CRITICAL REVIEW
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Biomass valorisation over polyoxometalate-based catalysts
Biomass valorisation over polyoxometalate-based catalysts

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The efficient utilization of biomass, the only globally available, renewable and abundant carbon-neutral source, is of high significance in green and sustainable chemistry. Polyoxometalates (POMs) and POM-based composites have been widely applied in green catalytic reactions, due to their tunable Brønsted/Lewis-acidity and redox properties enabling high reactivity in a wide range of chemical transformations. This review covers recent advances in the chemocatalytic conversion of biomass into chemicals and fuels over POMs and POM–metal composites. For biomass valorisation over POMs, the advances of acid catalysis including hydrolysis, dehydration, etherification, alcoholysis, transesterification and esterification are summarised. Furthermore, applications in chemical oxidation for the synthesis of organic acids and furan chemicals are discussed. For biomass valorisation over metal–POM composites, an overview of tandem reactions (e.g. hydrolysis–hydrogenation, hydrolysis–oxidation, and hydrogenolysis–hydrodeoxygenation) is highlighted. The future prospects of biomass valorisation over POM-based catalysts are finally presented.

1 Introduction

Since the industrial revolution, the ever-increasing consumption of fossil carbon resources including coal, crude oil and natural gas for energy and chemicals has resulted in enormous emissions of greenhouse gases (GHGs) into the atmosphere. The increasing demand for resources, the diminishing finite fossil reserves as well as the urgent need to reduce GHG emissions have driven the innovative development of alternative...
energy sources derived from green and sustainable feedstocks in a post-petroleum era.

Biomass, including carbohydrates, lignin, and lipids, among others, is an attractive alternative feedstock. It is the only globally available, renewable and abundant carbon-neutral source. Due to the relevant debate regarding “food versus fuel”, lignocellulosic biomass composed of non-edible cellulose (35–50%), hemicelluloses (20–35%) and lignin (10–25%) has attracted significant attention. A biorefinery that provides low-value/high-volume liquid fuels and low-volume/high-value chemicals, in particular from lignocellulosic biomass, has been the subject of intense research efforts.1,2

Polyoxometalates (POMs) are a unique class of anionic poly-nuclear metal-oxo clusters with structural diversity at the atomic level, with their negative charge being balanced by counterions. In general, POMs are mainly classified into isopolymolybdates [M2O9]x−, which feature only metal and oxygen atoms [M = typically high-valent (d0 or d1 electronic configuration) group V and VI transition metals (e.g., Mo, W, V)], and heteropolyoxometalates [XM2O12]x−, containing additionally a heteroelement X (e.g., Si and P).3,4 Due to the tunable Brønsted/Lewis-acidity and redox properties, POMs and POM-based composites have long been applied in heterogeneous catalysis.3–5 In the field of catalytic biomass valorisation, POMs have been employed as environmentally benign acid or oxidation catalysts3,4 in the synthesis of renewable chemicals and fuels including platform chemicals,6–8 organic acids, furans,9–11 and biodiesels.12–14 Similarly, metal–POM composites have also been used for biomass conversion into chemicals and fuels.6,15,16

Many excellent reviews on biosourced chemicals and fuels have been published, devoted to specific feedstock such as carbohydrates,1,9,17 cellulose,8,18,19 lignin,20 C5–C6 sugars,21,22 and glycerol,23,24 focusing on specific reactions such as hydrolysis,7,8,25–27 dehydration,21,23 esterification,12–14 oxidation,9,10 hydrogenolysis,24,28 and hydrodeoxygenation,29,30 or dealing with specific catalytic systems such as solid acids,8,14,25,31 metal catalysts,15 functionalised heterogeneous catalysts (e.g., carbon-based catalysts, metal–organic frameworks (MOFs), solid phase ionic liquid based catalysts, and magnetic iron oxide based catalysts).32 An updated and in-depth review on the theme of biomass valorisation over POM-based catalysts, to our knowledge, is not available. The aim of this review is to provide a detailed analysis integrating the state-of-the-art of the chemocatalytic conversion of biomass over POMs and metal–POM composites. While the focus is to show the wide applicability of POM-based catalysts in biorefinery, discussions on the relationship between the catalytic performance and the chemical/electronic/structural properties of the materials, as well as the reaction mechanisms, are also provided. For biomass valorisation over POMs, firstly the advances of acid catalysis including hydrolysis, dehydration, etherification, alcoholysis, transesterification and esterification are examined. Furthermore, applications in chemical oxidation for the synthesis of organic acids and furans are analysed. For biomass valorisation over metal–POM composites, an overview of tandem reactions (e.g. hydrolysis–hydrogenation, hydrolysis–oxidation, and hydrolysis–hydrodeoxygenation) is provided.

2 Properties and preparation of POM-based catalysts

Currently, most studies are focused on the Keggin and Wells–Dawson type of POM. The Keggin anion family is based on the \([\text{XM}_{12}\text{O}_{40}]^{−}\) anion (X = Si, P, etc.; M = Mo, W, etc.), while the Wells–Dawson anion family bears the chemical formula of \([\text{X}_{2}\text{M}_{18}\text{O}_{62}]^{1−}\).4 POMs are versatile catalysts due to the multiple active sites, including protons as Bronsted acids, substituted metals with strong Lewis acidity, or metals with redox properties, and thus they are usually applied in acid-catalysed and oxidation reactions.3 POMs with protons as the only counterions are usually called heteropolyacids (HPAs). Phosphotungstic acid (PTA, \(\text{H}_{3}\text{PW}_{12}\text{O}_{40}\), HPW), silicotungstic acid (STA, \(\text{H}_{4}\text{SiW}_{12}\text{O}_{40}\), HSiW), phosphomolybdic acid (PMA, \(\text{H}_{3}\text{PMo}_{12}\text{O}_{40}\), HPMo) and silicomolybdic acid (SMA, \(\text{H}_{3}\text{SiMo}_{12}\text{O}_{40}\), HSiMo) with strong Bronsted acidity are widely applied in acid catalysis. As for oxidation catalysis, the reported POMs \([\text{X}_{2}\text{M}_{18}\text{O}_{62}]^{1−}\) mainly contain P as the heteroelement X, and a combination of Mo and/or V as metal M.4,9,10

POMs are normally soluble in both water and polar organic solvents; thus inorganic cations (e.g. Cs+, Ag+, etc.) are usually employed as counter-cations to enhance the insolubility of POMs. In addition to inorganic cations, organic compounds with designable and flexible functional groups (e.g., organic amines, quaternary ammonium ions, organic surfactants, and ionic liquid cations) have also been adopted for the solidification of POMs.3,33 Meanwhile, various heterogeneous porous supports including transition metal oxides, clays, carbons, zeolites, mesoporous silicas, polymers, and MOFs, as well as magnetic nanoparticles (NPs) have been adopted for the immobilization of POMs.3,33 A variety of methods such as impreg-
nation, co-precipitation, deposition precipitation, equilibrium adsorption and ion exchange have been developed.\textsuperscript{3,5,12,33} Due to the increased thermal/hydrolytic/oxidative stability, these heterogeneous solidified/imobilised POMs have been widely applied as solid catalysts.\textsuperscript{3,5}

Metal–POM composites, containing both the metal sites (Ru, Au, Pd, Pt, etc.) and POM sites, can be prepared by impregnation, encapsulation, physical mixing and other methods.\textsuperscript{3,15,16} These hybrid materials have also been applied in a variety of one-pot conversions of biomass feedstock in a tandem reaction sequence including the hydrolysis–hydrogenation, hydrolysis–oxidation, and hydrogenolysis–hydrodeoxygenation combinations, owing to the facilitated migration of the substrates/intermediates between the metal sites and POM sites. Since the preparation and characterization of POM-based catalysts have been covered in other excellent reviews,\textsuperscript{3,5,12,33} in this review, the emphasis is on the functionality of POM-based catalysts in biomass transformations.

3 Biomass valorisation into renewable chemicals and fuels over POMs

3.1 Acid catalysis

3.1.1 Hydrolysis, dehydration and related reactions

3.1.1.1 Monosaccharide and derivative synthesis. As the most abundant and valuable component of lignocellulosic biomass, cellulose is a linear biopolymer consisting of glucose units connected through \(\beta\)-1,4-glycosidic bonds. The hydrolysis of cellulose or raw lignocellulosic biomass by acid catalysts leads to the generation of oligosaccharides or monosaccharides such as glucose.\textsuperscript{7,8,26} Further dehydration results in the formation of hydroxymethylfurfural (HMF),\textsuperscript{21,22,34–37} HMF has been widely accepted as an important platform chemical included in the “Top 10 + 4” list revised on the “Top 10” list described by the US Department of Energy (DOE).\textsuperscript{38} The “Top 10 + 4” list also includes other critical platform chemicals such as furfural (FAL), glycerol, levulinic acid (LA), lactic acid, sorbitol, which will be discussed in this review.

