Catalytic applications of layered double hydroxides in biomass valorisation

Yang Song,[1*] Simon Beaumont,[2] Xingguang Zhang,[3,4,5] Karen Wilson,[6*] Adam F. Lee[6*]

[1]Centre College, Danville, Kentucky 40422, USA
[2]Department of Chemistry, University of Durham, Durham DH1 3LE, UK
[3]Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing, Jiangsu 210037, PR China
[4]College of Chemical Engineering, Nanjing Forestry University, Nanjing, Jiangsu 210037, PR China
[5]Jiangsu Key Lab for the Chemistry & Utilization of Agricultural and Forest Biomass, Nanjing Forestry University, Nanjing, Jiangsu 210037, PR China
[6]Applied Chemistry & Environmental Science, RMIT University, Melbourne VIC3000, Australia

Abstract

Catalysis has a rich history of facilitating energy efficient, selective molecular transformations, and contributes to 90 % of current chemical manufacturing processes. In a post-petroleum era, catalysis will be pivotal in overcoming the scientific and engineering barriers to economically feasible processes for bioderived feedstocks to fuels and chemicals. Biomass is comprised of highly functional oxygenated molecules whose valorization requires catalysts with tunable acid-base and redox properties able to affect selective transformations of carbonyl, alcohol and carboxylic acid functions. Layered double hydroxides (LDH) of general formula $[M^{2+}{}_{(1-x)}.M^{3+}{}_{x}(OH)_2]^{x+}.[A^{n-}{}_{x/n}.zH_2O]^{x-}$ are attractive catalysts for biomass conversion due to their tunable composition and structure. This opinion discusses recent developments in the application of LDHs for biomass valorisation.

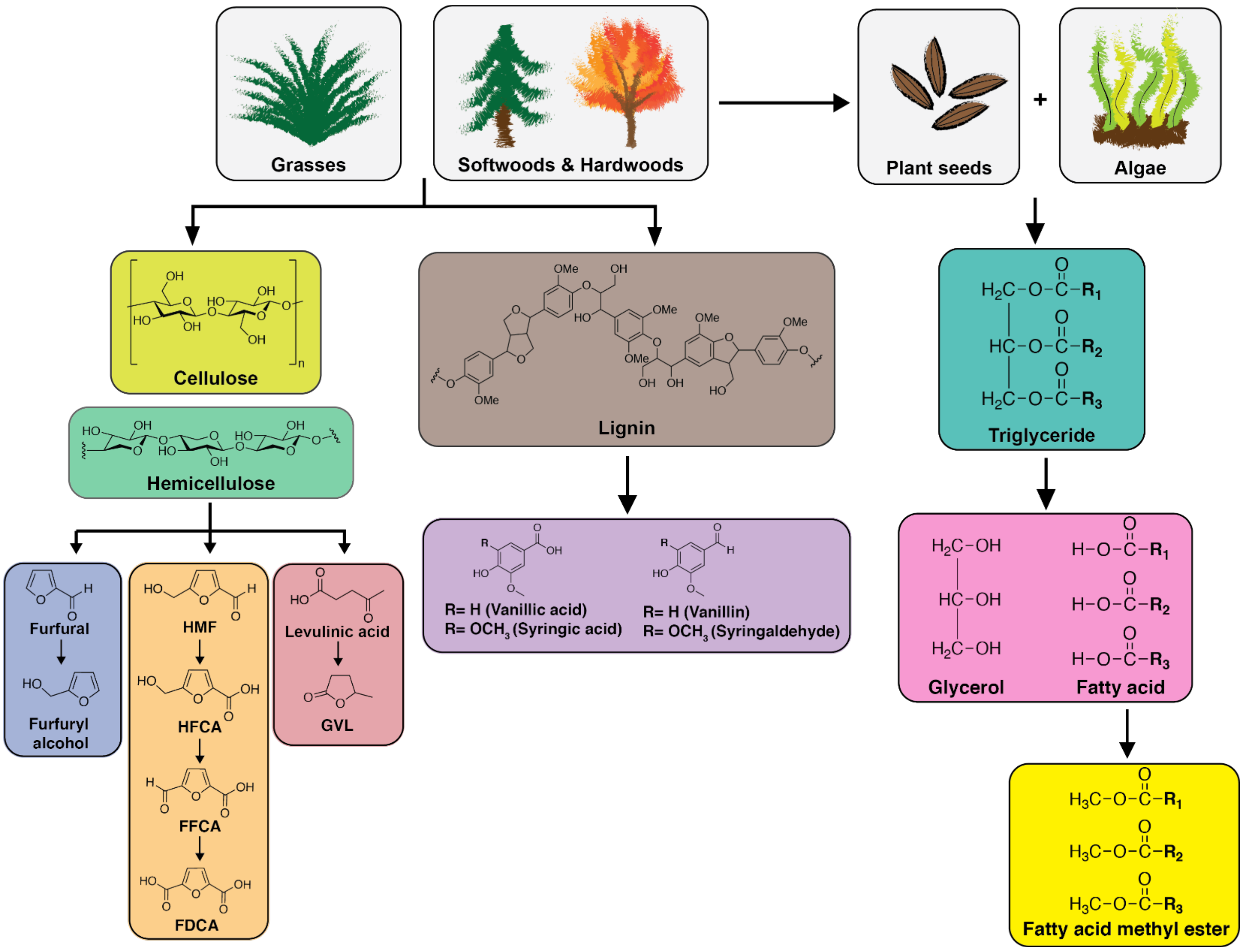
Introduction

Rising CO_2 emissions associated with continued use of coal and petroleum resources necessitate new chemical technologies to transform naturally-abundant biomass to raw materials, transport fuels and value-added chemicals;[1, 2] moreover, the new concept of ‘zero waste economy’ encourages utilisation of waste biomass as a feedstock.[3] If average global temperature rises are not to exceed 1.5 °C a large proportion of existing oil, gas and coal reserves must remain unused.[4]

Lignocellulosic biomass, such as agricultural and forestry residues, crops and wood, is a major biomass resource and recognised as a sustainable feedstock to replace fossil resources. It is also the most abundant biomass source inedible to humans, comprising cellulose and hemicellulose carbohydrate polymers embedded in a lignin matrix.[5] Lignin is a three-dimensional network of polyaromatic alcohols, whose upgrading offers an important source of renewable value-added chemicals.[6] Hemicellulose comprises pentose (xylose predominantly) and hexose units connected by different glycosidic bonds. Cellulose is a water insoluble, linear polysaccharide formed from glucose units linked via β-1,4-glycosidic bonds.[7]

Thermochemical (catalytic and non-catalytic) and biochemical (enzymatic) routes are the major approaches to biomass conversion, of which the former heterogeneously catalysed routes are attracting attention due to their potential to convert diverse biomass types into a targeted materials, fuels and chemicals.[8, 9] The complex nature of raw biomass hinders its direct utilisation as a feedstock. Efficient methods are therefore sought to deconstruct biomass into hemicellulose, cellulose and lignin fractions from which resulting C_5-C_6 sugars and aromatics can be transformed into polyalcohols and other platform chemicals (**Scheme 1**).[10-12] Routes to transform carbohydrates and lignin derived aromatics include dehydration, hydrolysis, hydrogenolysis, ketonisation and aldol condensation; all of which require careful tuning of catalyst acid:base properties. Considering the latter, layered double hydroxides (LDH) of general formula $[M^{2+}_{(1-x)}.M^{3+}_{x}(OH)_2]^{x+}.[A^{n-}_{x/n}.zH_2O]^{x-}$ are attractive catalysts for biomass conversion due to their tunable composition and associated redox or acid:base character, which can be controlled by judicious choice of M^{2+} or M^{3+}.[13, 14] Solid base and metal doped LDH catalysts find wide application in the conversion of oleochemical feedstocks to fuels, lubricants and surfactants via transesterification, decarboxylation and ketonisation. Furthermore, incorporation of redox active metals can promote bifunctional catalysis by coupling acid-base transformations with metal catalysed oxidation or hydrogenation, thereby improving process efficiency.

