofuels. Green Chemistry. 2010;12(9):1493-513.
34. Wright WRH, Palkovits R. Development of Heterogeneous Catalysts for the Conversion of Levulinic Acid to γ-Valerolactone. ChemSusChem. 2012;5(9):1657-67.
35. Palkovits R. Pentenoic Acid Pathways for Cellulosic Biofuels. Angewandte Chemie International Edition. 2010;49(26):4336-8.
36. Yan K, Liao J, Wu X, Xie X. A noble-metal free Cu-catalyst derived from hydrotalcite for highly efficient hydrogenation of biomass-derived furfural and levulinic acid. RSC Advances. 2013;3(12):3853-6.
37. Sen SM, Alonso DM, Wettstein SG, Gurbuz EI, Henao CA, Dumesic JA, et al. A sulfuric acid management strategy for the production of liquid hydrocarbon fuels via catalytic conversion of biomass-derived levulinic acid. Energy & Environmental Science. 2012;5(12):9690-7.
38. Braden DJ, Henao CA, Heltzel J, Maravelias CC, Dumesic JA. Production of liquid hydrocarbon fuels by catalytic conversion of biomass-derived levulinic acid. Green Chemistry. 2011;13(7):1755-65.
39. Heeres H, Handana R, Chunai D, Borromeus Rasrendra C, Girisuta B, Jan Heeres H. Combined dehydration/(transfer)-hydrogenation of C6-sugars (D-glucose and D-fructose) to [gamma]-valerolactone using ruthenium catalysts. Green Chemistry. 2009;11(8):1247-55.
40. Kopetzki D, Antonietti M. Transfer hydrogenation of levulinic acid under hydrothermal conditions catalyzed by sulfate as a temperature-switchable base. Green Chemistry. 2010;12(4):656-60.
41. Hengne AM, Rode CV. Cu-ZrO2 nanocomposite catalyst for selective hydrogenation of levulinic acid and its ester to [gamma]-valerolactone. Green Chemistry. 2012;14(4):1064-72.
42. Gilkey MJ, Xu B. Heterogeneous Catalytic Transfer Hydrogenation as an Effective Pathway in Biomass Upgrading. ACS Catalysis. 2016;6(3):1420-36.
43. Tang X, Hu L, Sun Y, Zhao G, Hao W, Lin L. Conversion of biomass-derived ethyl levulinate into [gamma]-valerolactone via hydrogen transfer from supercritical ethanol over a ZrO2 catalyst. RSC Advances. 2013;3(26):10277-84.
44. He J, Li H, Lu Y-M, Liu Y-X, Wu Z-B, Hu D-Y, et al. Cascade catalytic transfer hydrogenation–cyclization of ethyl levulinate to γ-valerolactone with Al–Zr mixed oxides. Applied Catalysis A: General. 2016;510:11-9.