So far, multiple POM-based catalysts have been reported for glucose synthesis.\textsuperscript{7,8,26} The representative POMs for fructose production are summarised in Table 1. Mizuno et al. found that highly negatively charged HPAs (e.g., \(\text{H}_2\text{BW}_{12}\text{O}_{40}\), \(\text{H}_2\text{AlW}_{12}\text{O}_{40}\), and \(\text{H}_2\text{GaW}_{12}\text{O}_{40}\), in particular \(\text{H}_2\text{BW}_{12}\text{O}_{40}\), displayed higher activity than other typical HPAs (e.g., HPW and HSiW) for the saccharification of polysaccharides, due to the high acidity and hydrogen-bonding accepting ability to decrease the crystallinity of polysaccharides (Table 1, entry 1).\textsuperscript{39} Wang et al. reported that a micellar HPA catalyst \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\) displayed a remarkable performance in the hydrolysis of polysaccharides (e.g., cellulose and starch), which is attributed to the facilitated access to catalytic sites by polysaccharide molecules, and the enhanced reaction rate and improved mass transport in the micellar catalyst.

| Entry | Substrate     | Solvent         | Catalyst                  | Temp. (°C) | Time (h) | Product     | Conv.% | Sel.% | Yield (%) | Ref. |
|-------|---------------|-----------------|---------------------------|------------|----------|-------------|--------|-------|-----------|------|
| 1     | Cellulose     | \(\text{H}_2\text{O}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 60         | 48       | Glucose    | N/A    | N/A  | 77        | 39   |
| 2     | Cellulose     | \(\text{H}_2\text{O}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 160        | 6        | Glucose    | N/A    | N/A  | 27        | 62   |
| 3     | Starch        | \(\text{H}_2\text{O}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 5        | Glucose    | 96     | 86   | 82        | 40   |
| 4     | Glycogen      | \(\text{H}_2\text{O}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 150        | 4        | Glucose    | N/A    | N/A  | 66        | 41   |
| 5     | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 97     | 94   | 63        | 42   |
| 6     | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 98     | 95   | 64        | 42   |
| 7     | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 98     | 95   | 64        | 42   |
| 8     | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2.7      | HMF        | 97     | 94   | 64        | 42   |
| 9     | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 98     | 95   | 64        | 42   |
| 10    | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 98     | 95   | 64        | 42   |
| 11    | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 98     | 95   | 64        | 42   |
| 12    | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 98     | 95   | 64        | 42   |
| 13    | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 98     | 95   | 64        | 42   |
| 14    | Fructose      | \(\text{DMSO}\)| \([\text{C}_{18}\text{H}_{33}\text{N(CH}_3)_3]\text{H}_2\text{PW}_{12}\text{O}_{40}\)| 120        | 2        | HMF        | 98     | 95   | 64        | 42   |
A variety of POMs have been evaluated for HMF generation. In addition to monophasic systems such as water, organic solvents and ionic liquids, innovative biphasic aqueous/organic systems have also been employed, which efficiently remove the produced HMF from the reactive aqueous phase to the organic phase, thus minimising side reactions. The representative POMs for the hydrolysis of polysaccharides/monosaccharides in monophasic and biphasic systems are summarised in Table 1. Wang and co-workers reported a micellar Brønsted–Lewis-surfactant-combined HPA catalyst Cr[(DS)H2PW12O40]3 (DS represents dodecyl sulfate, H3PW12O40, and H5PW11MO39 (M = Cr, Mn, Fe, Cu)) (Table 1, entries 1–12). The enhanced performance is mainly attributed to the Brønsted and Lewis acidities, as well as the micellar structure with hydrophobic groups. The same authors prepared a series of (HOC2H2CH2N(CH3)3)xH3-xPW12O40 (x = 1, 2 and 3) via choline chloride and Cr2O3, and the highest HMF yield of 75% was achieved over Ch3H2PW12O40 after 8 h at 140 °C (Table 1, entry 15). The hydrophilic head of Ch3H2PW12O40 concentrates the cellulose substrate, while the hydrophobic tail inhibits further hydration of HMF to by-product LA, thus benefitting HMF production. POMs encapsulated in MOFs (e.g. MIL-101) and immobilised on porous supports (e.g. MCM-41) have also been adopted for HMF generation. For instance, Hensen et al. reported PTA/MIL-101–PTA encapsulated in MIL-101 as a composite catalyst to convert sugars. The system achieved the same HMF yield of 63% from fructose in [EMIM]Cl at 80 °C after 1 h (Table 1, entry 17), and in DMSO at 130 °C after 30 min.

Furthermore, various POMs have been evaluated for the production of LA or levulinate ester from carbohydrates in consecutive reactions. Novel temperature-responsive HPA nanohybrids [(CH3)2NCH2CH2OH]xH5−nAlW12O40 (CH3H5−nAlW12O40)46,47 and Ch3H2PW12O40,52 HPA-based ionic liquid catalysts including [PyPs]xPW12O40 [PyPs = 1-(3-sulphopropyl)pyridinium]53 and [C6H5N2(CH3)3SO3H]3−H2PW12O40,55 HPAs with Brønsted and Lewis acidic sites H2PW12O40 (M = CuII, ZnII, CrIII, FeIII, SnIV, TiIV, and ZrIV; for Ti and Zr),54,55 combination of Zr-MCM-41 and HPW catalysts with tuneable Lewis and Bronsted acidity,50 as well as acid–base functional HPA nanospheres (C2H5O2N2)3–H2PW12O4051 were developed. Different reaction media including supercritical methanol, water–methanol mixtures,53 and water–methyl isobutyl ketone (MIBK)52,55 were also explored. For example, Wang and co-workers developed novel temperature-responsive CH3H5–nAlW12O40 catalysts, which dissolve at high temperature and precipitate from the reaction medium at room temperature. Among the tested catalysts, CH3H5AlW12O40 exhibited the highest LA yield of 74.8% with a cellulose conversion of 98.9% in one pot, due to the synergistic effects of the temperature-stimulus, and dual Lewis and Bronsted acidity (Table 1, entry 19).16 As shown in Fig. 1, the Bronsted acid sites are proposed to facilitate hydrolysis, isomerization and dehydration/rehydration pathways, while Lewis acid sites are beneficial for isomerization of glucose to fructose.

### 3.1.1.2 Acrolein synthesis

The significant surge in biodiesel production via transesterification of triglycerides with methanol is accompanied by a substantial increase of glycerol generation as a by-product (ca. 10 wt%). Acrolein synthesis via the dehydration of glycerol is a promising method for glycerol valorisation, as acrolein is an important intermediate for valued-added chemicals such as acrylic acid and amino-acid (L)-methionine. POMs supported on oxides (e.g. titania,73 niobia,74,75 alumina,76,77 silica, alumsilicate,78 and zirconium dioxide77,79) and molecular sieves (MCM-41,80 amino siloxane-functionalised MCM-41,80,81 Zr-MCM-41,82,83 SBA-15,84 and ZSM-585) have been reported for acrolein synthesis from glycerol. For example, Yun et al. prepared the Keggin type H3PW12O40/MCM-41 and Wells–Dawson type H2P2W18O62/MCM-41 for the dehydration of glycerol to acrolein. The selectivity to acrolein increased with the increasing ratio of Bronsted to Lewis acids, while the lower ratio of Bronsted/Lewis acids favoured the production of hydroxycetone as undesired side products.