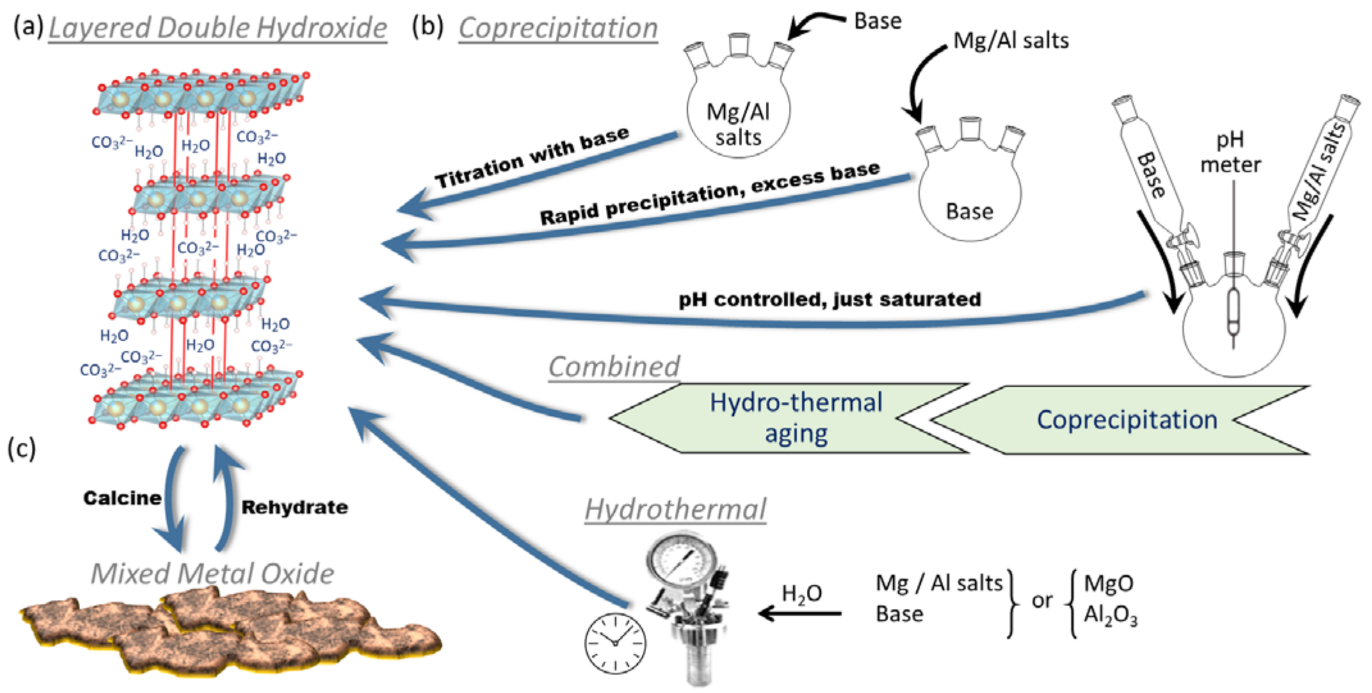
This opinion summarises the design and application of layered double hydroxides to biomass valorisation in the biorefinery context. Attention is paid to future research opportunities resulting from these recent advancements, and potential hurdles that might obstruct industrial implementation.



Scheme 1. Overview of biomass valorisation pathways involving LDH catalysts.

LDH synthesis

LDHs (anionic clays) are less abundant in nature than normal (cationic) clays, but simple and inexpensive to synthesise. The formation of positively charged mixed-valence mixed-metal (M^{2+}/M^{3+}) hydroxide layers (with interstitial charge-balancing anions and water molecules) requires synthetic approaches to intimately mix multiple metal precursors (**Scheme 2**). Co-precipitation is the method-of-choice, wherein metal precursors are homogenously mixed before controlled precipitation. Several variants exist (**Scheme 2b**): gradual titration with base (which risks sequential precipitation); gradual addition of metal precursor to excess base giving rapid precipitation; and precipitation at constant pH ensuring the solution is just supersaturated.[14] The latter typically entails gradual addition of both metal precursors while maintaining the pH such that the more soluble hydroxide precipitates. Hydrothermal synthesis (heating under autogenous pressure in an autoclave) can also be used prepare LDHs directly from separate oxides or hydroxides, usually affording more crystalline materials.[15] Aging or hydrothermally treating the co-precipitated LDH combines both methods and affords rapid synthesis and improved crystallinity.[16] Unless atmospheric CO_2 is rigorously excluded, the charge balancing anion is typically CO_3^{2-}, although other anions have been incorporated by exclusion of air and ion exchange.[17] Controlling pH during synthesis using inorganic (strong) bases can lead to erroneous catalysis: entrained alkaline hydroxides can leach under reaction conditions and behave as homogeneous catalysts; NH_4OH should therefore be used as a precipitant.[18] For catalytic applications, LDHs can be used directly, calcined to form mixed metal oxides, calcined and rehydrated to remove interlayer cations and reform the LDH,[19] or supported (*e.g.* on γ-alumina[20, 21] or alumina-coated SBA-15[22]) to increase active site accessibility, improve mechanical strength,[14] or enhance surface area.[23] LDH delamination in surfactant-solvent mixtures, which swell and exfoliate the lamella structure, is also attractive to prepare 2D nanosheets and composite or core-shell multifunctional materials.[24]



Scheme 2. Synthesis of LDH catalysts: (a) structural motif of a typical LDH comprising brucite-like layers with M^{2+}/M^{3+} atoms (yellow) at the centre of octahedra (turquoise) with oxygen (red) vertices, hydroxyl hydrogens are shown in white and the unit cell indicated by red lines; (b) LDH preparation methods (coprecipitation, hydrothermal or the combination of the two); and (c) calcination of LDH to form a disordered mixed metal oxide and subsequent rehydration to reverse this process.

