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Heteropolycompounds as catalysts for biomass product transformations

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Abstract

In the present review we show a variety of biomass product transformations through catalysis by both bulk and supported heteropolycompounds. The biomass sources considered include carbohydrates, oils and fats, and terpenes as main starting material groups. The products obtained and their applications are presented.

Keywords: Biomass, heteropolycompounds, carbohydrates, fat and oils, terpenes.

Introduction

Since some decades ago, chemical products are produced mainly from fossil resources. As fossil deposits are not renewable on a human civilization timescale, an alternative sustainable source will be required to sustain modern human lifestyle.

Biomass is an abundant and sustainable source of carbon structures that can be considered as valuable starting materials for production of fuels and chemicals. Vegetable biomass is generated from CO_2 and H_2O using sunlight as energy source *via* the process of photosynthesis. From these simple materials, plants produce a large quantity of more complex compounds that include cellulose, hemicellulose, lignin, lipids, sugars and terpenes, among others.

Once researchers have biomass as a potential chemical product source, the key challenge consists in finding some simple, green and economically affordable processes to obtain desirable compounds capable of replacing those that come from petrochemical sources.

Many biomass treatments involve the use of acidic catalysts. For example, the hydrolysis of cellulose is catalyzed by acids such as HCl, H_2SO_4, HF, and organic acids (oxalic, maleic and fumaric)[1]. Other catalysts were tested in order to reduce the generation of waste and allow facile catalyst separation and recycling. In this sense, solid acid catalysts usually represent a better option than liquid acid catalysts.

Catalysis by heteropolycompounds is a strategy used in basic research as well as in industry. They are stable solids that possess very strong acidity and are constituted by polyoxometalates incorporating anions having metal-oxygen octahedron MO_6 as the basic structural units[2], placed around a tetrahedral traditionally containing an element of the principal group, or rarely a transition metal. The heteropolycompounds, principally based on Keggin structure, exhibit the characteristic features of bulk-type catalysis (pseudoliquid bulk-type), in which the reagent molecules are absorbed between the polyanions (rather than in a polyanion) in the ionic crystal by replacing crystallization water or expanding the lattice, and the reaction occurs there[3].

The first heteropolyanion was prepared in 1826 by J. J. Berzelius[4]. It was a yellow solid corresponding to $[PMo_{12}O_{40}]^{-3}$, whose structure was determined by J. F. Keggin employing X-Ray diffraction[5]. Since then, heteropolycompounds with general formula $[XM_{12}O_{40}]^{-n}$ are called Keggin heteropolycompounds, where X corresponds to the central atom ($B^{(III)}$, $Si^{(IV)}$, $Ge^{(IV)}$, $P^{(V)}$, $As^{(V)}$, or transition metals with different oxidation states) and M is the addenda atom ($Mo^{(VI)}$ and $W^{(VI)}$, that could be replaced by other ions such as $V^{(V)}$, $V^{(IV)}$, $V^{(III)}$, $Co^{(III)}$, $Zn^{(II)}$, among many others).

Among heteropolycompounds, there is other well-known structure: the Wells-Dawson one. The first phosphostungstic compound with Wells-Dawson structure was prepared in 1892 by F. Kehrmann. Later, on the mid-twentieth century B. Dawson conducted the first crystallographic study of the above-mentioned material[6]. Since then, heteropolyanions with general formula $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)}$ are called Wells-Dawson heteropolycompounds. They are composed by MO_6 octahedral units (where M is the addenda atom, $Mo^{(VI)}$ and $W^{(VI)}$, that could be replaced by other ions such as $V^{(V)}$, $Fe^{(III)}$, $Ce^{(III)}$, $Cu^{(II)}$, $Ni^{(II)}$, $Co^{(II)}$, $Co^{(III)}$, $Cr^{(III)}$, $Sm^{(III)}$, $Lu^{(III)}$, $Eu^{(III)}$, $Mn^{(II)}$, $Mn^{(III)}$, $Zn^{(II)}$, among many others) that around a central tetrahedral unit in which is placed X (commonly $P^{(V)}$, $As^{(V)}$, $S^{(VI)}$)[7]. The Wells-Dawson structure could be considered as the union of two XM_9O_{39} units with Keggin structure.

It is important to mention a third important heteropolycompound: the Preyssler heteropolyanion. Its structure consists of a cyclic assembly of five XM_6O_{22} units, each one derived from the corresponding Keggin anion by the removal of two sets of three corner-sharing MO_6 octahedra[8]. The heteropolyanion $[NaP_5W_{30}O_{110}]^{-14}$ was first recognized by C. Preyssler in 1970, and it was formed as a byproduct in the preparation of a Dawson heteropolycompound. A complete crystallographic investigation was conducted by M. Alizadeh and collaborators in 1985, and thank to this the correct general formula was found[9,10].

Heteropolycompounds have intrinsic multifunctionality: they can be designed in order to enhance their redox or acidic properties by varying the atoms in their formula. In many cases, they can be used without appreciable loss of the catalytic activity[11]. However, they have low values of specific surface. It is well-known that an increase in the superficial area of a catalyst produces an increase in their catalytic activity. In this sense, several heteropolycompounds have been supported on a variety of substances having high specific surface values (such as silica, active carbon, acidic ion-exchange resins and organic polymers, among many others)[12]. In addition to the increased specific surface, supporting heteropolycompounds offers the possibility of having heterogeneous catalysis, making easier the separation of catalytic material from the reaction system.

The present review focuses on the use of heteropolycompounds as catalysts for biomass transformation to diverse chemical products with different applications. The considered biomass sources have been classified into three main groups: carbohydrates, oils and fats, and terpenes. All catalytic materials mentioned in this review and their corresponding abbreviations are summarized in a ‘Catalytic Materials’ section.

1. Carbohydrates

From a biochemical point of view, a large number of organic molecules such as carbohydrates, fats and oils, phospholipids and glycolipids, waxes, steroids, proteins and nucleotides are produced by living systems. Carbohydrates are the main structural components of the cell walls of plants, in which the carbohydrate polymers, namely cellulose and hemicellulose, are tightly bound to the lignin. Together, these three components form the known 'lignocellulosic biomass', a potential alternative source to produce fuels and chemicals.

Cellulose consists of a skeletal linear polysaccharide in which glucose-based monomer units are jointed together through β-1,4-glycosidic linkages[13]. Based on their different reactivity, it is feasible to separate cellulose and hemicellulose from lignin[14,15].

To produce chemicals and fuels from cellulose, usually requires obtaining the glucose monomer as the first step. In this regard, there are at least two main research routes: one of them focuses on achieving the depolymerization and hydrolysis of cellulose through an effective, low-cost and green protocol, while another directed to integrate the two-or multi-step batch processes into a one-pass continuous conversion by using a well-designed multifunctional catalyst in an efficient and environmentally friendly process[16]. Some studies were conducted in order to evaluate the effect of both Brönsted and Lewis acid sites on the hydrothermal decomposition of cellulose[17,18]. The effects of other factors on this reaction, such as the ionic strength and the adsorption behavior of the catalytic material by cellulose fiber, were also examined[19,20].