### 3.1.2 Ethersification and alcoholysis

Ethoxymethylfurfural (EMF) is a potential biofuel alternative due to its high energy density (30.3 MJ L−1) similar to gasoline (31.9 MJ L−1) and diesel (33.6 MJ L−1), as well as lower emission of soot, NOx and SOx. Thus, EMF production from HMF or monosaccharides has attracted much attention. The representative POM catalysts for EMF synthesis via ethersification, and dehydrative ethersification in monophasic and biphasic systems are summarised in Table 2. Chen et al. prepared MOF-based POMs [Cu-BTC/HPM] (NENU-5) (BTC = benzene-1,3,5-tricarboxylate, HPM = phosphomolybdic acid hydrate) for the conversion of HMF to EMF and ethyl levulinate (Fig. 2).87 [Cu-BTC/HPM] consisted of guest molecules of HPM in the pores of the insoluble Cu-BTC host and displayed remarkable catalytic activity and stability. Maximum EMF and ethyl levulinate (EL) yields of 68.4% and 20.2% were obtained at 140 °C after 12 h, respectively (Table 2).
unsaturated chains with chain lengths of 16 and 18 carbons, including stearic, oleic, linolenic and palmitic acids.\textsuperscript{12} For biodiesel production, parameters such as acid strength, structural porosity and surface hydrophobicity exert substantial impact on the catalytic performance.\textsuperscript{12,14} The representative inorganic cation/organo-solidified POMs and POMs supported on metal oxides, clays, zeolites, mesoporous silica, magnetic materials, and MOFs for biodiesel production are summarised in Table 3.

Guo and co-workers prepared novel organic–inorganic hybrid catalysts, HPA and ZrO\textsubscript{2} bifunctionalised organosilicas hollow nanospheres (H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}/ZrO\textsubscript{2}-Et-HNS).\textsuperscript{95} H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}/ZrO\textsubscript{2}-Et-HNS: due to the strong Bronsted and Lewis acidity, unique hollow nanospherical morphology and hydrophobic surface, this material displayed encouraging activity and recyclability for transesterification of yellow horn oil with methanol to biodiesel, as well as esterification of levulinic acid (LA) with methanol to methyl levulinate (discussed in 3.1.3.2). The hollow nanospherical morphology enhanced the accessibility of guest molecules to the acid sites, shortened the diffusion pathway and enhanced the diffusion efficiency. The hydrophobic surface of the hybrid catalysts induced by the incorporation of bridging ethyl groups facilitated the enrichment of the hydrophobic reactant and expulsion of the hydrophilic products, thus accelerating the reaction (Fig. 4).

Li et al. prepared core–shell structured HPW-PGMA-MNPs composed of iron oxide magnetic NPs (MNP) as the core, poly(glycidyl methacrylate) (PGMA) as the shell, and HPW as the surface acid group. HPW-PGMA-MNPs exhibited remarkable activity and good recyclability for the one-pot transformation of waste grease to biodiesel via simultaneous esterification of FFAs and transesterification of TAG with methanol, as a result of the firm attachment of HPW on MNPs via covalent binding, the stable PGMA shell, and the superparamagnetic properties of the MNPs (Fig. 5).\textsuperscript{96}

Shul et al. prepared bifunctional core–shell HPA-functionalised zeolitic imidazolate framework-8 (ZIF-8) NPs via imidazolium medium. The strong O–N bonding indicated the strong interaction between the Keggin structure in HPA and imidazolate units in ZIF-8 NPs. The optimised ZIF-8/HPA with both acidic and basic sites, and large surface areas displayed
notable activity and recyclability for the transesterification of rapeseed oil with methanol to biodiesel (Fig. 6).\textsuperscript{97}

3.1.3.2 Synthesis of levulinate esters. Levulinate esters have potential applications in the fragrance and flavouring industry, as blending agents in biodiesel, \textit{etc}. In particular, ethyl levulinate (EL) is a novel diesel miscible biofuel. Levulinate esters are generally obtained via esterification of levulinic acid (LA), one of the most important platform molecules in the “Top 10 + 4” list mentioned earlier. The typical POM-based catalysts for esterification of levulinic acid to alkyl levulinate are summarised in Table 4.

Guo and co-workers prepared ZrO$_2$-based organic–inorganic hybrid catalysts functionalised by Keggin-type HPA and hydrophobic alkyl groups \textit{i.e.}, benzene-terminally bonded and ethane/benzene-bridged organosilica moieties, H$_5$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Et/Ph)Si and H$_5$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Ph).\textsuperscript{125} H$_5$PW$_{12}$O$_{40}$/

Table 3 Biodiesel production over inorganic cation/organo-solidified POMs and POMs supported on metal oxides, clays, zeolites, mesoporous silica, magnetic materials, and MOFs

| Support          | Catalyst                        | Feedstock                        | Alcohol/feedstock mole ratio | Temp.$^{\text{a}}$ (°C) | Time (h) | Conv.$^{\text{b}}$/yield$^{\text{c}}$ (%) | Ref. |
|------------------|---------------------------------|----------------------------------|-----------------------------|-------------------------|---------|---------------------------------------|------|
|      |                                |                                  |                             |                         |         |                                       |      |
| Inorganic cation | Zn$_{1.2}$H$_{0.8}$PW$_{12}$O$_{40}$ | Waste cooking oil              | 2.5                         | 28                      | 65      | 12/97$^{\text{d}}$                     | 98   |
|      | Cs$_{1.2}$H$_{0.8}$PW$_{12}$O$_{40}$ | Yellow horn oil$^{\text{e}}$   | 1                           | 12                      | 60      | 0.2/96$^{\text{e}}$                    | 99   |
|      | Cs$_{1.2}$H$_{0.8}$PW$_{12}$O$_{40}$ | Jatropha oil                    | 3                           | 25                      | 65      | 0.6/91$^{\text{f}}$                     | 100  |
| Organo-solidified | (C$_2$H$_5$O$_2$N$_2$)$_2$HPW$_{12}$O$_{40}$ | Eruca sativa gars (ESG) oil | 9                           | 9                       | 65      | 12/91$^{\text{g}}$                     | 101  |
|      |                                | [H$_2$CH$_2$COOH]H$_5$PW$_{12}$O$_{40}$ | Palmitic acid               | 6                       | 12      | 90/3/93$^{\text{h}}$                    | 102  |
| Ionic liquid    | [MIM-PSSH]H$_5$PW$_{12}$O$_{40}$ | Palmitic acid                   | 7                           | 13                      | 80      | 5/92$^{\text{i}}$                      | 103  |
| Oxide           | Ta$_2$O$_5$/SiO$_2$[H$_5$PW$_{12}$O$_{40}$/R] [R = Me or Ph] | Soybean oil (20% myristic acid) | 2                           | 90                      | 65      | 24/90$^{\text{j}}$                     | 104–106 |
|      |                                | Oleic acid                      | 10                          | 6                       | 100     | 4/88$^{\text{k}}$                      | 107  |
|      |                                | Used cooking oil                | 3                           | 18                      | 200     | 20/92$^{\text{h}}$                     | 108  |
|      |                                | Palmatic acid                   | 1                           | 14                      | 65      | 4/81$^{\text{h}}$                      | 109  |
|      |                                | Jatropha oil                    | 4                           | 19                      | 65      | 0.8/84$^{\text{h}}$                    | 110  |
|      |                                | Eruca sativa gars oil           | 5                           | 90                      | 65      | 24/75–99$^{\text{h}}$                  | 111  |
|      |                                | Yellow horn oil                 | 5                           | 90                      | 65      | 24/63–76$^{\text{h}}$                  | 95   |
| Clay            | 20%HPW/metaakolin flint        | Oleic acid                      | 5                           | 30                      | 130     | 2/97$^{\text{h}}$                      | 112  |
|      |                                | Oleic acid                      | 5                           | 8                       | 165     | 5/100$^{\text{h}}$                     | 113  |
| Carbon          | H$_5$PW$_{12}$O$_{40}$/ACF      | Palmitic acid                   | 1.4                         | 97                      | 60      | 6/88$^{\text{h}}$                      | 114  |
|      |                                | Jatropha oil$^{\text{d}}$      | 4                           | 20                      | 65      | 0.66/87$^{\text{h}}$                   | 115  |
| Zeolite         | 30%HPW$_{12}$O$_{40}$/Hb        | Oleic acid                      | 0.1                         | 20                      | 60      | 6/84$^{\text{h}}$                      | 116  |
|      | 30%SiW$_{12}$/Hb               | Oleic acid                      | 0.1                         | 20                      | 60      | 10/86$^{\text{h}}$                     | 117  |
| Mesoporous silica | 23%H$_5$PW$_{12}$O$_{40}$/SBA-15 | Oleic acid                      | 0.3                         | 40                      | 40      | 4/90$^{\text{h}}$                      | 118  |
|      |                                | Waste cooking oil              | 0.3                         | 8                       | 65      | 8/86$^{\text{h}}$                      | 119  |
|      |                                | Canola oil                     | 3                           | 26                      | 200     | 6/97$^{\text{h}}$                      | 120  |
|      |                                | Laurie acid                    | 0.1                         | 40                      | 60      | 6/100$^{\text{h}}$                     | 121  |
|      |                                | Oleic acid                     | 0.1                         | 40                      | 65      | 16/81$^{\text{h}}$                     | 123  |
|      |                                | Grease                         | 4                           | 33                      | 122     | 24/98$^{\text{h}}$                     | 96   |
|      |                                | Rapseseed oil                  | 4                           | 10                      | 200     | 2/98$^{\text{h}}$                      | 97   |
|      |                                | Soyabean oil                   | 10                          | 35                      | 110     | 6/96$^{\text{h}}$                      | 124  |