The gamut of physicochemical characterization techniques associated with solid catalysts (TEM, SEM, IR, BET, DSC, TGA, XRD UV-Vis, ESR, NMR, XAFS, ICP, XRF etc.) is commonly deployed with LDHs, and reviewed elsewhere.[25] XRD measures basal reflections (interlayer spacings are ~24 Å for most small anions) and is essential in confirming successful LDH synthesis.[26] Solid state NMR and XAFS provides complementary local coordination information for amorphous materials invisible to XRD (e.g. individual hydroxides in poorly synthesised materials).[27] IR can highlight exchange of interlayer anions,[28] or the identification of acid/base sites through probe molecule titration.[29]

Holocellulose derived platform molecules

Isomerisation and dehydration of C_5 and C_6 sugars

Base catalysed isomerisation of glucose to fructose is an important route to 5-hydroxymethylfurfural (HMF), a versatile platform chemical to produce diverse value-added chemicals and liquid fuels.[30] Glucose-to-fructose isomerisation proceeds by the Lobry de Bruyn−Alberda van Ekenstein (LdB−AvE) transformation, initiated by abstraction of an α-hydrogen by base.[13, 31, 32] Heterogenous base catalysts for this transformation are desirable for large-scale industrial applications, with LDHs promising candidates due to their tunable basicity, nanostructure and stability. Due to the reversibility of the glucose↔fructose isomerisation,[33] many reports aim to shift the equilibrium forward. A MgAl-LDH modified by the introduction of sodium *n*-dodecyl sulfate as interlayer species[34] increased the catalyst hydrophobicity, with continuous flow operation used to remove reactively-formed fructose. Consequently, reaction selectivity increased (~92 % fructose selectivity at 30 % conversion). MgAl-LDHs were also studied for glucose isomerisation;[35] well-dispersed (primary) particles with small crystallites exhibited higher basicity and were more effective. Solvent effects in glucose isomerisation have been explored for MgAl-LDH, with 80 % fructose selectivity at 56 % glucose conversion obtained in ethanol.[31] LDH activity was regenerated by calcination and aqueous treatment.

LDHs can exhibit acidic and basic properties. Bifunctional metal doped LDHs, synthesised by impregnating aqueous solutions of metal chlorides (Sn, La, Cr, Fe, Zr or Ni) on MgAl-LDH,[36, 37] are reportred for the one-pot conversion of xylose to furans and furan derivatives. A NiAl-LDH catalyst in combination with Amberlyst-15 converted xylose to furfural in high yield (46 %), wherein Ni^{2+} was proposed to provide additional Lewis acidity to supplement the support Brønsted basicity for xylose isomerisation to xylulose, with Amberlyst-15 catalysing the subsequent dehydration.[37] In a more elaborate one-pot cascade, (2-furanylmethylene)malononitrile was produced from xylose with 44 % yield over a Cr/MgAl-LDH and Amberlyst-15 combination via stepwise isomerisation, dehydration and Knoevenagel condensation.[36]

Hydrogenation, hydrogenolysis and hydrodeoxygenation

Hydrotreatment of sugars and platform chemicals is important for biorefinery applications, and encompasses direct hydrogenation of C=C, carboxylic acid and carbonyl functions, and/or hydrogenolysis and hydrodeoxygenation to reducing oxygen content via C-O cleavage or dehydration/hydrogenation respectively. Hydrogenation accesses key chemical intermediates such as furfuryl alcohol, tetrahydrofurfuryl alcohol (THFA), 2-methylfuran, furan, tetrahydrofuran, from xylose derived furfural, while hydrogenation of levulinic acid (LA) can yield γ-valerolactone (GVL),[37] a promising green fuel additive and solvent. The flexible composition of LDH allows preparation of Ni[38] or Cu_xNi_y[39] doped MgAl-LDH precursors that transform on calcination into highly dispersed Ni or bimetallic CuNi nanoparticles (NPs) supported on MgAlO mixed metal oxides. CuNi materials exhibited excellent activity for furfural hydrogenation in batch (150 °C, 40 bar H_2), with selectivity to furfuryl alcohol highest over Cu NPs, while THFA production increased for Cu:Ni ratios of 1:1-1:3 [39] In contrast, calcined MgAlNi-LDHs with Mg:Ni of 1:2 show high yield (>92 %) for furfuryl alcohol in flow (180 °C and 1 bar H_2) with minimum deactivation.[38] Calcined CuCr-LDHs with Cu:Cr ratios of 0.5-2 are also active for furfural (200 °C, 60 bar H_2) and levulinic acid hydrogenation (200 °C, 70 bar H_2), with furfuryl alcohol and GVL yields increasing to 83 and 90 % respectively with Cr content.[40,41] A related family of calcined CuFe-LDHs show a similar increase in GVL yield with Fe content under identical reaction conditions, however the furfuryl alcohol yield decreased from 84 to 16 % with Fe content, with 2-methylfuran (2-MF) the favoured product via subsequent ring hydrogenation and hydrogenolysis of furfuryl alcohol.[42,41] A CoFeAl-LDH with composition $Co_3Fe_{0.25}Al_{0.75}$ produced high (80-99 %) furfural conversion and 83 % 2-MF selectivity under continuous operation at 180 °C and a more desirable 1 bar H_2 pressure. Fe substitution into the Co lattice was proposed to increase 2-MF production, however high Fe contents resulted in metallic Fe phases and deactivation.[43] Comparison of 5 wt% Ru doped CoFe- and NiFe-LDH for 2,5-DMF production from HMF revealed CoFe-LDH favours 2,5-DMF production (98.2% yield in batch at 10 bar H_2).[44] In this instance, Ru promoted 2,5-DMF production under harsher conditions than for undoped $Co_3Fe_{0.25}Al_{0.75}$ systems,[43] possibly reflecting a suboptimal 2:1 Co:Fe ratio in the support.

Growth and calcination of NiZrAl-LDH[45], synthesized by hydrothermal crystallization of Al and Zr precursors on a Ni foam, yielded a highly active catalyst for vapour phase GVL production from levulinic acid, attributed to cooperative interaction of dispersed Ni nanoparticles with Lewis acid sites and improved active site accessibility imparted by the foam support. A challenge to using Ni-LDH catalysts is the strong hydrogenation activity of Ni, which can over-hydrogenate furfural to THFA rather than furfuryl alcohol in batch. However, when the LDH possesses strong surface basic sites proximate to Ni sites, and the reaction is continuously operated under reduced H_2 pressure, side reactions are suppressed thereby improving selectivity to furfuryl alcohol.[38] While Cu-LDHs appear attractive due to their high selectivity towards furfuryl alcohol and GVL, the requisite elevated pressures 60-70 bar H_2 and high reaction temperatures are commercially undesirable. Furthermore, although calcined CuCr-LDHs offers 91 % GVL yields at 100 % LA conversion, use of toxic Cr is problematic.[41] Catalytic transfer hydrogenation of furfural by methanol has been explored over Cu_2Al-LDHs at 240 °C to circumvent gaseous hydrogen use, wherein furfuryl alcohol yields of 90 % are reported. Reduction of Cu favoured hydrogenolysis, with reduced Cu_3Al-LDH catalysts effective for converting furfural to 2-MF and HMF to 2,5-DMF in 88 % and 95 % yields respectively.[46]