Furthermore many research groups are also looking for benign and convenient processes to prepare diverse chemical products from both disaccharide sucrose and the most abundant monosaccharides in nature: glucose, fructose, and xylose.

1.1. Hydrolysis of cellulose and hemicellulose: glucose and xylose production

In nature, there are two main types of sugars: hexoses and pentoses. Among hexoses, the most common monosaccharide is glucose, which may be obtained from cellobiose, cellulose, starch, sucrose, lactose, and natural lignocellulose biomass such as rice plant straw, palm empty fruit bunch (EFB) fiber, and Japanese cedar sawdust, corncob, corn stover and bagasse, among many other possible sources. The preparation process takes place through a hydrolysis reaction usually achieved by using an acid catalyst.

The challenge in this kind of transformation is to have a convenient reaction rate while minimizing side reactions, to have a good yield of the desired monosaccharide.

Tian *et al.* used $H_3PW_{12}O_{40}$ (PW) to catalyze the hydrolysis of cellulose (Figure 1) to glucose under hydrothermal conditions. Results showed a remarkably high yield of glucose (50.5%) and selectivity higher than 90% at 453 K for a reaction time of 2 h, with a mass ratio of cellulose to PW of 0.42[21].

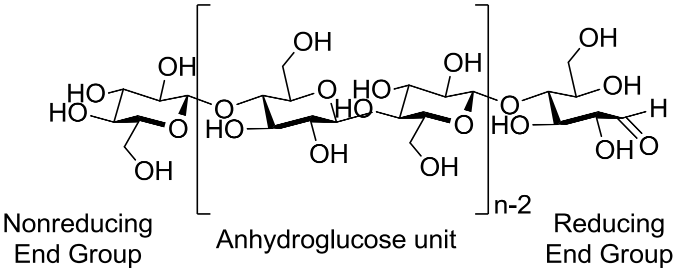


Figure 1. Cellulose structure.

Heteropolyacids PW and $H_4SiW_{12}O_{40}$ (SiW) and their salts of metal cations, whose general formula corresponds to $M_{3/n}PW_{12}O_{40}$ (M^{n+} = Ag^+, Ca^{2+}, Co^{2+}, Y^{3+}, Sn^{4+}, Sc^{3+}, Ru^{3+}, Fe^{3+}, Hf^{4+}, Ga^{3+}, Al^3), were used as catalysts for the hydrolysis of cellulose and lignocellulose to glucose and total reducing sugars (TRS)[22]. Initially, the hydrolysis of cellobiose was attempted by using some Brönsted acids including heteropolyacids and mineral acids. Results after 24 h showed that glucose yield follows the order: PW> SiW > $HClO_4$ > H_2SO_4 > H_3PO_4. Then, the authors tested the activity of salt catalysts and calculated the initial rates for glucose formation. The turnover frequency (TOF) per mole of catalyst was estimated and the highest reaction rates were observed for catalysts with moderate Lewis acidity, such as Sn^{4+}, Sc^{3+}, Ru^{3+}, Fe^{3+}, and Ga^{3+}. They also noted that the catalysts with moderate Lewis acidity show higher TOFs for glucose formation than PW. Regarding cellulose hydrolysis, PW and $Sn_{0.75}PW_{12}O_{40}$ catalysts in a water system at 423 K gave a higher yield of total reducing sugars than H_2SO_4.

Sucrose (α-D-glucopyranosyl β-D-fructofuranoside or β-D-fructofuranosyl α-D-glucopyranoside) is a nonreducing sugar and it is the major disaccharide in most diets. This disaccharide is one of the main carbohydrate feedstocks of low molecular weight to produce chemicals.

Sun *et al.*[23] tested the one-pot depolymerization of cellulose, starch and sucrose into glucose using some heteropolyacid ionic liquids $[C_4H_6N_2(CH_2)_3SO_3H]_{3-n}H_nPW_{12}O_{40}$ ($[MIMPSH]_nH_{3-n}PW_{12}O_{40}$, n= 1, 2, 3, where MIMPSH refers to 1-(3-sulfonic acid) propyl-3-methyl imidazolium) as catalysts in a water-methyl isobutyl ketone (water-MIBK) biphasic system. The cellulose hydrolysis process was efficient using [MIMPSH]$H_2PW_{12}O_{40}$ as catalyst, and the conversion of cellulose and the yield of glucose reached 55.1% and 36.0%, respectively, at 413 K for 5 h. Regarding starch and sucrose depolymerization, they proceeded efficiently at 323 and 363 K, respectively, and when catalyzed by [MIMPSH]$H_2PW_{12}O_{40}$ they gave glucose in high yields (>90%) in both cases (Figure 2).

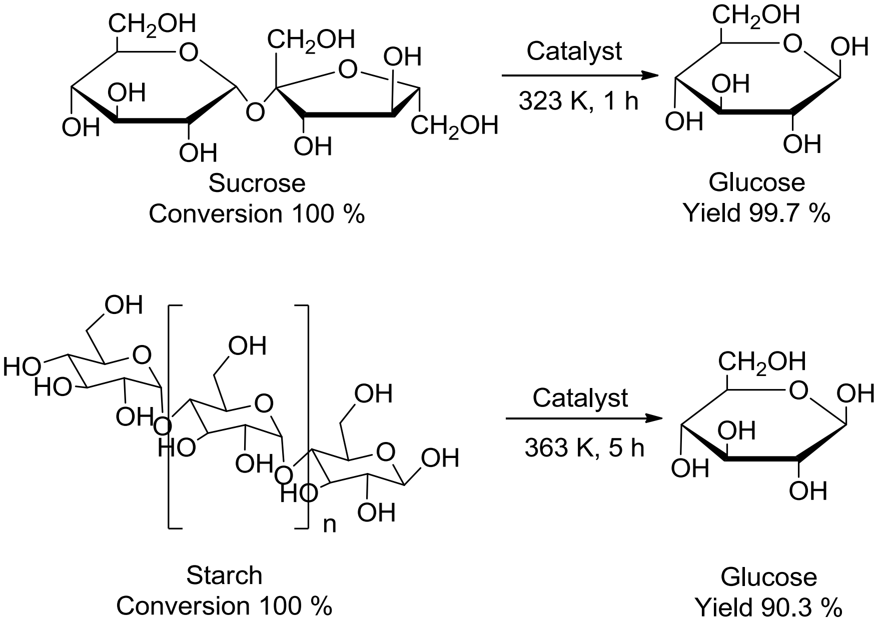


Figure 2. Glucose production from starch and sucrose.