$^{\text{a}}$Temp. = temperature. $^{\text{b}}$Conv. = conversion. $^{\text{c}}$Yield. $^{\text{d}}$Assisted by ultrasonic energy. $^{\text{e}}$Microwave.
ZrO$_2$-Si(Et/Ph)Si and H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Ph) exhibited excellent catalytic activity and stability for the esterification of LA. The authors attributed the superior catalytic performance to the strong Brønsted and Lewis acidity, unique textural properties and the hydrophobic surface that inhibit the strong adsorption of the hydrophilic by-products. In particular, the ordered 2D hexagonal mesostructured H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Ph)Si exhibited higher activity than 3D wormhole-like H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Ph) and H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Et), due to the higher diffusion efficiency in the ordered mesoporous structure (Fig. 7). The same authors developed HPA and ZrO$_2$ bifunctionalised organosilica nanohybrids PW$_{12}$/ZrO$_2$-Si(Et)Si with a 1D hollow tubular nanostructure, a 2D hexagonal periodic mesostructure and a 3D interconnected mesostructure. Among these, HPW and ZrO$_2$-bifunctionalised organosilica nanotubes PW$_{12}$/ZrO$_2$-Si(Et)Si-NTs exhibited the highest activity for alkyl levulinates by LA esterification (Fig. 8).

### 3.2 Oxidation

The carbohydrate feedstock has high oxygen content; thus oxidation into oxygen-containing chemicals or oxygen removal via dehydroxylation, hydrolysis, or hydrodeoxygenation is a convenient pathway. The catalytic oxidation of carbohydrates and their derivatives provide a variety of value-added fine chemicals, including organic acids (e.g. formic acid, glycolic acid, gluconic acid, lactic acid, and acrylic acid), as well as furan chemicals (e.g. 2,5-diformylfuran).

#### 3.2.1 Organic acid synthesis

#### 3.2.1.1 Oxidation of carbohydrates to formic acid. Formic acid (FA) is a versatile chemical finding widespread applications. It is used as a H$_2$ donor in hydrogenation reactions, as well as a hydrogen storage compound in the context of hydrogen economy. Research studies have been focused on sustainable FA generation from oxidation of monosaccharides, oligosaccharides, and bio-polymers such as cellulose, hemicellulose, lignin and even algae, under mild conditions with

### Table 4 Esterification of levulinic acid to alkyl levulinate over POM-based catalysts

| Catalysts | Reaction conditions$^a$ | Conv.$^b$/yield (%) | Ref. |
|-----------|-------------------------|---------------------|-----|
| HPW/desilicated-ZSM-5 | 0.25 wt%/6/78/4 | 94$^b$ | 127 |
| H$_3$SiW$_{12}$O$_{40}$/SiO$_2$ | 0.1 g/50/65/6 | 73 | 128 |
| H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Ph)Si | 2 wt%/7/65/3 | 99.9 | 129 |
| H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Ph)Si-1.0 | 2 wt%/7/65/3 | 99.9 | 125 |
| H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Et) | 2 wt%/7/65/3 | 68 |  |
| H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Si(Ph)-1.0 | 2 wt%/7/65/3 | 72 |  |
| H$_3$PW$_{12}$O$_{40}$/ZrO$_2$-Et-HNS-2.0 | 2 wt%/7/65/1 | 92 | 95 |
| PW$_{12}$/ZrO$_2$-Si(Et)Si-NTs | 2 wt%/7/65/1.5 | 99.9 | 126 |
| [Cu-BTC][HPM] | N/A/N/A/120/6 | >99 | 130 |

$^a$Reaction conditions: Amount of catalyst wt%/molar ratio of alcohol to substrate/reaction temperature in °C/reaction time in h. $^b$Conv. = conversion.
molecular oxygen or air as an oxidant. The oxidative conversion of cellulose includes the hydrolysis of highly polymerised cellulose into glucose over acid sites and the subsequent oxidative C–C bond cleavage of glucose into FA over redox sites, while overoxidation leads to the formation of CO₂ which is the thermodynamically favoured product. Keggin-type phosphovanadomolybdates, H₃₊₊ₙPV₉Mo₁₂−ₙO₄₀ (HPA-n), with n = 0–6, are typical catalysts for the oxidative conversion of biomass to FA (Fig. 9). The representative H₃₊₊ₙPV₉Mo₁₂−ₙO₄₀ (HPA-n) catalysts for the oxidation of carbohydrates to formic acid are summarised in Table 5.

Wasserscheid et al. firstly reported the oxidation of carbohydrate-based biomass to FA over H₃₊₊ₙPV₉Mo₁₂−ₙO₄₀. An FA yield of around 50% with nearly full conversion was obtained from monosaccharides (glucose and xylose) and disaccharides (cellobiose and sucrose) at 80 °C and 3 MPa O₂ after 26 h (Table 5, entry 1). However, water-insoluble cellulose only offered an FA yield of 1% under the same reaction conditions. Wasserscheid et al. further investigated the activity of H₃₊₊ₙPV₉Mo₁₂−ₙO₄₀ (n = 0–6) in selective oxidation of biomass to FA, and found that a higher degree of V-substitution enhanced the catalytic activity. The highest activity was obtained over HPA-5 (Table 5, entry 3), probably due to the formation of pervanadyl (VO²⁺) cations that are known to be a strong oxidative species.

The addition of inorganic or organic acids can further increase the FA yield due to the facilitated hydrolysis of cellulose. Fu et al. reported an FA yield of 34% with full cellulose conversion over HPA-2 combined with HCl at 170 °C and 1 MPa O₂ after 9 h (Table 5, entry 14). Wu et al. reported an FA yield of 61% with 100% cellulose conversion over HPA-2 and H₂SO₄ at 180 °C after 5 min (Table 5, entry 15). Wasserscheid et al. obtained 22% FA from oxidative conversion of cellulose over HPA-2 and p-toluenesulfonic acid (TSA) at 90 °C and 3 MPa O₂ after 66 h. The FA generation over a combination of HPA-2 and p-TSA can be expanded to a wide range of feedstocks including lignocellulose (e.g., xylan, lignin,

Table 5 Oxidation of carbohydrates to formic acid over H₃₊₊ₙPV₉Mo₁₂−ₙO₄₀ (HPA-n)