Hydrogenation and ring opening of furanic species via hydrogenolysis is desirable to produce high value α,ω-diols including 1,4 butanediol, 1,5 pentanediol or 1,6 hexanediol, widely used in polyester and polyurethane production.[47] MgAl-LDH supported Pt nanoparticles catalyse furfural hydrogenolysis to 1,2 pentane diols in 73 % yield. [48] Cu doped MgAl-LDH is also effective for furfuryl alcohol hydrogenolysis, with 1,2- and 1,5-pentanediol yields of 29 and 51 % respectively; cooperation between metallic Cu and basic $Mg_3AlO_{4.5}$ is proposed, wherein Cu nanoparticles of 1.7 nm maximise activity and chemoselectivity.[49]

Aldol condensation

Aldol condensation is a valuable route to bio-fuels wherein short chain, biomass derived C_2-C_4 oxygenates are coupled to grow hydrocarbon chains. Acetone self-condensation (derived from fermentation or acetic acid ketonisation in fast pyrolysis oil) offers a route to aromatic products or branched hydrocarbons, while condensation of longer methyl ketones offers jet fuel and diesel range hydrocarbons and lubricants.[50] Selectivity of the condensation reaction is important, with trimers of methyl ketones required for jet fuel, while linear hydrocarbons are more suited for diesel.[51] Aqueous-phase aldol condensation of furfural or HMF with acetone permits the sustainable production of second generation biofuels from sugars.[52] C_8-C_{15} adducts obtained from an initial condensation are then dehydrated to a stable enone intermediate, for subsequent conversion to jet fuel alkanes by hydrogenation or hydrodeoxygenation. These reactions involve an enol or enolate ion reacting with a carbonyl, creating a C-C bond to give a hydroxyaldehyde or hydroxyketone, with an α,β-unsaturated carbonyl moiety finally formed by dehydration. A comprehensive study of MgAl-LDH preparation methods on their reactivity for aldol condensation of furfural with acetone was recently reported;[53] the optimum Mg_3Al catalyst exhibited 95 % furfural conversion, with 70 % selectivity towards C_8 products (from acetone addition to furfural) and 22 % towards the C_{13} product (from C_8 coupling with another furfural molecule). In situ MgAl-LDH rehydration increased activity. Calcined and reconstructed MgGa-LDHs (Mg:Ga between 2-4) were also explored for furfural aldol condensation to explore whether substitution of Al^{3+} with Ga^{3+} alters the LDH Brønsted basicity or Lewis acidicity.[54] Reconstructed MgGa-LDHs were more active than the corresponding mixed oxides, with reactivity decreasing with Mg:Ga ratio whereas product selectivity was almost invariant. A related study of MgAl-LDH explored the impact of water:toluene solvent ratio; added water ($\leq$50 vol%) increased the C_8 product yield from 14 to 70 %, attributed to partitioning of this intermediate in the organic phase and hindering subsequent reaction.[55] Calcined LiAl-LDHs (Li:Al of 0.5) synthesised by mechanochemical methods have been explored for aldol condensation of acetone and furfural, and exhibit higher base site loadings and reaction rates than Mg_3Al-LDH.[56] Calcined MgFe-LDH (Mg:Fe of 1 to 10) are also active for acetone and furfural condensation, with a balance of acid and base sites necessary to achieve both condensation and dehydration steps to form the stable enone; while increasing Mg content enhanced furfural conversion, dehydration was favoured over acidic materials with Mg:Fe≤ 5. [57] The versatility of LDHs in condensation reactions is further demonstrated in the coupling of furfural and levulinic acid over Mg_3Al-LDH,[58] isobutyraldehyde and formaldehyde to produce hydroxypivaldehyde over CaAl-LDH,[59] and the Guerbet reaction of ethanol to 1-butanol over calcined Mg_3Al-LDH.[60] Coupling MgAl-LDH with a hydrogenation catalyst is an attractive route to bi- and tri-cyclopentanes, potential aviation fuels, from the condensation and hydrodeoxygenation of furfural derived cyclopentanol.[61]

Interpreting the preceding catalyst performance is hampered by alkali carbonate/hydroxide use during LDH synthesis. Alkali-free LDH syntheses are urged to avoid artefacts, especially during liquid phase reactions,[62, 63]

Oxidation of carbohydrates and platform chemicals

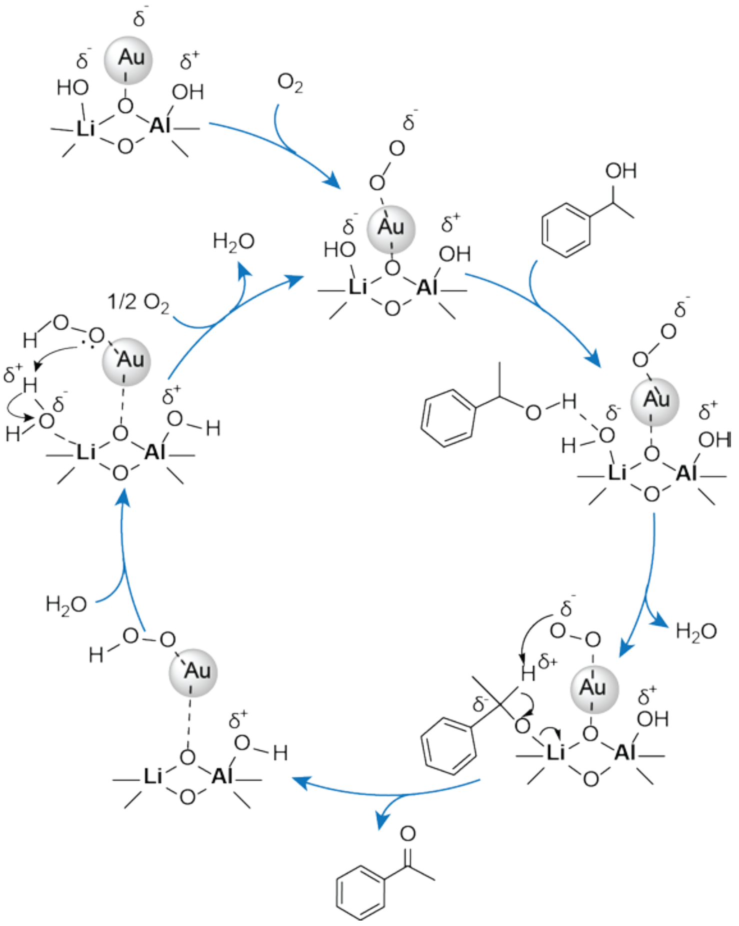
Catalytic oxidation of biomass derived platform chemicals opens routes to dicarboxylic acids, important intermediates for the sustainable production of biobased polymers.[64] [65] [66] Gluconic acid produced from glucose oxidation finds widespread use in the food, detergent, and pharmaceutical industries.[67] However, selective oxidation of carbohydrates and bioderived platform molecules such as furfural and HMF is often performed in aqueous alkaline media,[68] necessitating water tolerant, robust solid base catalysts.[69,70]