Cheng *et al.*[24,25] have used micellar heteropolyacid catalysts in the transformation of polysaccharides into water-soluble products. In their investigations, they studied the preparation of glucose from sucrose, starch and cellulose using $[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ as catalyst. Glucose yields and selectivity were 82.4 and 85.7%, 39.3 and 89.1%, corresponding to starch and cellulose, respectively. Sucrose conversion into the corresponding monosaccharides reached about 100% in 60 min at 353

K in water. Hydrolysis of cellulose has also been attempted with high surface area solid heteropolyacids. For instance, the selective hydrolysis of microcrystalline cellulose to sugars in an aqueous phase at 433 K for 6 h, using as catalysts a series of insoluble heteropolytungstate cesium salts, $Cs_xH_{3-x}PW_{12}O_{40}$ (Cs_xPW, x = 1.0, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5 and 3.0), was studied by Tian *et al.* [26]. They found that the conversion of cellulose, the yields for TRS and glucose, and selectivity are strongly related to the cesium content, and also to the acidity of the catalyst. CsPW was the material that showed the best catalytic performance, and this was attributed to its strong protonic acidic sites.

Ogasawara *et al.*[27] have studied the saccharification of non-pretreated crystalline cellulose (microcrystalline) catalyzed by SiW, $H_6CoW_{12}O_{40}$, $H_5BW_{12}O_{40}$ (BW), $H_5AlW_{12}O_{40}$, and $H_5GaW_{12}O_{40}$ in a water reaction system at 333 K. All considered materials efficiently catalyze the reaction to obtain glucose (main product) and cellobiose in high yields. The highest total yields of glucose (77%) and cellobiose (5%) were obtained using BW as catalyst. The same reaction system is also useful to produce glucose from cellobiose and starch after 6 h, giving 82% and 85% yield, respectively. Those authors also tested the direct conversion of nonpurified natural lignocellulose biomass. They used three lignocellulose biomass samples: rice plant straw, palm EFB fiber, and Japanese cedar sawdust. The samples used have different contents of holocellulose (cellulose + hemicellulose), lignin, extractives (oil), and ash. In all cases, water-soluble saccharides were obtained as a mixture in high yields (Figure 3).

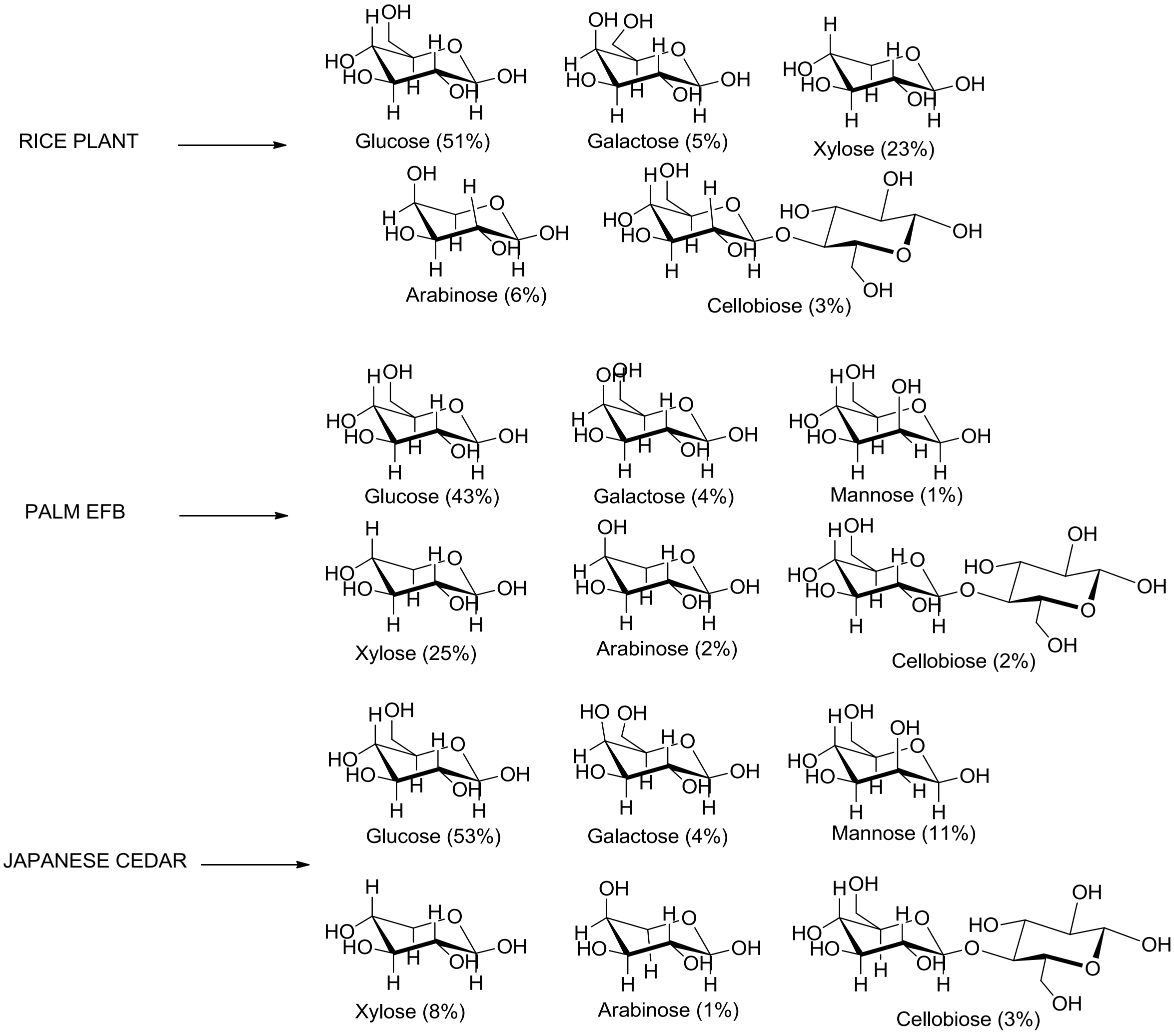


Figure 3. Monosaccharide production from rice plant straw, palm EFB fiber, and Japanese cedar sawdust.

The use of microwave irradiation for cellulose hydrolysis was introduced by Li and coworkers, using PW as catalyst [28].A glucose yield of 75.6% was obtained from cellulose powder pretreated by ball-milling to reduce the size of the crystalline cellulose, working at 363 K for 3 h under microwave irradiation. These researchers also investigated, under the same reaction conditions, the hydrolysis of real lignocellulosic biomass: corncob, corn stover and bagasse. Results indicated that glucose yields were 37.2%, 43.3% and 27.8%, respectively.

Glycogen, a biopolymer of cellulose, was used by Klein and collaborators as starting material for glucose production[29]. In their work, PW and SiW were employed as catalysts and, after 2 h at 373 K, complete conversion into glucose was achieved. The same result was obtained by using microwave irradiation, and preparation of glucose was also achieved through sonication of an aqueous solution.