| Entry | Substrate | Feed conc. (mg mL⁻¹) | Catalyst | Temp. (°C) | O₂ (MPa) | Time (h) | Conv. (%) | Yield (%) | Ref. |
|-------|-----------|----------------------|----------|------------|----------|----------|-----------|-----------|------|
| 1     | Glucose   | 30                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 80        | 3        | 26       | >98       | 47        | 144  |
| 2     | Glucose   | 25                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 100       | 5 (air)  | 3        | 100       | 52        | 136  |
| 3     | Glucose   | 18                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 90        | 3        | 8        | 100       | 60        | 135  |
| 4     | Glucose   | 18                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 90        | 3        | 7        | 100       | 85²      | 141  |
| 5     | Cellobiose| 30                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 80        | 3        | 26       | >98       | 47        | 134  |
| 6     | Glucose   | 72                   | [MIMP₃]HPMo₆VO₄₀ | 180       | 1        | 1        | 100       | 55        | 140  |
| 7     | Sucrose   | 30                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 80        | 3        | 26       | >98       | 48        | 134  |
| 8     | Sucrose   | 34                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 90        | 2        | 48       | 96        | 76²      | 141  |
| 9     | Xylan     | 30                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 80        | 3        | 26       | N/A       | 33        | 134  |
| 10    | Xylan     | 27                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90 | 3 | 24 | 97 | 53 | 138 |
| 11    | Xylan     | 50                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90 | 3 | 24 | 100 | 58 | 135 |
| 12    | Cellobiose| 30                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 80        | 3        | 26       | N/A       | 1         | 134  |
| 13    | Cellobiose| 30                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + HCl | 180       | 0.6      | 3        | 100       | 68        | 144  |
| 14    | Cellobiose| 10                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 170       | 1        | 9        | 100       | 34        | 136  |
| 15    | Cellobiose| 27                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + H₂SO₄ | 180       | 3        | 0.08     | 100       | 61        | 137  |
| 16    | Cellobiose| 27                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90        | 3        | 66       | N/A       | 22        | 139  |
| 17    | Cellobiose| 27                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90        | 3        | 24       | N/A       | 31        | 145  |
| 18    | Cellobiose| 50                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90        | 3        | 24       | 76        | 28        | 135  |
| 19    | Cellobiose| 67                   | [MIMP₃]HPMo₆VO₄₀ | 180       | 1        | 1        | 93        | 51        | 140  |
| 20    | BM cellulose| 10                  | Co₅H₂₀₅Mo₉V₁₂O₄₀ | 160       | 2(O₂ + N₂) | 5       | N/A       | 66        | 146  |
| 21    | Lignin    | 30                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 80        | 3        | 26       | N/A       | 14        | 134  |
| 22    | Lignin    | 27                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90 | 3 | 24 | N/A | 31–32 | 138 and 145 |
| 23    | Lignin    | 50                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90 | 3 | 24 | N/A | 32 | 135 |
| 24    | Poplar sawdust| 30        | H₃₊₊₉PV₉Mo₁₀O₄₀ | 80        | 3        | 26       | N/A       | 19        | 134  |
| 25    | Pomace    | 33                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90 | 3 | 24 | N/A | 55 | 139 |
| 26    | Cane trash| 33                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90 | 3 | 24 | N/A | 49 | 139 |
| 27    | Beech wood| 27                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90 | 3 | 24 | N/A | 35 | 138 |
| 28    | Beech wood| 16                   | H₃₊₊₉PV₉Mo₁₀O₄₀ + p-TSA | 90 | 2 | 48 | N/A | 61² | 141 and 145 |
| 29    | Bagasse   | 10                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 180       | 0.6      | 3        | 100       | 61        | 144  |
| 30    | Hay       | 10                   | H₃₊₊₉PV₉Mo₁₀O₄₀ | 180       | 2        | 3        | 100       | 55        | 144  |

² Feed conc. = feed concentration. ³ Temp. = temperature. ⁴ Conv. = conversion. ⁵ Water : 1-hexanol (1 : 1).
beech wood, pomace, and cane trash), as well as the third-generation biomass (e.g., algae) (Table 5, entries 10, 16, 22, and 25–27).  

Similarly, high FA yields from cellulose, xylan, and lignin were obtained over HPA-5 with p-TSA as an additive (Table 5, entries 11, 18 and 23).

The H⁺ cation in HPA-n can be exchanged by organic compounds and transition metal cations. Liu et al. prepared a series of heteropolyanion-based ILs with PMO11VO40⁻⁴⁻ anions and –SO₃H functionalised cations including –SO₃H functionalised methylimidazolium (MIMPS), –SO₃H functionalised pyridinium (PyPS) and TEAPS.  

The –SO₃H functionalised cations are responsible for cellulose hydrolysis to glucose, while the PMO11VO40⁻⁴⁻ anions catalyze the glucose oxidation to FA. [MIMPS]₃HPMo11VO40 provided the highest FA yield of 51% from cellulose at 180 °C and 1.0 MPa O₂ (Table 5, entry 19).

Novel process technologies such as in situ extraction of FA are adopted to further increase FA yields. Albert et al. reported a water–organic biphasic system to effectively boost the FA selectivity compared with monophasic aqueous media. FA yields of up to 85% and 61% were obtained from glucose and beech wood over HPA-5 in the biphasic system (Table 5 entries 4, 8 and 28). The in situ extraction of FA with long-chain primary alcohols such as 1-hexanol and 1-heptanol prevented the decrease of pH of the aqueous phase, and resulted in a higher FA selectivity and yield.

In addition to Keggin-type POMs, Lindqvist-type isopolyoxometalates [V₆W₆O₃₆]₅⁻ have also been applied in the biomass oxidation to FA. Albert et al. found that K₅V₃W₅O₁₉ selectively oxidised hemicellulose and lignin to FA, while being inactive for cellulose conversion.  

3.2.1.2 Oxidation of carbohydrates to glycolic acid. Glycolic acid (2-hydroxy acetic acid) is an important C₂ α-hydroxy acid used as a precursor for the biodegradable polymer polyglycolic acid.  

The reaction pathway of carbohydrate conversion to glycolic acid is proposed in Fig. 10. Glucose from the hydrolysis of cellulose undergoes multiple retro-aldol reactions to glycolaldehyde, which is converted to glycolic acid through oxidation. Similarly, fructose from glucose isomerization also undergoes successive retro-aldol reactions and oxidation to provide glycolic acid and FA.  

Han et al. reported heteromolybdic acid H₃PMO₁₂O₄₀ exhibiting high activity for one-pot conversion of α-cellulose into glycolic acid. A glycolic acid yield of 49% together with 10% FA were obtained at 180 °C and 0.6 MPa O₂ after 1 h.

3.2.1.3 Oxidation of glycerol to lactic acid. Lactic acid (2-hydroxypropionic acid), as one of the US DOE’s top 10 carbohydrate-derived chemicals, has widespread applications in the food, pharmaceutical and chemical industries such as building blocks of biodegradable plastic polylactic acid.  

The reaction pathway of glycerol conversion to lactic acid is shown in Fig. 11. Glycerol undergoes dehydration/oxidation to form dihydroxyacetone (DHA) in equilibrium with glyceraldehyde (GCA). The pyruvaldehyde (PAL) obtained from the dehydration of DHA further undergoes a benzylid acid-type rearrangement to provide lactic acid. The oxidation of glycerol into lactic acid in water over representative POM-based catalysts is summarised in Table 6.

Wang and co-workers reported H₃PMO₉SO₄₀ (HPMo) with optimal Brunsted acidic and redox properties exhibiting a lactic acid selectivity of 90% at 88% glycerol conversion. HPMO loaded on carbonised willow catkins (HPMo/C) achieved an even higher lactic acid selectivity of 94% at 98% glycerol conversion (Table 6).  

The preparation of HPMO/C catalysts is shown in Fig. 12, including (1) surface oxidation of the carbon support; (2) covalent binding of ethanediamine to the surface carboxylic groups; and (3) functionalization with 1-bromodecane and immobilization of HPMo into a lipid-like layer. The inclusion of HPMo in a lipid-like layer prevents HPMo leaching; thus the HPMo/C exhibits high catalyst stability.

In addition, novel HPMo@lipid(n)/GO catalysts were developed with HPMo embedded in lipid-like bilayers that are covalently bonded to graphene oxide (GO). The coupling of the surface carboxylic groups on functionalised graphene oxide (GO) with diamine provided a covalently linked GO-NH₂ monolayer. Then the functionalisation of the GO-NH₂ monolayer with 1-bromodecane, followed by embedding of HPMo into the lipid-like bilayer, provided HPMO@lipid(n)/GO hybrid materials (Fig. 13). The optimal HPMo@lipid(4)/GO catalyst featured balanced hydrophobic and hydrophilic properties, and the capillary-like microreactor configuration formed by the lipid-like bilayer structure. It achieved a high lactic acid yield of 90% with a glycerol conversion of 97% at 60 °C and 1
MPa O₂ after 3.5 h (Table 6). The capillary reactor of HPMo@lipid(n)/GO enhanced the adsorption of glycerol and oxygen molecules, and concentrated them around HPMo, thus improving glycerol conversion. The oxidative ability of HPMo enhanced by GO and optimised by the length of the alkyl chain, combined with the balanced hydrophobicity of the lipid bilayer and the hydrophilicity of HPMo, led to high selectivity to lactic acid.