The three functional groups (conjugated furan, aldehyde and hydroxy group) makes HMF a versatile intermediate to valuable chemicals and biofuels.[71, 72] HMF oxidation yields 2,5-diformylfuran (DFF), 5-formyl-2-furancarboxylic acid (FFCA), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), and principally 2,5-furandicarboxylic acid (2,5-FDCA), a potential replacement for terephthalic acid in bio-based polyesters. 2 wt% Au/MgAl-LDH catalysts are reported for the aqueous phase oxidation of HMF to 2,5-FDCA,[73,74] however, the use of Na_2CO_3/NaOH precipitants was problematic due to entrained alkali.[75] Alkaline-free 2 wt% Au/MgAl-LDH were subsequently prepared[74] but ineffective for 2,5-FDCA formation due to competitive adsorption between HMF and reactively-formed HMFCA; NaOH addition promoted solution phase HMF activation, but could be circumvented by using high Au loadings; optimising the HMF:Au ratio enabled high 2,5-FDCA yields. A 2wt% Pd/Mg_5Al-LDH yielded near quantitative 2,5-FDCA production from HMF, however catalysis was likely influenced by the presence of brucite,[76] while a bimetallic $Pd_{0.2}Pt_{0.8}$/MgAl-LDH achieved ~100 % 2,5-FDCA yield in the absence of aqueous base[77] (since extended to the aerobic oxidation of sugars to sugar acids[78]). Calcined $Mn_{0.70}Cu_{0.05}Al_{0.25}$-LDHs are also effective for HMF oxidation to 2,5-diformylfuran under 8 bar O_2.[79] NiFe-LDH nanosheets on carbon fibers are effective electrocatalysts for the direct oxidation of HMF to 2,5-FDCA with >90 % selectivity, but required 1 M KOH. [80]

Lignin depolymerisation

Lignin is a more complex three-dimensional polymer than holocellulose,[6] but contains prominent molecular targets for chemical deconstruction. Lignin depolymerisation is attractive for the production of aromatic-rich platform molecules, but is challenging due to the formation of recalcitrant intermediates and competing use as a solid fuel. LDH-derived catalysts have been use for lignin depolymerization, targeting the β-aryl ether unit with its characteristic β-O-4 ether linkage, which comprises up to 60 % of lignin.[81]

Au/LDH catalysts were recently reported (**Scheme 3**)[82] effective for the oxidative depolymerization of lignin β-O-4 model compounds, with ~90 % conversion of a β-O-4 model compound in 24 h at 120 °C using O_2. The most active Au/LiAl-LDH catalyst produced 20 wt% ethyl acetate-soluble products and ~10 wt% monomers (mainly vanillin and vanillic acid,) from Indulin AT Kraft lignin (derived from pine). When applied to γ-valerolactone extracted lignin from maple, a 56 wt% yield of ethyl acetate-soluble products was obtained with 40 wt% yield of GC-MS identifiable monomers,[83] representing the largest monomer yield from lignin under such conditions to date. High activity was attributed to electron transfer between Au nanoparticles and the basic LiAl-LDH, facilitating O_2 activation and alcohol deprotonation.



Scheme 3. Proposed catalytic cycle for Au/LiAl-LDH catalysed alcohol oxidation.

Oleaginous feedstocks

Basic LDH catalysts are widely used for the conversion of triglycerides (TAG) to biodiesel fatty acid methyl esters (FAME), and the ketonisation[84] or decarboxylation of fatty acids[85] for the synthesis of lubricants or green diesel respectively. MgAl-LDHs deliver near quantitative transesterification of TAGs in poor and high quality oil feeds[86] including refined and acidic cottonseed oil (9.5 wt% fatty acids), and animal fat feed (45 wt% water) in 3 h at 200 °C. However, many catalytic studies employ LDHs precipitated using Na or K hydroxide/carbonate and hence are unreliable due to potential homogeneous contributions from leached alkalis.[18, 75] Alkali-free precipitation using NH_3OH and NH_3CO_3 has been used to synthesise MgAl-[63] and ZnAl-LDHs[87] prior to hydrothermal reconstruction.

Microporous LDHs are unsuitable for bulky C_{16}-C_{18} TAGs. Intercalation[88,89] to swell the layers, and macropore incorporation,[90] offer significant benefits for base site accessibility and diffusion of long chain TAGs. Ordered, hierarchical materials possessing bimodal pore architectures can be prepared through dual-templating approaches, wherein co-precipitation of divalent and trivalent metal cations occurs within the interstices of an infiltrated polystyrene (PS) colloidal crystal[91, 92] resulted in an alkali-free macroporous-microporous LDH catalyst.[90] Macropores provided large conduits to transport bulky TAGs to active base sites at the surface of LDH nanocrystallites, promoting triolein transesterification almost ten-fold versus a conventional MgAl-LDH of identical composition. Alternatively alkali- and nitrate-free MgAl-LDH coatings have been grown on alumina[93] and alumina coated macro-mesoporous SBA-15.[22] The resulting coatings are more active for the transesterification of C_4–C_{18} triglycerides than bulk LDH counterparts, again attributed to improved accessibility of bulky TAGs to base sites.

Poor thermal and oxidative stability of biodiesel, coupled with variable fuel properties depending on oil source (e.g. degree of unsaturation, chain length), limits FAME based transportation fuels, with >C_{18} FAME molecules exhibiting poor viscosity and cloud and pour points.[94] In contrast, green diesel produced from TAGs and free fatty acids[95] by 250-350 °C hydrotreating, involving catalytic cracking or deoxygenation via decarboxylation (DCX), hydrodecarbonylation (HDC) or hydrodeoxygenation (HDO), offers hydrocarbon fuels closer to fossil derived fuels.[96,97, 98,99 100] Oleic acid direct decarboxylation over MgAl-LDHs proceeds with ~100 % conversion at 400 °C. However, such H_2 free processes require catalysts with high Mg content and temperatures >350 °C to avoid saponification, which result in poor yields of desired C_{17} due to competing cracking.[101] $Ni_{0.67}Al_{0.33}$-LDHs are effective for hydrotreatment of stearic acid and tristearin to C_{10}-C_{17} hydrocarbons, with the 56 % yield of C_{17} alkanes double that achievable over Ni/Al_2O_3 catalysts.[85] Ru and Pd doped MgAl-LDHs have been used to hydrotreat Jatropha oil to produce diesel range hydrocarbons, with 87-91 % C_{15}-C_{18} oil yields observed for both catalysts.[102] Pt/ZnAl-LDH exhibits ~98 % decarboxylation of oleic acid but inferior selectivity to C_{17} products relative to Pt/SAPO-34 zeolite, suggesting this transformation needs strong acid catalysts.[103] Despite the potential of LDHs are precursors to metal/metal oxide nanoparticles on calcination/reduction, their application in hydrotreating is not widespread,[99] and there is scope for redox (e.g. Ni, Co, Cu, Fe) LDH formulations which have proven successful in HDO of platform chemicals as highlighted in an earlier section.

Catalyst deactivation

LDH deactivation in biomass upgrading occurs either ex situ through base site neutralisation by atmospheric CO_2 adsorption,[104] or in situ through active site blocking (coking and/or irreversible adsorption of organic species[72]) or the loss of active sites due to particle sintering, leaching,[105] or a change in phase/oxidation state.[32, 34] Coking and fouling are partially reversible by calcination for catalysts with thermal stability ≥400 °C,[31, 34, 106] however such treatments inevitably promote structural transformation and are hence best avoided by e.g. continuous processing to avoid by-product formation.[34] Metal leaching from LDHs is problematic in the presence of reactively-formed acids[34] or in acidic media,[107] and from supported metal nanoparticles (e.g. Au from PdAu/MgAl-LDH during HMF oxidation[108] or Pd from Pd/MgAl-LDH during furanics decarbonylation[109]); however, related studies did not observe metal leaching from Au/Mg-Al or Au/Li-Al LDHs during HMF oxidation[74] or lignin depolymerisation[82] respectively under mild conditions.