Similarly to the case of glucose in the family of hexoses, xylose is the most common pentose. Ogasawara *et al.*[27] and reported the synthesis of xylose (yield, 73%) from xylan using BW as catalyst in a water reaction system at 333 K for 3 h (Figure 4).

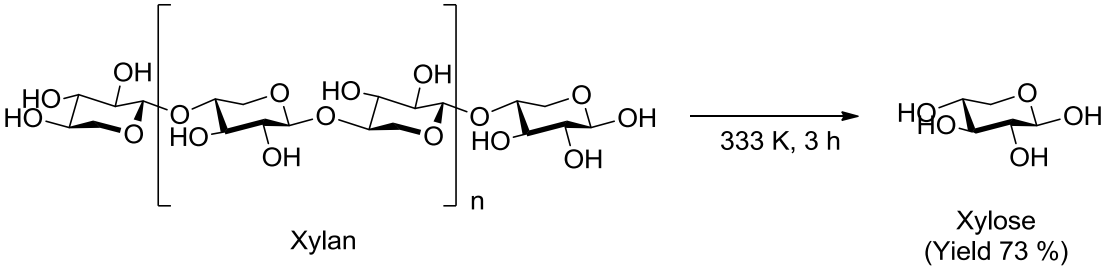


Figure 4. Xylose production from xylan.

1.2. Monosaccharide derivatives

1.2.1. Hexose derivatives

1.2.1.1. Alkyl glycosides production

By the reaction of a sugar with an aliphatic alcohol, some alkyl glycosides are formed, which are used as biodegradable surfactants or chemical intermediates. Glycoside derivatives with surfactant properties could be prepared using fatty alcohols: in this way the sugar is the hydrophilic part and the fatty alcohol, the hydrophobic part. Sugars such as glucose, fructose, mannose, and xylose and several disaccharides (for example, lactose, cellobiose, and maltose) can be used as the hydrophilic section, although glucose is usually the preferred carbohydrate (then, they are named alkyl glucosides)[30].

Methyl and ethyl α,β-glucosides were prepared using cellulose as starting material. Deng and coworkers catalyzed these transformations using PW and SiW in methanol or ethanol medium at 468 and 453 K, respectively. Results showed that it was possible to achieve yields of methyl and ethyl glucosides of 57% and 63%. The authors found that a too high concentration of catalyst, too high temperatures or too long reaction times lead to the transformation of methyl and ethyl glucosides into methyl or ethyl levulinates. Catalytic conversions are summarized in Figure 5[31–33].

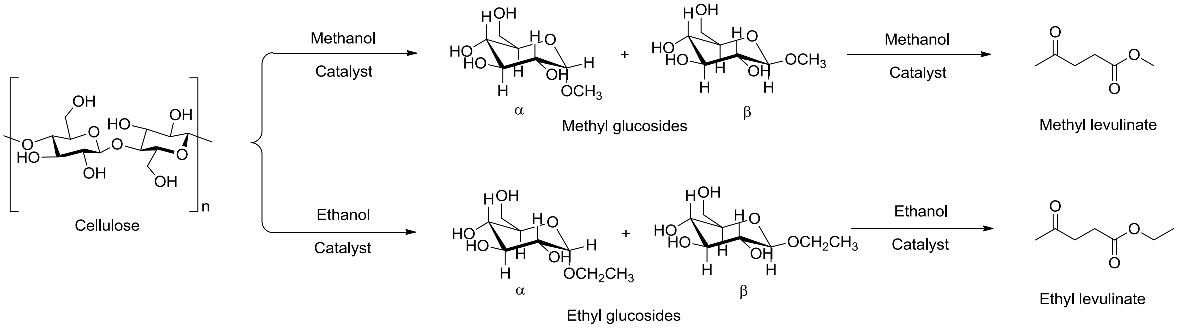


Figure 5. Catalytic conversions from cellulose to alkyl glucosides and then, into alkyl levulinates.

Recently, the direct conversion of cellulose into surfactants by one pot hydrolysis and glucosidation with fatty alcohols in ionic liquid medium has been presented[34–36]. Thus, octyl- α,β-glycosides surfactants were prepared in one pot by employing PW as catalyst in ionic liquid medium starting from cellulose and octanol. Under the optimized reaction conditions and after 1 h of reaction, 74.9% of mass yield of octyl- α,β-glycosides was obtained at almost complete conversion.

1.2.1.2. Mannose production

Mannose is a C-2 epimer of glucose. Epimerization is useful for the production of rare sugars from more common ones and also for the production of some pharmaceuticals[37–39]. Ju *et al.*[40] performed the epimerization of aldoses using $H_3PMo_{12}O_{40}$ (PMo), $Ag_3PMo_{12}O_{40}$ (Ag_3PMo), and $Sn_{0.75}PMo_{12}O_{40}$ as catalysts. First, the authors studied the epimerization of glucose to mannose with the three molybdenum-based heteropolycompounds (Figure 6). In all tested cases, near equilibrium of glucose conversions was obtained and high selectivity values were achieved: greater than 90% after working for 1 h at 353 and 373 K. From this it can be concluded that the cation does not participate in activating the reaction. The pH was varied in the range from 1.1 to 4.5, conditions that produce no significant differences in the results. The researchers also replaced Mo with W in the Keggin structure, which resulted in a loss of activity. The PMo catalyst was also used in the epimerization of xylose and mannose. In both cases, the selected catalyst was highly active and selective to the desired product. Although mannose epimerization was effective, showing that the catalyst is also active in the reverse reaction, the observed reaction rate for this reaction was lower than that for glucose epimerization. The authors published the apparent activation barriers for glucose epimerization using PMo, Ag_3PMo, and $Sn_{0.75}PMo_{12}O_{40}$: their corresponding values were 96 ± 4, 99 ± 4, and 97 ± 3 kJ/mol, respectively.

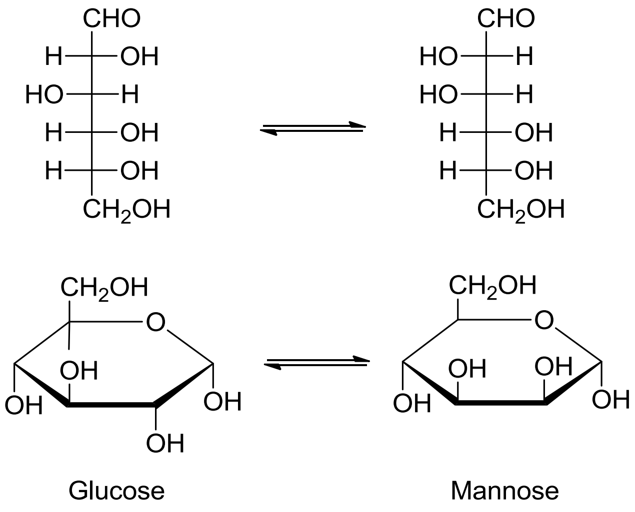


Figure 6. Reversible catalytic epimerization of D-glucose to D-mannose.