3.2.1.4 Dehydration–oxidation of glycerol to acrylic acid. Acrolein and acrylic acid (AA) are critical chemicals derived from glycerol. AA is generally obtained by a two-step tandem reaction including glycerol dehydration to acrolein over a solid acid and subsequent oxidation of acrolein over Mo- and V-based catalysts (Fig. 14). AA synthesis is also realised via a two-step tandem reaction via allyl alcohol as an intermediate. In this context, the direct oxidative dehydration of glycerol to acrylic acid over bifunctional catalysts is highly desired. Zhang et al. reported that the incorporation of vanadium species into CsPMo and CsPW promoted the formation of acrylic acid from glycerol conversion, due to the synergism between the Keggin anions and the cesium/vanadium species at the secondary structure. The combination of Cs(VO)₀.₂PMo and Cs(VO)₀.₂PW as solid solution catalysts changed the oxidation ability and surface acidity, and improved selectivity for acrylic acid. Consequently, H₀.₁Cs₂.₅(VO)₀.₂(PMo₁₂O₄₀)₀.₂₅(PW₁₂O₄₀)₀.₇₅ displayed the highest acrylic acid yield up to 60% and satisfactory resistance to coke deposition.¹⁵³

3.2.2 Synthesis of furan derivatives. Maleic anhydride (MA) is an important precursor for polyester resins, additives, pharmaceuticals, and so on. Yin et al. reported a vanadium-substituted HPA catalyst (H₅PV₂Mo₁₀O₄₀) for the aerobic oxidation of HMF to maleic anhydride (MA).¹⁵⁴ An MA yield of 41.8% and total yields of MA and maleic acid of 50.9% were achieved under optimised conditions (acetonitrile, 90 °C, 10 bar O₂, 8 h). A novel mechanism initialised by the C–C bond cleavage between the hydroxymethyl group and furan sketch of HMF via an ET-OT process, without the formation of 2,5-diformylfuran (DFF), 5-formyl-2-furancarboxylic acid (FFCA), 2,5-furan dicarboxylic acid (FDCA), and 5-hydroxymethyl-2-furancarboxylic acid (HMFC), was proposed for MA formation (Fig. 15).

| Table 6 | Oxidation of glycerol to lactic acid in water over POM-based catalysts |
|---------|------------------------------------------------------------------------|
| Catalysts | Reaction conditions | Yield (%) | Ref. |
| 30%H₃PMo₁₂O₄₀/C | 10/60/5/5 | 92 | 149 |
| AlPMo₁₂O₄₀ | 10/60/10/5 | 85 | 151 |
| Ag₃PMo₁₂O₄₀ | 10/60/10/5 | 93 | 152 |
| H₃PMo₁₂O₄₀@lipid/GO | N/A/60/10/3.5 | 90 | 150 |
| a Reaction conditions: Catalyst amount (mg mL⁻¹)/reaction temperature °C/oxygen pressure bar/reaction time h. |

Fig. 12 Synthetic progress of HPMo-modified carbon catalysts.¹⁴⁹ Reproduced from ref. 149 with permission from WILEY, copyright 2015.

Fig. 13 Synthetic strategy for the assembly of HPMo@lipid(n)/GO hybrid catalyst materials, where n represents the length of the diamine carbon chain (n = 2, 4, 6, 8, and 10).¹⁵⁰ Reproduced from ref. 150 with permission from The Royal Society of Chemistry, copyright 2017.

Fig. 14 Two-step and one-step conversion of glycerol to acrylic acid.¹⁵³ Reproduced from ref. 153 with permission from American Chemical Society, copyright 2016.

4 Biomass valorisation into renewable chemicals and fuels over metal–POM composites

Metal NP–POM composites are referred to either metal NPs supported on heterogenised POMs or both metal NPs and POMs immobilised on an additional support. Such an intimate contact between the metal and POMs has the advantage of facilitated migration of the substrate/intermediates between the metal and acid sites at a nanometer distance. This section...

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describes how metal–POMs can be used in catalytic biorefinery to achieve a one-pot tandem catalytic process. The use of physical mixtures of metal catalysts and POMs as catalysts is also included to provide readers a more comprehensive overview.

4.1 Hydrolysis, hydrogenation and related reactions

4.1.1 Hydrolysis/hydrogenation of polysaccharides. The hydrolysis of polysaccharides (e.g., cellulose and inulin) and disaccharides (e.g., cellobiose) generates monosaccharides. These monosaccharides undergo hydrogenation to yield hexitols (e.g., sorbitol) as important products in the food, cosmetic and pharmaceutical industries. Since the pioneering works from Kou, Liu, and Fukuoka, which proved the feasibility of one-pot reaction combining polysaccharide/disaccharide hydrolysis and monosaccharide hydrogenation, many catalytic systems have been developed. In the context of using metal–POM composites as catalysts, several factors including the substrate concentration, hydrophobicity, acidity of metal–POMs, and size of metal NPs seem to have great impact on the catalytic activity and product selectivity. The hydrogenation activity is sufficiently higher compared with the hydrolysis rate; thus hydrolysis is generally believed to be the rate-determining step.

Sels and co-workers reported the direct combination of H₄SiW₁₂O₄₀/H₃PW₁₂O₄₀, or water-tolerant Cs₂.₅H₂.₅SiW₁₂O₄₀ (CsSiW)/Cs₂.₅H₂.₅PW₁₂O₄₀ (CsPW) with Ru/C to convert cellulose to hexitols. Palkovits et al. adopted physical mixtures of H₄SiW₁₂O₄₀/H₃PW₁₂O₄₀ and Ru/C for the transformation of cellulose and biomass feedstock spruce to sugar alcohols. High yields of C₄–C₆ sugar alcohols up to 81% and 65% were obtained at 160 °C starting from cellulose and spruce, respectively.

Wang and co-workers reported Ru/C₅₃PW₁₂O₄₀ catalysts for the transformation of cellobiose and cellulose into sorbitol. Ru/C₅₃PW₁₂O₄₀ catalysts exhibited full cellobiose conversion, and a high sorbitol yield of 86% at 140 °C. It is proposed that the reversible Bronsted acid sites were generated on the Cs₁₃PW₁₂O₄₀ surface by spillover H species from H₂ dissociation on Ru NPs. However, the surface area and porosity of Cs₁₃PW₁₂O₄₀ are relatively low, leading to inefficient diffusion of the reactant and product.

Chen et al. encapsulated PTA H₅PW₁₂O₄₀ inside the mesoporous cavities of MIL-100(Cr), and developed a Ru-PTA/MIL-100(Cr) catalyst to convert cellulose and cellobiose into sorbitol (Fig. 16). The ratio of the acid site density to the number of Ru surface atoms (n₅₃/Ru₅₃) in the catalytic performance was analysed in detail. The optimum n₅₃/Ru₅₃ values between 8.84 and 12.90 led to the maximum conversion of cellulose and cellobiose into sorbitol. The Ru-PTA/MIL-100(Cr) catalysts with optimal acid/metal ratios exhibited high sorbitol yields of 97.1% and 57.9% at full cellobiose and cellulose conversion, respectively. However, the Ru-PTA/MIL-100(Cr) catalysts suffered from poor reusability, which might have resulted from the adsorption of insoluble substances such as oligomeric products on catalysts.

Isosorbide, a precursor of various biopolymers, pharmaceuticals and other chemicals, is obtained from the combined hydrolytic hydrogenation of cellulose to sorbitol and further dehydration of sorbitol. Sels and co-workers reported such an approach using a physical mixture of H₄SiW₁₂O₄₀ and Ru/C. 52% isosorbide was obtained from purified microcrystalline cellulose, while 63% isosorbide was generated from crude wheat straw pulps obtained by organosolv fractionation.

The hydrolysis of polysaccharides and subsequent hydrogenolysis with C–C and C–O cleavage can provide high value diols such as ethylene glycol (EG) and propylene glycol (PG). For instance, García-Bosch et al. reported a Ru-STA/AC catalyst to achieve a 1,2-PDO yield of 40% and selectivity up to 50% from fructose at 140 °C. Zhang and co-workers reported the combination of RANEY® nickel and W species for EG synthesis. The EG yield increased in the following order: H₃SiW₁₂O₄₀ < H₃PW₁₂O₄₀ < WO₃ < H₂WO₄ (Fig. 17). The W species catalysed the cleavage of the C–C bonds in cellulose by a retro-aldol reaction pathway to generate glycolaldehyde, which undergoes further hydrogenation to form EG.