Conclusions

LDHs find broad application in biomass conversion, either as tunable acid-base catalysts or as precursors to mixed metal oxide catalysts. For the latter, intermixing of redox active M^{2+} and M^{3+}cations (e.g. Cu, Co, Fe, Ni, Pd) in the parent LDH facilitates well-defined metal and oxide nanoparticles on thermal processing. MgAl- and M^{2+} substituted-LDHs are most studied, however ZnAl- and MgGa-LDHs offer greater hydrothermal stability and broader acidity, and hence opportunities for higher performance catalysts. The influence of M^{2+}:M^{3+} ratio on catalytic performance is evident in HDO of furanics, and may translate to hydrotreating of oleaginous feedstocks. Syntheses that improve LDH active site accessibility, such as thin film, delamination and templating strategies, are essential to broaden their applications, particularly to transformations involving bulky reactants. LDH incorporation into nanocomposites, e.g. core-shell nanoparticles, is uncommon for biomass applications, but could unlock new thermal (and photo-[110]) catalytic cascades for atom-economical one-pot transformations.[111] Despite well-documented concerns regarding alkali precipitation, much of the recent LDH literature still adopts such synthetic protocols. For liquid phase catalysis, which underpins biomass conversion to value-added chemicals, entrained alkali is a potential source of product contaminant (and reactor corrosion), and impairs reproducibility of academic studies and the development of commercial processes; hydrothermal or alkali-free precipitation routes to LDHs must be pursued.

References

1. S. Zhou, L. Zhou, Y. Zhang, J. Sun, J. Wen and Y. Yuan, *Journal of Materials Chemistry A*, 2019, **7**, 4217-4229.
2. J. A. Melero, J. Iglesias and A. Garcia, *Energy & Environmental Science*, 2012, **5**, 7393-7420.
3. E. Calcio Gaudino, G. Cravotto, M. Manzoli and S. Tabasso, *Green Chemistry*, 2019, **21**, 1202-1235.
4. M. Jakob and J. Hilaire, *Nature*, 2015, **517**, 150.
5. C.-H. Zhou, X. Xia, C.-X. Lin, D.-S. Tong and J. Beltramini, *Chemical Society Reviews*, 2011, **40**, 5588-5617.
6. R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx and B. M. Weckhuysen, *Angewandte Chemie International Edition*, 2016, **55**, 8164-8215.
   **This review provides the most detailed background on the various isolation techniques of lignin and lignin valorization up to date.
7. D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chemical Society Reviews*, 2012, **41**, 8075-8098.
8. I. Delidovich, K. Leonhard and R. Palkovits, *Energy & Environmental Science*, 2014, **7**, 2803-2830.
9. H. Li, Z. Fang, R. L. Smith and S. Yang, *Progress in Energy and Combustion Science*, 2016, **55**, 98-194.
10. X. Zhang, K. Wilson and A. F. Lee, *Chemical Reviews*, 2016, **116**, 12328-12368.
11. X. Zhang, L. J. Durndell, M. A. Isaacs, C. M. A. Parlett, A. F. Lee and K. Wilson, *ACS Catalysis*, 2016, **6**, 7409-7417.
12. X. Zhang, A. I. M. Rabee, M. Isaacs, A. F. Lee and K. Wilson, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 14704-14712.
13. K. Yan, Y. Liu, Y. Lu, J. Chai and L. Sun, *Catalysis Science & Technology*, 2017, **7**, 1622-1645.
    **This review provides details on the application of LDH and LDH-derived catalysts towards upgrading of biomass-derived molecules.
14. F. Cavani, F. Trifirò and A. Vaccari, *Catalysis Today*, 1991, **11**, 173-301.
15. D. M. Roy, R. Roy and E. F. Osborn, *American Journal of Science*, 1953, **251**, 337-361.
16. F. Kovanda, T. Rojka, P. Bezdička, K. Jirátová, L. Obalová, K. Pacultová, Z. Bastl and T. Grygar, *Journal of Solid State Chemistry*, 2009, **182**, 27-36.
17. A. I. Khan and D. O'Hare, *Journal of Materials Chemistry*, 2002, **12**, 3191-3198.
18. H. E. Cross and D. R. Brown, *Catalysis Communications*, 2010, **12**, 243-245.
19. K. Takehira, *Applied Clay Science*, 2017, **136**, 112-141.
20. J. J. Creasey, A. Chieregato, J. C. Manayil, C. M. A. Parlett, K. Wilson and A. F. Lee, *Catalysis Science & Technology*, 2014, **4**, 861-870.
21. R. Xu and H. C. Zeng, *Chemistry of Materials*, 2001, **13**, 297-303.
22. J. J. Creasey, C. M. A. Parlett, J. C. Manayil, M. A. Isaacs, K. Wilson and A. F. Lee, *Green Chemistry*, 2015, **17**, 2398-2405.
23. Q. Wang and D. O'Hare, *Chemical Reviews*, 2012, **112**, 4124-4155.
    **This provides a comprehensive review of LDH synthesis
24. J. Yu, Q. Wang, D. O'Hare and L. Sun, *Chemical Society Reviews*, 2017, **46**, 5950-5974.
    **A comprehensive review of LDH delamination methods.
25. V. Rives, *Materials Chemistry and Physics*, 2002, **75**, 19-25.
26. D. G. Evans and R. C. T. Slade, in *Layered Double Hydroxides*, eds. X. Duan and D. G. Evans, Springer Berlin Heidelberg, Berlin, Heidelberg, 2006, DOI: 10.1007/430_005, pp. 1-87.
27. M. Vucelic, W. Jones and G. D. Moggridge, *Clays and Clay Minerals*, 1997, **45**, 803-813.
28. S. P. Newman and W. Jones, *Journal of Solid State Chemistry*, 1999, **148**, 26-40.
29. F. Prinetto, G. Ghiotti, R. Durand and D. Tichit, *The Journal of Physical Chemistry B*, 2000, **104**, 11117-11126.
30. I. Delidovich and R. Palkovits, *ChemSusChem*, 2016, **9**, 547-561.
31. M. Yabushita, N. Shibayama, K. Nakajima and A. Fukuoka, *ACS Catalysis*, 2019, **9**, 2101-2109.
32. W. Y. Hernández, J. Lauwaert, P. Van Der Voort and A. Verberckmoes, *Green Chemistry*, 2017, **19**, 5269-5302.
    **This review provides a detailed overview of the integration of LDH and LDH-derived catalysts in the lignocellulosic feedstock biorefinery. The review highlights the versatility of LDH catalysts and their application in each fraction of the biomass.
33. M. Moliner, Y. Román-Leshkov and M. E. Davis, *Proceedings of the National Academy of Sciences*, 2010, **107**, 6164-6168.
34. I. Delidovich and R. Palkovits, *Catalysis Science & Technology*, 2014, **4**, 4322-4329.
35. I. Delidovich and R. Palkovits, *Journal of Catalysis*, 2015, **327**, 1-9.
    *This article discusses the tunability of Mg-Al LDH and the properties of Mg-Al LDH synthesized using various methods and the effect on the catalytic activity of glucose to fructose isomerization.
36. M. Shirotori, S. Nishimura and K. Ebitani, *Catalysis Science & Technology*, 2014, **4**, 971-978.
37. M. Shirotori, S. Nishimura and K. Ebitani, *Chemistry Letters*, 2016, **45**, 194-196.