1.2.1.3. 5-Hydroxymethylfurfural and derivatives production

5-Hydroxymethylfurfural (HMF) is a versatile and key intermediate[41,42] that can be prepared from biomass through the dehydration of sugars such as the monosaccharides fructose and glucose (Figure 7), the disaccharide sucrose[43] and also from the polysaccharide cellulose[44], among many others[45]. The dehydration process is more efficient and selective to HMF when the process starts from ketohexoses rather than from aldohexoses. Besides, glucose can condense to form oligosaccharides, which can react with HMF, resulting in cross-polymerized materials[46].

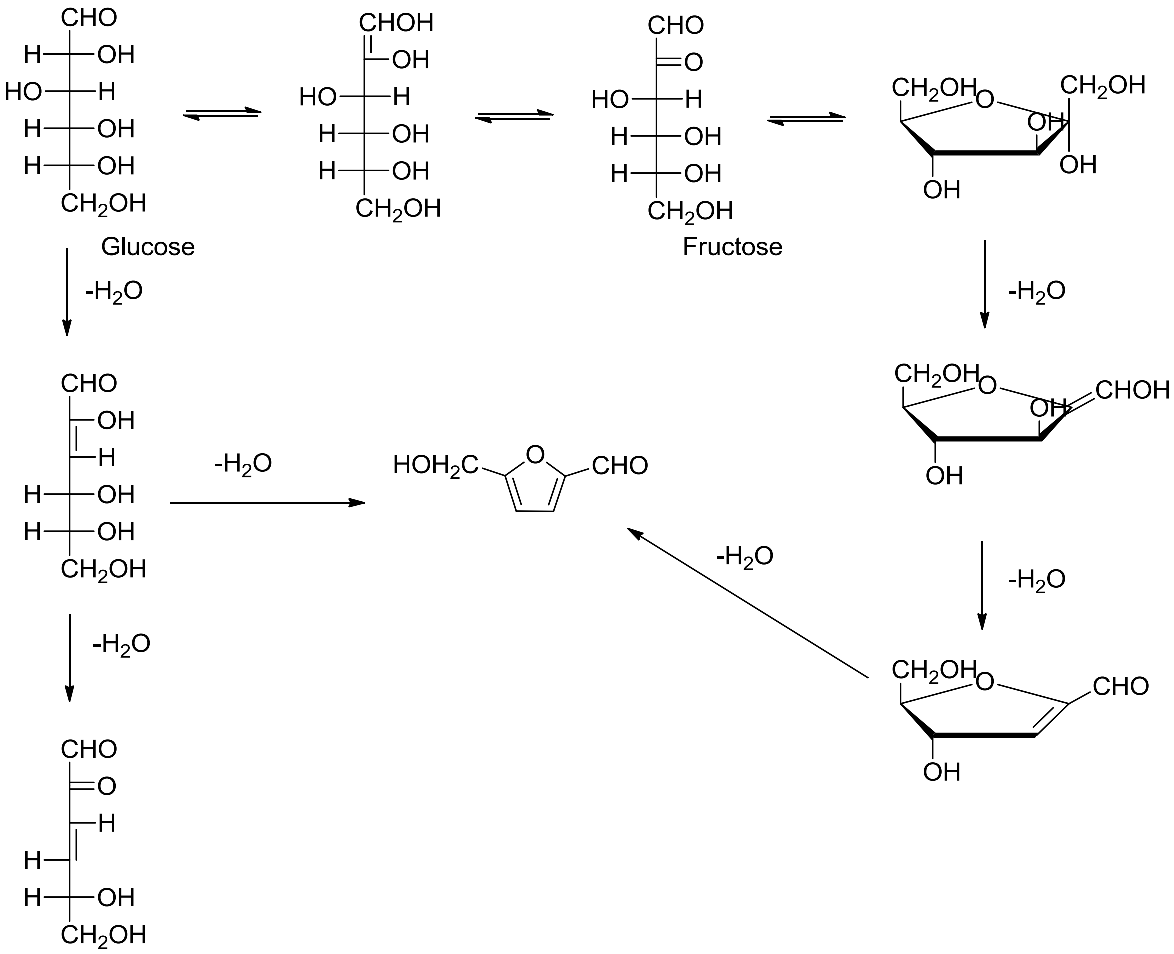


Figure 7. HMF preparation by dehydration of fructose and glucose.

HMF was obtained through the dehydration of glucose in ionic liquids at 393 K for 3 h using different heteropolyacids: PW, PMo, SiW, and 12-molybdosilicic acid ($H_4SiMo_{12}O_{40}$, SiMo)[47]. Both the acidity and activity decrease in the order PW > PMo > SiW > SiMo, while the selectivity order is the following: SiMo > PMo > SiW > PW. By using PW, it is possible to reach 98% conversion of glucose, and a high selectivity to HMF, 99%. A reaction mechanism for the dehydration of glucose to HMF catalyzed by PMo is proposed

(Figure 8). Dehydration of glucose to HMF usually starts from the isomerization of glucopyranose to fructofuranose[48].