Similarly, Guerrero-Ruiz et al. adopted Ru NPs supported on an HPA-carbon material [activated carbon (AC), high surface area graphite (HSAG)] for the hydrolytic hydrogenolysis of cellulose to alkanediols. Among the various POMs tested, Ru/AC-HPA and Ru/HSAG-HPA catalysts based on tungsten-based HPA (PTA and STA) exhibited better performance in terms of EG selectivity.
4.1.2 Hydrolysis/hydrogenation of 5-hydroxymethylfurfural/furfural. HMF is obtained from acid-catalysed dehydration of carbohydrates. A variety of fuels and commodity chemicals such as FDCA, DFF, 2,5-dimethylfuran (2,5-DMF) and alkyl levulinate are further produced from HMF. For instance, selective hydrogenation–hydrogenolysis of HMF provided 2,5-DMF (Fig. 17), which is a potential substitute for ethanol and other fossil energy sources. Yadav et al. reported a Pd-Cs2.5H0.5PW12O40/K-10 clay that exhibited 98% conversion of HMF with 81% selectivity to 2,5-DMF under mild reaction conditions (90 °C, 1 MPa H2). H2 was dissociatively adsorbed on Pd sites, and the aldehyde group of HMF was hydrogenated into the hydroxyl group, thus generating bis(hydroxymethyl) furan (BHMF) as an intermediate. Further hydrogenolysis of the hydroxyl groups of BHMF to 2,5-DMF was facilitated by the acid sites of the Cs2.5H0.5PW12O40/K-10 clay. While HMF is a key platform chemical from cellulose, furfural is an important platform molecule derived from hemicellulose for the synthesis of value-added products including furfuryl alcohol (FAL) and alkyl levulinate (AL). Furfural hydrogenation into intermediate FAL and subsequent acid-catalysed alcohololysis of FAL provide AL as an important bio-based fuel additive and a precursor for γ-valerolactone (Fig. 19). The Au-HSiW/ZrO2 catalyst achieved a high AL yield of 80.2% with full furfural conversion at 100 °C. The Au surface sites catalysed the transfer hydrogenation reaction of furfural to FAL using 2-propanol as a H-donor, while the acidic HSiW sites catalysed the alcoholysis of FAL to yield AL. Among HSiW/HPW/HPMo impregnated, ZrO2 supported Au catalysts, a linear relationship between the acidity of Au-HPA/ZrO2 catalysts and AL yield was established.

4.1.3 Hydrogenolysis/dehydration of glycerol to diol/acrolein. The biodiesel production via transesterification of plant oils and animal fats with short chain alcohols generates a large amount of glycerol as a by-product. Thus, the transformation of bioglycerol into value-added chemicals via hydrogenolysis, dehydration, and other reactions is of significance. In particular, the selective hydrogenolysis of glycerol to value-added C3 chemicals including 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), and propanols is promising to valorize the surplus glycerol. The dehydration of glycerol to 3-hydroxypropaldehyde (3-HPA) on Bronsted acid sites followed by subsequent hydrogenation on the metal center lead to the formation of 1,3-PDO. The dehydration of glycerol into acetol over either metal sites or Lewis acid sites and consecutive hydrogenation over metal sites (e.g. Ru and Cu) result in the formation of 1,2-PDO. Propanol is usually formed via 1,2-PDO as an intermediate (Fig. 20). 1,3-PDO has the highest economic value among the three, and functions as a monomer to make polypropylene terephthalate as polyester fibers.

A series of alkaline metals, including Li, K, Rb and Cs, were used to modify the Pt-H4SiW12O40/ZrO2 catalyst. Li+ exhibited the best promotional effect in glycerol hydrogenolysis, providing 53.6% 1,3-PDO selectivity and 43.5% glycerol conversion at 180 °C, 5 MPa (Table 7). A linear relationship between 1,3-PDO yield and concentration of Bronsted acid sites was observed, indicating that the hydrogenolysis of glycerol to 1,3-PDO proceeded via dehydration of glycerol to 3-HPA on
Bronsted acid sites followed by hydrogenation of the dehydration product 3-HPA on nearby metal sites. Furthermore, Pt-HSiW/ZrO\(_2\) exhibited superior performance in glycerol hydrogenolysis to 1,3-propanediol among HSiW, HPW and HPMo modified Pt/ZrO\(_2\) catalysts, due to the higher concentration of Bronsted acid sites. In parallel, a close correlation between the 1,2-PDO yield and the concentration of Lewis acid sites was obtained. Thus, the Bronsted acid sites are proposed to facilitate the selective generation of 1,3-PDO, while the Lewis acid sites favor the generation of 1,2-PDO.

Zhu and co-workers reported that the Pt-H\(_4\)SiW\(_{12}\)O\(_{40}\)/ZrO\(_2\) catalyst afforded a high 1-propanol yield of 80% and long-term stability of 160 h at 200 °C and 5 MPa H\(_2\) (Table 7).\(^{177}\) The Pt-H\(_4\)SiW\(_{12}\)O\(_{40}\)/ZrO\(_2\) catalyst exhibited higher activity and propenol selectivity than its counterparts with Pd, Cu, and Ni as metal sites. ZrO\(_2\) interacts strongly with Pt sites, and prevents the crystallisation of Pt NPs in calcination at high temperatures. The small Pt particle size with high exposure of the Pt active species on the surface resulted in superior activity of Pt-H\(_4\)SiW\(_{12}\)O\(_{40}\)/ZrO\(_2\). The Pt-H\(_4\)SiW\(_{12}\)O\(_{40}\)/ZrO\(_2\) catalysts also displayed high resistance to the impurities in crude glycerol.

Acrolein, an important precursor for the production of adhesives, polymers, and detergents, can be obtained via the dehydration of glycerol over POMs/HPAs. H\(_2\) co-feeding and incorporation of platinum-group metals prevent coking and enhance the catalyst stability.\(^{73,181}\) Pd incorporation showed a larger stability enhancement effect than the incorporation of its Pt and Ru counterparts.\(^{83,182}\) For instance, Pd-H\(_3\)PW\(_{12}\)O\(_{40}\)/Zr-MCM-41 exhibited high catalytic activity and stability, showing a slight decrease of glycerol conversion from 97% to 87% after 50 h.\(^{83}\)

### 4.2 Oxidation of carbohydrates and derivatives

The hydrolysis of cellulose and cellobiose and further oxidation lead to the generation of gluconic acid, an important food additive and intermediate for the synthesis of fine chemicals and pharmaceuticals.\(^{6}\) For metal NP–POM nanocomposites, the acidic sites facilitate the hydrolysis of cellulose and cellobiose to glucose, while the metal (usually Au) NPs facilitate the oxidation of glucose into gluconic acid (Fig. 21). Han et al. reported a Au/Cs\(_x\)HPW\(_{12}\)O\(_{40}\) acidic/oxidative bifunctional catalyst, achieving a high gluconic acid yield of 96.4% with nearly complete cellobiose conversion.\(^{183}\) Cs\(_x\)HPW\(_{12}\)O\(_{40}\) was inert to the deep oxidation of gluconic acid, and passivated the oxidative activity of Au NPs; thus Au/Cs\(_x\)HPW\(_{12}\)O\(_{40}\) nanocomposites effectively prevented over-oxidation of gluconic acid. XPS analysis and DFT calculations demonstrated that the strong metal–support interfacial interaction effectively modulates the electronic structures of Au NPs, and subsequently the reactivity of the active oxygen species on the Au surface, thus resulting in the selective oxidation to gluconic acid. Several Au/Cs\(_x\)H\(_{1-x}\)PW\(_{12}\)O\(_{40}\) catalysts were developed for the same reaction. 97% gluconic acid was attained over Au/Cs\(_{1-x}\)H\(_x\)PW\(_{12}\)O\(_{40}\), which bears stronger acidity and smaller Au NP size compared to other samples, at 145 °C for 3 h.\(^{184}\) Indeed, both the acidity of POMs and mean-size of the Au NPs are crucial parameters in the conversion of cellobiose into gluconic acid. Cs\(_x\)H\(_{1-x}\)PW\(_{12}\)O\(_{40}\) with stronger acidity not only facilitated the conversion of cellobiose, but also accelerated the desorption of gluconic acid and inhibited the consecutive degradation. The Au NPs with smaller size accelerated the oxidation of glucose, leading to high selectivity for gluconic acid.