38. M. Manikandan, A. K. Venugopal, K. Prabu, R. K. Jha and R. Thirumalaiswamy, *Journal of Molecular Catalysis A: Chemical*, 2016, **417**, 153-162.
39. J. Wu, G. Gao, J. Li, P. Sun, X. Long and F. Li, *Applied Catalysis B: Environmental*, 2017, **203**, 227-236.
40. K. Yan and A. Chen, *Energy*, 2013, **58**, 357-363.
41. K. Yan, J. Liao, X. Wu and X. Xie, *RSC Advances*, 2013, **3**, 3853-3856.
42. K. Yan and A. Chen, *Fuel*, 2014, **115**, 101-108.
43. T. P. Sulmonetti, B. Hu, Z. Ifkovits, S. Lee, P. K. Agrawal and C. W. Jones, *ChemCatChem*, 2017, **9**, 1815-1823.
44. Q. Li, P. Man, L. Yuan, P. Zhang, Y. Li and S. Ai, *Molecular Catalysis*, 2017, **431**, 32-38.
45. W. Li, G. Fan, L. Yang and F. Li, *ChemCatChem*, 2016, **8**, 2724-2733.
46. J. Zhang and J. Chen, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 5982-5993.
47. J. He, K. Huang, K. J. Barnett, S. H. Krishna, D. M. Alonso, Z. J. Brentzel, S. P. Burt, T. Walker, W. F. Banholzer, C. T. Maravelias, I. Hermans, J. A. Dumesic and G. W. Huber, *Faraday Discussions*, 2017, **202**, 247-267.
48. T. Mizugaki, T. Yamakawa, Y. Nagatsu, Z. Maeno, T. Mitsudome, K. Jitsukawa and K. Kaneda, *ACS Sustainable Chemistry & Engineering*, 2014, **2**, 2243-2247.
49. H. Liu, Z. Huang, F. Zhao, F. Cui, X. Li, C. Xia and J. Chen, *Catalysis Science & Technology*, 2016, **6**, 668-671.
50. M. Balakrishnan, E. R. Sacia, S. Sreekumar, G. Gunbas, A. A. Gokhale, C. D. Scown, F. D. Toste and A. T. Bell, *Proceedings of the National Academy of Sciences*, 2015, **112**, 7645.
51. L. Wu, T. Moteki, Amit A. Gokhale, David W. Flaherty and F. D. Toste, *Chem*, 2016, **1**, 32-58.
52. G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446-1450.
    **This article provides an overview of the value for cellulose- and hemicellulose- derived priducts and their conversion to second generation biofuels.
53. L. Hora, V. Kelbichová, O. Kikhtyanin, O. Bortnovskiy and D. Kubička, *Catalysis Today*, 2014, **223**, 138-147.
    **This article focuses on the physical properties of Mg-Al LDH and Mg-Al mix metal oxide. The authors report the effectivness of the catalyst by varying the synthesis route and other modificaitons.
54. O. Kikhtyanin, L. Čapek, Z. Tišler, R. Velvarská, A. Panasewicz, P. Diblíková and D. Kubička, *Frontiers in Chemistry*, 2018, **6**, 176.
55. A. Parejas, D. Cosano, J. Hidalgo-Carrillo, R. J. Ruiz, A. Marinas, C. Jiménez-Sanchidrián and J. F. Urbano, *Catalysts*, 2019, **9**.
56. L. Stepanova, R. Mironenko, O. Belskaya and V. J. C. f. S. E. Likholobov, *Catalysis for Sustainable Energy*, 2017, **4**, 8-16.
57. J. Kocík, K. Frolich, I. Perková and J. Horáček, *Journal of Chemical Technology & Biotechnology*, 2019, **94**, 435-445.
58. G. Liang, A. Wang, X. Zhao, N. Lei and T. Zhang, *Green Chemistry*, 2016, **18**, 3430-3438.
59. W. Bing, L. Zheng, S. He, D. Rao, M. Xu, L. Zheng, B. Wang, Y. Wang and M. Wei, *ACS Catalysis*, 2018, **8**, 656-664.
60. K. K. Ramasamy, M. Gray, H. Job, C. Smith and Y. Wang, *Catalysis Today*, 2016, **269**, 82-87.
61. X. Sheng, N. Li, G. Li, W. Wang, J. Yang, Y. Cong, A. Wang, X. Wang and T. Zhang, *Scientific Reports*, 2015, **5**, 9565.
62. D. P. Debecker, E. M. Gaigneaux and G. Busca, *Chemistry – A European Journal*, 2009, **15**, 3920-3935.
63. D. G. Cantrell, L. J. Gillie, A. F. Lee and K. Wilson, *Applied Catalysis A: General*, 2005, **287**, 183-190.
64. R. Beerthuis, G. Rothenberg and N. R. Shiju, *Green Chemistry*, 2015, **17**, 1341-1361.
65. J. Zhang, J. Li, Y. Tang, L. Lin and M. Long, *Carbohydrate Polymers*, 2015, **130**, 420-428.
66. J. Becker, A. Lange, J. Fabarius and C. Wittmann, *Current Opinion in Biotechnology*, 2015, **36**, 168-175.
67. T. Matsumoto, S. Shimada, K. Yamamoto, T. Tanaka and A. Kondo, *Fuel Cells*, 2013, **13**, 960-964.
68. C. Basheer, S. Swaminathan, H. K. Lee and S. Valiyaveettil, *Chemical Communications*, 2005, DOI: 10.1039/B414429E, 409-410.
69. M. J. Climent, A. Corma and S. Iborra, *Green Chemistry*, 2011, **13**, 520-540.
70. J. M. Fraile, J. I. García and J. A. Mayoral, *Catalysis Today*, 2000, **57**, 3-16.
71. Z. Zhang and K. Deng, *ACS Catalysis*, 2015, **5**, 6529-6544.
    *This review discusses recent advances of the catalytic prouction of 2,5-FDCA and other derivaties.
72. Z. An, W. Wang, S. Dong and J. He, *Catalysis Today*, 2019, **319**, 128-138.
73. N. K. Gupta, S. Nishimura, A. Takagaki and K. Ebitani, *Green Chemistry*, 2011, **13**, 824-827.
74. L. Ardemani, G. Cibin, A. J. Dent, M. A. Isaacs, G. Kyriakou, A. F. Lee, C. M. A. Parlett, S. A. Parry and K. Wilson, *Chemical Science*, 2015, **6**, 4940-4945.
    *This article gives insight into the reaction mechanism of HMF to 2,5-FDCA using Au/Mg-Al LDH by using operando Au L_{III}-Edge XAS technique and detailed kinetic analysis.
75. J. M. Fraile, N. García, J. A. Mayoral, E. Pires and L. Roldán, *Applied Catalysis A: General*, 2009, **364**, 87-94.
76. Y. Wang, K. Yu, D. Lei, W. Si, Y. Feng, L.-L. Lou and S. Liu, *ACS Sustainable Chemistry & Engineering*, 2016, **4**, 4752-4761.
77. H. Choudhary and K. Ebitani, *Chemistry Letters*, 2016, **45**, 613-615.
78. R. Tomar, J. Sharma, S. Nishimura and K. Ebitani, *Chemistry Letters*, 2016, **45**, 843-845.