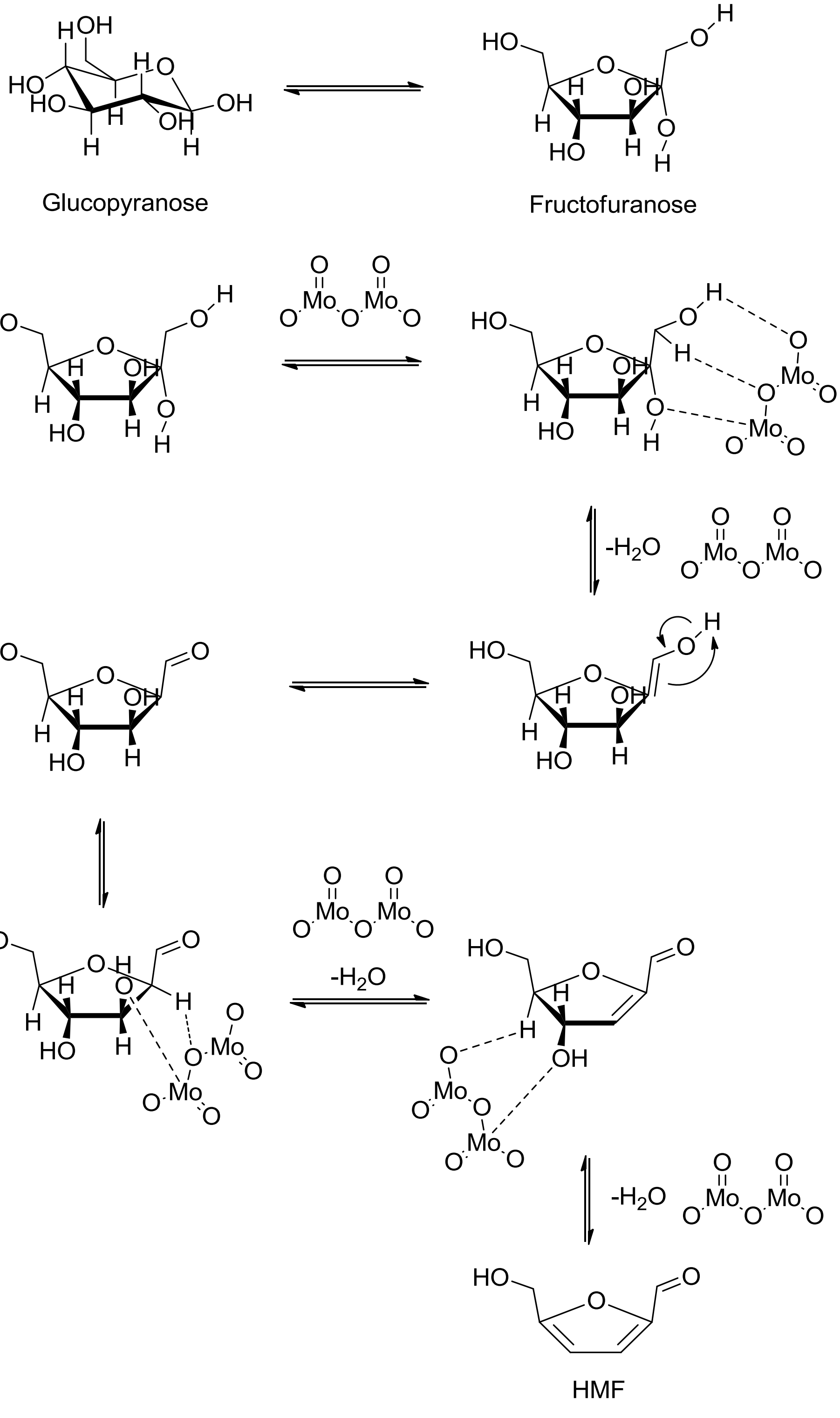


Figure 8. Proposed reaction mechanism for the dehydration of glucose to HMF catalyzed by PMo.

Another process employing ionic liquids for the dehydration of glucose was reported by Hu *et al.*[49]. They combined PW with boric acid, and tested this catalytic system in a [BMIM]Cl medium. In less than 1 h, an HMF yield of 51.9% was achieved working at 413

K. Furthermore, the authors tested the effect of using different reaction solvents, including caprolactam, dimethyl acetylamide, dimethyl formamide, DMSO, and tetraethyl ammonium chloride. Results showed that with all the above-mentioned solvents, the HMF yield was lower than with [BMIM]Cl, except for tetraethyl ammonium chloride, which was found to be a good solvent for the studied reaction.

A Brønsted-Lewis surfactant-combined heteropolyacid catalyst, $Cr[(DS)H_2PW_{12}O_{40}]_3$, where DS represents $OSO_3C_{12}H_{25}$ (dodecyl sulfate), was presented by Zhao *et al.*[50]. This catalytic material was used for the cellulose depolymerization and glucose conversion to HMF in a single process in water at 423 K for 2 h, achieving a HMF yield above 77%. The authors also tested some untreated lignocellulosic biomass sources as starting materials: corn stover and husk of *Xanthoceras Sorbifolia Bunge* (XSB).Working at 423 K for 2 h, 57.3% and 62.5% of dry weight of corn stover and husk of XSB were transformed into HMF, giving yield values of 30.8% and 35.5%, respectively. Another surfactant-combined heteropolyacid catalyst was prepared by Lu *et al.*[51] by employing $(CTA)H_4PW_{11}TiO_{40}$ (CTA, hexadecyltrimethylammonium) HMF yields of 53.7% and 50.8 % for fructose and glucose were obtained in water, and 66.4%, 55.9% and 40.6% for sucrose, cellobiose and cellulose in a biphasic solvent system, respectively. A water-tolerant cetyltrimethyl ammonium salt of Cr(III)-substituted polyoxometalate $C_{16}H_3PW_{11}CrO_{39}$ (C_{16}, cetyltrimethyl ammonium) was also used by Zheng *et al.*[52] for the conversion of fructose and glucose into HMF, obtaining high conversion (90.3% and 84.2%, respectively) and moderate yield (40.6% and 35.2%, respectively) values.

PW supported on SiO_2 was used by Alam and coworkers for HMF production in N, N-dimethylacetamide-LiCl solvent under microwave irradiation. Systems were heated at 393 K for 2 min, and several weed sources were used as starting materials: Indian doab, Water hyacinth, Foxtail and Wild Elephant foot yam. Results showed that the best results were obtained employing Foxtail straw, giving an HMF yield of 32%[53].

As it was previously indicated, HMF preparation from glucose usually starts *via* isomerization of glucose into fructose. This is a more efficient and selective route and therefore a number of researchers have investigated the formation of HMF from fructose. Thus, HMF was also prepared using $Ag_3PW_{12}O_{40}$ (Ag_3PW) as catalyst using fructose as starting material, working at 393 K in a water-MIBK medium for 1 h[54]. HMF prepared from fructose gave yield and selectivity values of 77.7% and 93.8%, respectively. On the other hand when glucose was used, even with some higher temperature (403 K), and longer reaction time (4 h) an HMF yield of 76.3% was obtained, corresponding to a selectivity of 85.3%. Silicotungstic acid exchanged with silver, was tested for the dehydration of fructose and sucrose in superheated water, at 393 K. As a result, 82.7% and 62.5% HMF yields were obtained from fructose and sucrose, respectively[55].

Shimizu and coworkers evaluated the activity of some solid acid catalysts: PW, $FePW_{12}O_{40}$ and $Cs_{2.5}PW$ for fructose dehydration. These three systems achieved a conversion of 100% at 393 K in a reaction time of 2 h, with values of selectivity of 95%, 97% and 91%, respectively. The reaction was typically performed using fructose (1.7 mmol), DMSO (10 g) and a catalyst (0.02 g) under evacuation at 0.97×10^5 Pa[56]. A solid acid catalyst based on $Cs_{2.5}PW$ was also used in a biphasic system consisting of water–MIBK for the dehydration of fructose. The reaction conditions included the use of 2 mL of 30 wt% of fructose solution, 0.128 g of catalyst in 6 mL of MIBK at 298 K for 1 h. Conversion of fructose into HMF was achieved in high selectivity (94.7%) and relatively high yield (74.0%)[57].

Other researchers also used fructose as starting material for HMF preparation and BW as catalyst (3 mol % of fructose). After 4 h in a DMSO medium, at 343 K, HMF was obtained with 89% yield[27]. PW and SiW catalysts, in 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) as reaction solvent gave 99% yield and selectivity of HMF after 5 min at 353 K. In this case, reuses were evaluated and after ten catalytic cycles, HMF yields were almost constant[58].