45. Song J, Wu L, Zhou B, Zhou H, Fan H, Yang Y, et al. A new porous Zr-containing catalyst with a phenate group: an efficient catalyst for the catalytic transfer hydrogenation of ethyl levulinate to [gamma]-valerolactone. Green Chemistry. 2015;17(3):1626-32.
46. Tang X, Zeng X, Li Z, Li W, Jiang Y, Hu L, et al. In Situ Generated Catalyst System to Convert Biomass-Derived Levulinic Acid to γ-Valerolactone. ChemCatChem. 2015;7(8):1372-9.
47. Song J, Zhou B, Zhou H, Wu L, Meng Q, Liu Z, et al. Porous Zirconium–Phytic Acid Hybrid: a Highly Efficient Catalyst for Meerwein–Ponndorf–Verley Reductions. Angewandte Chemie. 2015;127(32):9531-5.
48. Iglesias J, Melero JA, Morales G, Moreno J, Segura Y, Paniagua M, et al. Zr-SBA-15 Lewis Acid Catalyst: Activity in Meerwein Ponndorf Verley Reduction. Catalysts. 2015;5(4):1911-27.
49. Kuwahara Y, Kaburagi W, Osada Y, Fujitani T, Yamashita H. Catalytic transfer hydrogenation of biomass-derived levulinic acid and its esters to γ-valerolactone over ZrO2 catalyst supported on SBA-15 silica. Catalysis Today. 2017;281, Part 3:418-28.
50. Enumula SS, Gurram VRB, Kondeboina M, Burri DR, Kamaraju SRR. ZrO2/SBA-15 as an efficient catalyst for the production of [gamma]-valerolactone from biomass-derived levulinic acid in the vapour phase at atmospheric pressure. RSC Advances. 2016;6(24):20230-9.
51. Li H, Fang Z, Yang S. Direct Conversion of Sugars and Ethyl Levulinate into γ-Valerolactone with Superparamagnetic Acid–Base Bifunctional ZrFeOx Nanocatalysts. ACS Sustainable Chemistry & Engineering. 2016;4(1):236-46.
52. Bui L, Luo H, Gunther WR, Román-Leshkov Y. Domino Reaction Catalyzed by Zeolites with Brønsted and Lewis Acid Sites for the Production of γ-Valerolactone from Furfural. Angewandte Chemie. 2013;125(31):8180-3.
53. Luo HY, Consoli DF, Gunther WR, Román-Leshkov Y. Investigation of the reaction kinetics of isolated Lewis acid sites in Beta zeolites for the Meerwein–Ponndorf–Verley reduction of methyl levulinate to γ-valerolactone. Journal of Catalysis. 2014;320:198-207.
54. Wang J, Jaenicke S, Chuah G-K. Zirconium-Beta zeolite as a robust catalyst for the transformation of levulinic acid to [gamma]-valerolactone via Meerwein-Ponndorf-Verley reduction. RSC Advances. 2014;4(26):13481-9.
55. Huang L, Zhu Y, Huo C, Zheng H, Feng G, Zhang C, et al. Mechanistic insight into the heterogeneous catalytic transfer hydrogenation over Cu/Al2O3: Direct evidence for the assistant role of support. Journal of Molecular Catalysis A: Chemical. 2008;288(1–2):109-15.
56. Jae J, Zheng W, Lobo RF, Vlachos DG. Production of Dimethylfuran from Hydroxymethylfurfural through Catalytic Transfer Hydrogenation with Ruthenium Supported on Carbon. ChemSusChem. 2013;6(7):1158-62.
57. Sawadjoon S, Lundstedt A, Samec JSM. Pd-Catalyzed Transfer Hydrogenolysis of Primary, Secondary, and Tertiary Benzylic Alcohols by Formic Acid: A Mechanistic Study. ACS Catalysis. 2013;3(4):635-42.
58. Gandarias I, Arias PL, Requies J, El Doukkali M, Güemez MB. Liquid-phase glycerol hydrogenolysis to 1,2-propanediol under nitrogen pressure using 2-propanol as hydrogen source. Journal of Catalysis. 2011;282(1):237-47.
59. Pellet RJ. Hydrogen Transfer Catalysis by Platinum on Zeolites. Journal of Catalysis. 1998;177(1):40-52.
60. Subramanian T, Pitchumani K. Selective Reduction of Nitroarenes by using Zeolite-Supported Copper Nanoparticles with 2-Propanol as a Sustainable Reducing Agent. ChemCatChem. 2012;4(12):1917-21.
61. Hansen TS, Barta K, Anastas PT, Ford PC, Riisager A. One-pot reduction of 5-hydroxymethylfurfural via hydrogen transfer from supercritical methanol. Green Chemistry. 2012;14(9):2457-61.
62. Lv J, Rong Z, Wang Y, Xiu J, Wang Y, Qu J. Highly efficient conversion of biomass-derived levulinic acid into [gamma]-valerolactone over Ni/MgO catalyst. RSC Advances. 2015;5(88):72037-45.

63. Geboers J, Wang X, de Carvalho AB, Rinaldi R. Densification of biorefinery schemes by H-transfer with Raney Ni and 2-propanol: A case study of a potential avenue for valorization of alkyl levulinates to alkyl γ-hydroxypentanoates and γ-valerolactone. Journal of Molecular Catalysis A: Chemical. 2014;388–389:106-15.

64. Yang Z, Huang Y-B, Guo Q-X, Fu Y. RANEY[registered sign] Ni catalyzed transfer hydrogenation of levulinate esters to [gamma]-valerolactone at room temperature. Chemical Communications. 2013;49(46):5328-30.

65. Kuwahara Y, Kaburagi W, Fujitani T. Catalytic transfer hydrogenation of levulinate esters to [gamma]-valerolactone over supported ruthenium hydroxide catalysts. RSC Advances. 2014;4(86):45848-55.

66. Amarasekara AS, Hasan MA. Pd/C catalyzed conversion of levulinic acid to γ-valerolactone using alcohol as a hydrogen donor under microwave conditions. Catalysis Communications. 2015;60:5-7.

67. Al-Shaal MG, Calin M, Delidovich I, Palkovits R. Microwave-assisted reduction of levulinic acid with alcohols producing γ-valerolactone in the presence of a Ru/C catalyst. Catalysis Communications. 2016;75:65-8.

68. Zhu S, Xue Y, Guo J, Cen Y, Wang J, Fan W. Integrated Conversion of Hemicellulose and Furfural into γ-Valerolactone over Au/ZrO2 Catalyst Combined with ZSM-5. ACS Catalysis. 2016;6(3):2035-42.

69. Hwang DW, Kashinathan P, Lee JM, Lee JH, Lee Uh, Hwang J-S, et al. Production of [gamma]-butyrolactone from biomass-derived 1,4-butanediol over novel copper-silica nanocomposite. Green Chemistry. 2011;13(7):1672-5.

70. Cui J, Tan J, Deng T, Cui X, Zheng H, Zhu Y, et al. Direct conversion of carbohydrates to [gamma]-valerolactone facilitated by a solvent effect. Green Chemistry. 2015;17(5):3084-9.