79. F. Neaţu, N. Petrea, R. Petre, V. Somoghi, M. Florea and V. I. Parvulescu, *Catalysis Today*, 2016, **278**, 66-73.
80. W.-J. Liu, L. Dang, Z. Xu, H.-Q. Yu, S. Jin and G. W. Huber, *ACS Catalysis*, 2018, **8**, 5533-5541.
81. W. Schutyser, T. Renders, S. Van den Bosch, S. F. Koelewijn, G. T. Beckham and B. F. Sels, *Chemical Society Reviews*, 2018, **47**, 852-908.
**This review provides insight of various depolymerization methods of lignin that reach beyond the use of LDH catalysts. Notable, it gives detailes regarding the products obtained from various lignin depolymerization methods and their role in an integrated biorefinery.
82. Y. Song, J. K. Mobley, A. H. Motagamwala, M. Isaacs, J. A. Dumesic, J. Ralph, A. F. Lee, K. Wilson and M. Crocker, *Chemical Science*, 2018, **9**, 8127-8133.
83. Y. Song, A. H. Motagamwala, S. D. Karlen, J. A. Dumesic, J. Ralph, J. K. Mobley and M. Crocker, *Green Chemistry*, 2019, **21**, 3940-3947.
*This article compares recent literature lignin depolymerization methods using lignin that has been previously oxidized, highlighting the superior ability of Au/Li-Al LDH to depolymerize lignin without the need for prior oxidation.

84. B. Smith, L. Li, D. D. Perera-Solis, F. L. Gildea, L. V. Zholobenko, W. P. Dyer and C. H. Greenwell, *Inorganics*, 2018, **6**.
85. E. Santillan-Jimenez, T. Morgan, J. Shoup, A. E. Harman-Ware and M. Crocker, *Catalysis Today*, 2014, **237**, 136-144.
86. N. Barakos, S. Pasias and N. Papayannakos, *Bioresource Technology*, 2008, **99**, 5037-5042.
87. A. N. Tajuddin, C. J. Manayil, A. M. Isaacs, M. A. C. Parlett, F. A. Lee and K. Wilson, *Catalysts*, 2018, **8**.
88. O. Meyer, F. Roessner, R. A. Rakoczy and R. W. Fischer, *ChemCatChem*, 2010, **2**, 314-321.
89. G. Fan, F. Li, D. G. Evans and X. Duan, *Chemical Society Reviews*, 2014, **43**, 7040-7066.
90. J. J. Woodford, J.-P. Dacquin, K. Wilson and A. F. Lee, *Energy & Environmental Science*, 2012, **5**, 6145-6150.
91. E. Géraud, V. Prévot, J. Ghanbaja and F. Leroux, *Chemistry of Materials*, 2005, **18**, 238-240.
92. E. Géraud, S. Rafqah, M. Sarakha, C. Forano, V. Prevot and F. Leroux, *Chemistry of Materials*, 2007, **20**, 1116-1125.
93. J. J. Creasey, A. Chieregato, J. C. Manayil, C. M. A. Parlett, K. Wilson and A. F. Lee, *Catalysis Science & Technology*, 2014, **4**, 861-870.
94. G. Knothe, *Topics in Catalysis*, 2010, **53**, 714-720.
95. Y. Liu, R. Sotelo-Boyás, K. Murata, T. Minowa and K. Sakanishi, *Energy & Fuels*, 2011, **25**, 4675-4685.
96. A. N. Kay Lup, F. Abnisa, W. M. A. W. Daud and M. K. Aroua, *Applied Catalysis A: General*, 2017, **541**, 87-106.
97. G. W. Huber and A. Corma, *Angewandte Chemie-International Edition*, 2007, **46**, 7184-7201.
98. I. Hachemi, N. Kumar, P. Mäki-Arvela, J. Roine, M. Peurla, J. Hemming, J. Salonen and D. Y. Murzin, *Journal of Catalysis*, 2017, **347**, 205-221.
99. A. Kiméné, R. Wojcieszak, S. Paul and F. Dumeignil, *Journal of Chemical Technology & Biotechnology*, 2019, **94**, 658-669.
100. L. Hermida, A. Z. Abdullah and A. R. Mohamed, *Renewable and Sustainable Energy Reviews*, 2015, **42**, 1223-1233.
101. J.-G. Na, B. E. Yi, J. N. Kim, K. B. Yi, S.-Y. Park, J.-H. Park, J.-N. Kim and C. H. Ko, *Catalysis Today*, 2010, **156**, 44-48.
102. S. J. Patil and P. D. Vaidya, *Fuel Processing Technology*, 2018, **169**, 142-149.
103. M. Ahmadi, A. Nambo, J. B. Jasinski, P. Ratnasamy and M. A. Carreon, *Catalysis Science & Technology*, 2015, **5**, 380-388.
104. K. K. Rao, M. Gravelle, J. S. Valente and F. Figueras, *Journal of Catalysis*, 1998, **173**, 115-121.
105. I. Sádaba, M. López Granados, A. Riisager and E. Taarning, *Green Chemistry*, 2015, **17**, 4133-4145.
106. K. Kaneda and T. Mizugaki, *Green Chemistry*, 2019, **21**, 1361-1389.
107. M. De bruyn, C. Sener, D. D. Petrolini, D. J. McClelland, J. He, M. R. Ball, Y. Liu, L. Martins, J. A. Dumesic, G. W. Huber and B. M. Weckhuysen, *Green Chemistry*, 2019, **21**, 5000-5007.
108. H. Xia, J. An, M. Hong, S. Xu, L. Zhang and S. Zuo, *Catalysis Today*, 2019, **319**, 113-120.
109. N. An, D. Ainembabazi, C. Reid, K. Samudrala, K. Wilson, A. F. Lee and A. Voutchkova-Kostal, *ChemSusChem*, **n/a**.
110. S. Kumar, M. A. Isaacs, R. Trofimovaite, L. Durndell, C. M. A. Parlett, R. E. Douthwaite, B. Coulson, M. C. R. Cockett, K. Wilson and A. F. Lee, *Applied Catalysis B: Environmental*, 2017, **209**, 394-404.
111. M. A. Isaacs, C. M. A. Parlett, L. J. Durndell, J. C. Manayil, S. K. Beaumont, S. Jiang, N. Hondow, K. Wilson and A. F. Lee, https://doi.org/10.26434/chemrxiv.8248250.v1).