Different loadings of PW were encapsulated in metal-organic framework (MOF) MIL-101 and tested for the dehydration of carbohydrates in ionic liquids. The HMF yield was 63% and the selectivity was 77% after 0.5 h when working with the best PW (3.0 g)/MIL-101 at 403 K in DMSO using fructose as starting material. In this case, they achieved similar results replacing ionic liquids by DMSO, but the introduced change allowed avoiding proton leaching. On the other hand, it was established that glucose was not converted to an appreciable degree by using the same catalytic material in ionic liquid at 373 K[59].

When a heteropolyacid salt composed of an ionic liquid-forming cation functionalized with a propanesulfonate group, 1-(3-sulfonic acid) propyl-3-methyl imidazolium, and PW ($[MIMPSH]_3PW$) was used as catalyst for the conversion of fructose to HMF a maximum yield of HMF (99.1%) was obtained after 2 h at 393 K, using sec-butanol as solvent. Most interesting, the catalyst could be separated from the reaction mixture at the end of the reaction, and it was reused six times showing no appreciable loss of activity[60].

A supported ionic liquid catalyst, Poly(1-vinyl-3-propane sulfonate imidazolium)-PW (poly(VMPS)-PW), was prepared and used for HMF preparation from both glucose and fructose. HMF yield values were 83% and 26% using fructose and glucose as starting materials, respectively[61].

A series of acid-base bifunctional PW heteropolyacids ($(C_6H_{15}O_2N_2)_xH_{3-x}PW_{12}O_{40}$, Ly_xPW) were designed by Zhao and collaborators using different ratios of PW with the amino acid lysine in order to control their acid/base properties. Those materials were employed in the dehydration of fructose to HMF using choline chloride as solvent at 383 K. After 1 min of subjecting Ly_2PW to the above-mentioned reaction conditions, an HMF yield greater than 92% was obtained. Since the rate-determining step of fructose dehydration is the enolisation of fructose, Ly_2HPW bearing protons and NH_2 groups can produce the concerted activation of fructose at the C−OH bond of the anomeric cation by the proton and at the C−H of C1 of the fructose via hydrogen bonding by N, facilitating the conversion of fructose to HMF[62].

2,5-Diformylfuran

2,5-Furandicarboxaldehyde, or 2,5-diformylfuran (DFF), is a versatile compound commonly used due to its applications as a monomer, a starting material for the synthesis of some pharmaceuticals and antifungal agents, for the preparation of furan–urea resins and functional polymers, and also as a component for foundry sand binders, among many others[63,64]. One of most widely employed route to DFF preparation consists in the oxidation of HMF, which is prepared by the dehydration of sugars.

The one-pot conversion of fructose to DFF was studied employing $H_4PMo_{11}VO_{40}$ ($PMo_{11}V$), $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$), $H_4PW_{11}VO_{40}$ ($PW_{11}V$), PMo and $H_5SiMo_{11}VO_{40}$ ($SiMo_{11}V$) as catalysts[65]. Among them, PMo presented the highest catalytic activity towards DFF conversion from fructose. The authors expanded their study by using inulin, glucose and sucrose as starting materials, and established a DFF yield order according to the reactant used: fructose > inulin > sucrose > glucose. Finally, although PMo presented good catalytic activity, the authors decided to prepare some heterogeneous materials replacing protons with Cs atoms and $Cs_{2.5}PMo$, gave a 69.3% DFF yield after 2 h at 433 K in DMSO. Trying to combine acidity and redox properties a series of acidic cesium salts of molybdovanadophosphoric heteropolyacids ($Cs_xH_{3-x}PVMo_{11}O_{40,-}Cs_xPVMo$) were used as catalyst for the one pot reaction[66] (Figure 9). The catalyst combined adequate acid site density for the acid-promoted fructose dehydration and certain vanadium content (for the metal-promoted aerobic oxidation of HMF). Those properties could be adjusted by varying cesium and vanadium contents in the Cs_xPVMo heteropolycompound. In this sense, the authors defined a parameter referred to the ratio of acid site density to the molar concentration of vanadium (nH/nV) for studying a large series of catalysts. Then, Cs_3PVMo, with an nH/nV ratio of 2.56, is considerably more active and selective to afford the one-pot reaction with a DFF yield greater than 60% (based on the fructose used). Moreover, the above-mentioned catalyst can be recycled at least four times with a minimum loss of activity.

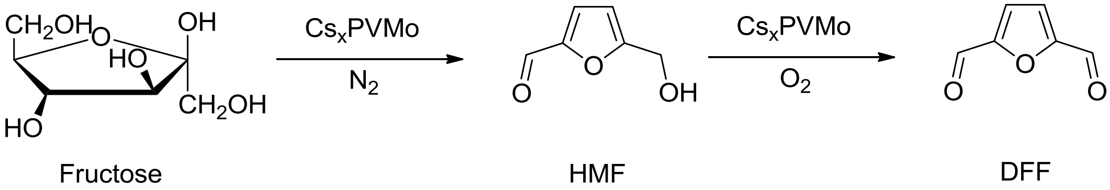


Figure 9. Preparation of DFF from fructose.

5-Ethoxymethylfurfural

5-Ethoxymethylfurfural (EMF), a liquid with a boiling point of 508 K, is proposed to be one of the potential liquid biofuels due to its high energy density (8.7 kWh/L), substantially higher than that of ethanol (6.1 kWh/L), and comparable to that of standard gasoline (8.8 kWh/L) and diesel fuel (9.7 kWh/L)[67]. Then, EMF has been prepared from fructose by a one-pot reaction using a SO_3H-functionalized polymer including PW in its structure (poly(VMPS)-PW), in ethanol at 383 K for 10 h (Figure 10). EMF yield was higher than 70%, and after five catalytic cycles there was a low loss of activity[68].