### 4.3 Hydrodeoxygenation/deoxygenation of biomass-derived oxygenates

Due to the high oxygen content in biomass feedstock, hydrodeoxygenation (HDO) is an effective method to remove (part of) oxygen to convert biomass-derived oxygenates into drop-in bio-fuels and chemicals.\(^{20,29,30}\) The HDO process generally involves a combination of different reactions including hydrosis, hydrogenation, hydrogenolysis, dehydrogenation, decarboxylation and decarbonylation.\(^{29}\) Based on the structures of sub-

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**Table 7** Hydrogenolysis and dehydration of aqueous glycerol over metal NP–POM bifunctional catalysts

| Catalysts                        | H\(_2\) (MPa) | Temp.\(^a\) (°C) | Time (h) | WHSV (h\(^{-1}\)) | Conv.\(^b\) (%) | Sel.\(^c\) (1,2-PD) |
|---------------------------------|--------------|------------------|---------|------------------|----------------|---------------------|
| 5 wt%Ru/C(3 wt%) + 15 wt%PTA/ZrO\(_2\) (6 wt%) | 6            | 180              | 8       | —                | 44             | 64.3                |
| 1 wt%Pt-20 wt%Li\(_2\)H\(_2\)SiW/ZrO\(_2\) | 5            | 180              | —       | 0.09             | 43.5           | 14.2                |
| 2 wt%Pt-15 wt%H\(_2\)SiW\(_2\)O\(_4\)/ZrO\(_2\) | 5            | 180              | 0.09    | 24.1             | 16.5           | 48.1                |
| 2 wt%Pt-15 wt%H\(_2\)SiW\(_2\)O\(_4\)/ZrO\(_2\) | 5            | 200              | 0.05    | 99.7             | 5.1            | 90.0                |
| 2 wt%Pt-15 wt%H\(_4\)PW\(_{12}\)O\(_{40}\)/ZrO\(_2\) | 0.1          | 250              | 1.02    | 98.6             | —              | 97                  |
| 0.5 wt%Pd/Cs\(_x\)H\(_{1-x}\)PW\(_{12}\)O\(_{40}\) | 0.1          | 275              | 2.80    | 79               | —              | 96                  |
| 1 wt%Pd-30 wt%H\(_2\)PW\(_{12}\)O\(_{40}\)/C | 0.1          | 260              | 0.08    | 90               | —              | 70                  |
| 2 wt%Pd-30 wt%H\(_2\)PW\(_{12}\)O\(_{40}\)/Zr-MCM-41 | 0.1          | 320              | 0.35    | 90               | —              | 83                  |

\(^a\) Temp. = temperature. \(^b\) Conv. = conversion. \(^c\) Sel. = selectivity.
strates, the HDO process can be mainly classified into the HDO of ketones, ethers, carboxylic acids, esters, angelica lactones, furanic compounds, carbohydrates, and aromatic compounds.

For the HDO of aliphatic and aromatic ketones, the reaction pathway involves the hydrogenation of ketones to a secondary alcohol on metal sites (mostly Pt) followed by dehydration of the alcohol to alkene on acid sites, and finally hydrogenation of the alkene to alkane on metal sites. Kozhevnikov et al. investigated the gas-phase deoxygenation of aromatic ether anisole, aliphatic diisopropyl ether (DPE), and aliphatic ester ethyl propanoate (EP) over bifunctional catalysts comprising Pt, Ru, Ni, and Cu as the metal components and Cs2.5H0.5PW12O40 as the acid component (Fig. 22). For the HDO of anisole, the model compound of lignin, consecutive hydrogenation of the aromatic ring, elimination of methoxylcyclohexane, and further hydrogenation to cyclohexane can be facilitated by bifunctional catalysts. 0.5% Pt/Cs2.5H0.5PW12O40 achieved a high cyclohexane selectivity of 89% with an anisole conversion of 87% under mild conditions (100 °C and 1 bar of H2), and the physical mixture of Pt/C and Cs2.5H0.5PW12O40 (0.35% Pt content) provided 100% yield of cyclohexane. The Pt/C + Cs2.5H0.5PW12O40 physical mixture displayed higher activity and resistance to deactivation than Pt/Cs2.5H0.5PW12O40. For the deoxygenation of DPE, the combined Pt/C + Cs2.5H0.5PW12O40 catalysts achieved an increased DPE conversion of 99% and a propane selectivity of 93%. Similarly, for the deoxygenation of EP, the Pt/Cs2.5H0.5PW12O40 catalyst under H2 showed much better stability compared with Cs2.5H0.5PW12O40, due to the decreased catalyst coking in the presence of Pt and H2.

Recently, interest in the one-pot HDO of furan derivatives and carbohydrates to alkanes has considerably increased. Zhang et al. reported the first one-pot HDO of high carbon furans (HCFs) and δ-furfurylidenelevulinic acid (FDLA) to long-chain alkanes over Pd/C combined with HPW. The total yield of alkanes as high as 93.2% including an 89.5% yield of decane was obtained under relatively mild conditions (3 MPa H2, 170 °C, 4 h). The consecutive pathways include (a)
the hydrogenation of unsaturated alkenyls, keto-carbonyls and furans of FDLA over metal sites, (b) the formation of a 5-(2-(tetrahydrofuran-2-yl)ethyl)dihydrofuran-2(3H)-one (DC) intermediate via the intramolecular dehydration reaction, (c) the hydrogenolysis and HDO of furans and lactones over metal–acid sites, and (d) the generation of alkanes via HDO of aldehyde/alcohol via hydrogenation-dehydration-hydrogenation steps (Fig. 23).

One-pot conversion of cellulose to n-hexane has also been studied. Sels and co-workers reported the combination of tungstosilicic acid (TSA) and hydrothermally TSA-treated Ru/C (ht-STA-Ru/C) catalysts to convert microcrystalline cellulose into 52% n-hexane in a biphasic decane/water system. The direct conversion of cellulose to straight-chain alkanes mainly proceeded via HMF rather than sorbitol as an intermediate. This is in contrast to the widely accepted pathway, in which hydrolytic hydrogenation of cellulose to sorbitol and consecutive HDO to n-hexane is proposed. The kinetic study indicated that the hydrothermal treatment of Ru/C with TSA effectively enhanced the selectivity towards HMF hydrogenation and suppressed the glucose hydrogenation ability. The cellulose hydrolysis to glucose, dehydration of glucose to HMF, ring opening hydrolysis of 2,5-dimethylfuran (DMF) to 2,5-hexanediol, as well as ring-opening hydrolysis of 2,5-dimethyltetrahydrofuran (2,5-DMTHF) to 2,5-hexanediol were favoured over TSA in the aqueous phase, while the hydrogenation of the intermediates to the straight-chain alkanes was facilitated over ht-STA-Ru/C (Fig. 24).

5 Conclusions and outlook

Recent progress in the chemocatalytic conversion of biomass into chemicals and fuels over POMs and POM–metal composites are summarised. For biomass valorisation over POMs, the advances of acid catalysis and chemical oxidation are discussed. For biomass valorisation over metal–POM composites, an overview of the types of tandem reactions enabled by a metal–POM combination is presented. Despite these encouraging developments, there are still considerable challenges/opportunities ahead for biomass valorisation using POM-based catalysts.

As shown in this review, a variety of methods have been adopted to transform POMs into insoluble solids or immobilize POMs on porous supports so that they can be used as recyclable heterogeneous catalysts. However, leaching still seems to be a common issue, thus compromising the catalyst stability. Future efforts should be directed to the detailed study of the POM–support interaction, and the kinetics and thermodynamics of POM adsorption/desorption on various support materials. Furthermore, new combinations of POMs anchored on emerging porous materials, such as nitrides, carbides, covalent organic frameworks (COFs), and porous organic frameworks (POFs), may be studied.

In addition, most of the reported POMs for biomass utilisation are focused on the Keggin and Wells–Dawson-type POMs, and there is still unexplored potential for application of POMs with other structures (e.g., Lindqvist-type). Due to the tunable Brønsted/Lewis-acidity and redox properties, the POMs are generally applied in acid catalysis and chemical oxidation for biomass valorisation, while POM–metal composites are widely applied in the related tandem reactions. Beyond these, attention can be paid to explore other types of reactions in biomass valorisation over POM-based catalysts. For instance, it is envisaged that tungsten-containing POMs are active for retro-aldol condensation to break C–C linkages in carbohydrates. Metal–POM composites should also be effective in making organonitrogen chemicals, which appears to be a new direction in biomass conversion.

POMs have been proven as effective supports to stabilize a range of single atom catalysts (SACs), exhibiting excellent performance in CO oxidation, selective hydrogenation, and Suzuki–Miyaura coupling reaction. Compared to their NP counterparts, SAC-POMs have maximal atom utilization, together with strong and tunable interactions between single metal atoms and POMs. We put forward SAC-POMs to be potentially efficient catalytic systems to enable both oxidative (e.g., conversion of the –OH group into the –COOH group) and reductive (e.g., C=O hydrogenation and hydrodeoxygenation) transformations of biomass to value-added fine chemicals under mild conditions.

Finally, a deep understanding of the relationship between the catalytic performance and the chemical/electronic/structural properties of the POM-based catalysts will be of significance for biomass utilisation. It is also of high interest to develop a new generation POM-based catalytic system for biomass valorisation in the future. We hope that this review has highlighted the usefulness of POMs in catalytic biorefinery, and will encourage more researchers to delve into this exciting field.

Conflicts of interest

There are no conflicts to declare.

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