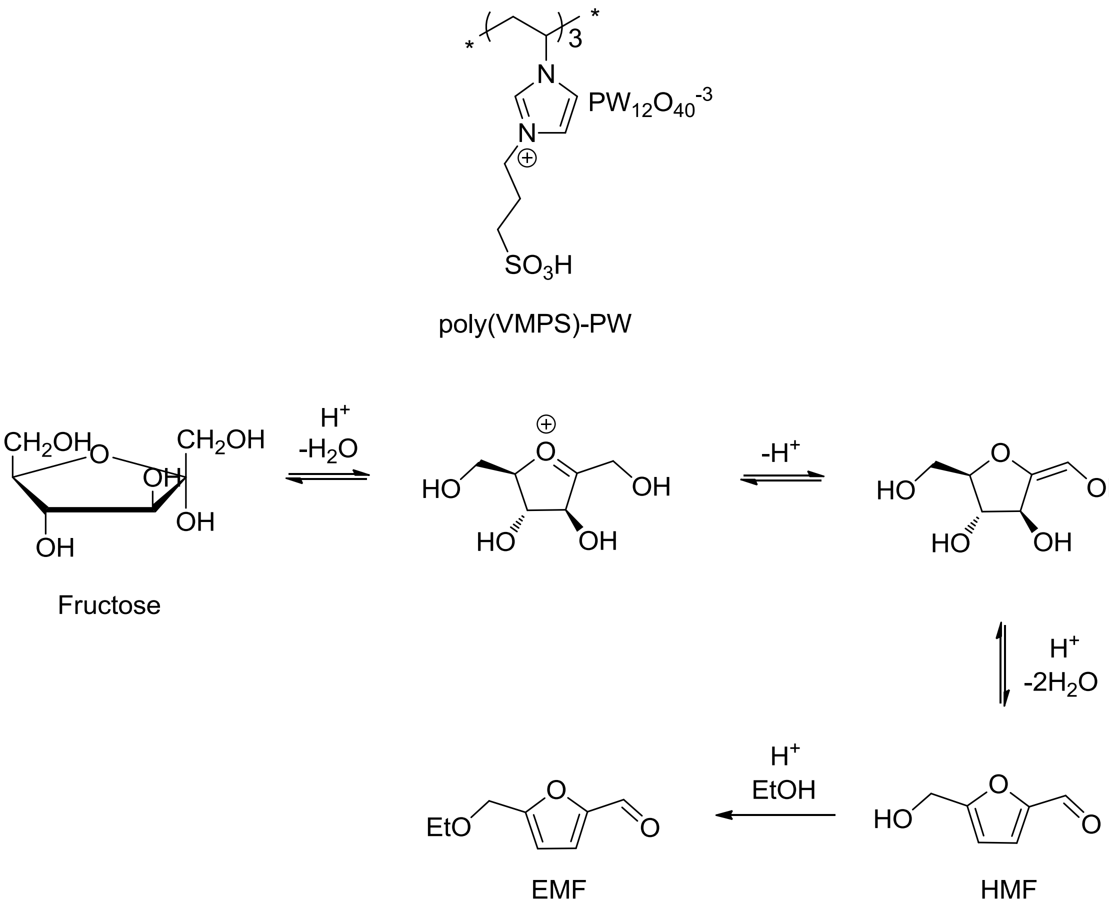


Figure 10. 5-Ethoxymethylfurfural (EMF) preparation from fructose.

Another efficient process for the dehydration of fructose into HMF and then etherification of HMF into EMF has been developed in a one-pot process using ethanol-DMSO as solvent and catalyzed by PW as catalyst at 413 K. Both HMF and ethyl levulinate are obtained as by-products, and they can be easily separated from the reaction system and used as excellent fuel additives. The yield of the desired product was 64% under the optimized reaction conditions[69].

EMF has been prepared from fructose, sucrose, and inulin with PW as catalyst[70].A ratio of THF: ethanol (3: 5, v/v) at 403 K under microwave heating, gave 76% EMF yield from fructose. The authors observed that the fructose moiety in sucrose and inulin was converted to EMF selectively, but the glucose moieties cannot be converted into EMF.

As in previous reactions, heteropolyacids have been supported on different carriers or in the form of hybrid materials for the synthesis of EMF. Thus, highly dispersed SiW/MCM-41 nanospheres were prepared by SiW precursor impregnation on MCM-41 silica nanospheres and used in the etherification of the hydroxyl group of HMF in the presence of anhydrous ethanol as reactant and solvent, at 363 K for 4 h under a nitrogen atmosphere. The best catalytic results in the EMF preparation were obtained with 40% SiW/MCM-41, and after five catalytic cycles its activity was almost constant[71].

The synthesis of EMF through the etherification of HMF and the dehydrative etherification of fructose was also studied by supporting PW on K-10 clay. Working in an ethanol medium at 373 K, the 30 wt% PW/ K-10 clay material was found to have the highest catalytic activity, achieving an EMF yield of 91.5% after 10 h using HMF as the starting reactant. Although the use of bulk PW presented higher HMF conversion and EMF yield values, the use of the heterogeneous 30 wt% PW/ K-10 clay material demonstrated several advantages such as the recycling possibility and also an easier product separation. When fructose was used as starting material, an EMF yield of 61.5% was obtained[72].

Bing, *et al.*[73] performed the direct conversion of fructose into EMF catalyzed by an organic-inorganic hybrid solid catalyst [methylimidazolebutylsulfate]$_3$PW$_{12}$O$_{40}$ ([MIMBS]$_3$PW). As a first step, the authors studied the etherification of HMF with ethanol and found that by using [MIMBS]$_3$PW as catalyst at 343 K, the EMF yield was 90.7%, corresponding to an HMF conversion of 98.1%. Two control experiments were done using the precursors of the prepared catalyst, PW and MIMBS. Although a relatively high yield of EMF was obtained using PW (85.3% yield corresponding to a 100% conversion value), the catalyst had a weak aspect: it was soluble in the reaction mixture. When the neutral salt MIMBS was used, almost no HMF was converted into EMF. Then, when studying the one-pot dehydrative etherification of fructose into EMF, it could be seen that at 343 K, the desired process was not favored and at 383 K, the system was favored but promoted side reactions. Working at 363 K, a high EMF yield of 90.5% was obtained from fructose after 24 h. The catalytic activity of [MIMBS]$_3$PW was tested, and it was found that after six catalytic runs, EMF yields remained at around 90%.

1.2.1.4. Gluconic acid production

D-Gluconic acid and its salts are important building blocks for the food industry, and they also have pharmaceutical applications (sodium gluconate is widely used as a chelating agent)[30]. Thus, An *et al.*[74] prepared gold nanoparticles loaded onto Keggin-type insoluble polyoxometalates such as Cs$_x$PW and used them for the direct conversion of cellobiose and cellulose into gluconic acid in water by combining hydrolysis and oxidation reactions (Figure 11). Working at 418 K for 3 h, cellobiose conversion and gluconic acid selectivity values were greater than or equal to 95% for materials with low cesium contents (x= 1.2, 1.7 and 2.2). A further increase in cesium content causes a decrease in the obtained conversion and selectivity. According to the characterization results, a stronger material acidity favored both the activity and the selectivity for the conversion of cellobiose into gluconic acid. The authors also studied the effect of the size of Au nanoparticles on the oxidation of cellobiose and glucose into gluconic acid preparing catalytic materials with a mean Au size between 2.5 and 20 nm. It was found that as the Au nanoparticle size decreases, cellobiose conversion and gluconic acid selectivity increase. As to glucose conversion, selectivity was greater than 99% with each tested catalyst. The TOF, i.e. the moles of glucose converted per unit of time at the initial stage per mole of surface Au atoms, was also calculated. Those materials with a smaller Au nanoparticle size exhibited higher TOFs for the desired oxidation reaction.

In the case of cellulose conversion into gluconic acid, the Au/Cs_xPW system undergoes serious deactivation during repeated use. This problem was solved by using Au/Cs_3PW in combination with PW: working at 418 K and using both ball-milled cellulose and microcrystalline cellulose as starting materials, gluconic acid yields were 85% and 39%, respectively. The combined catalytic material could be recovered and used repeatedly

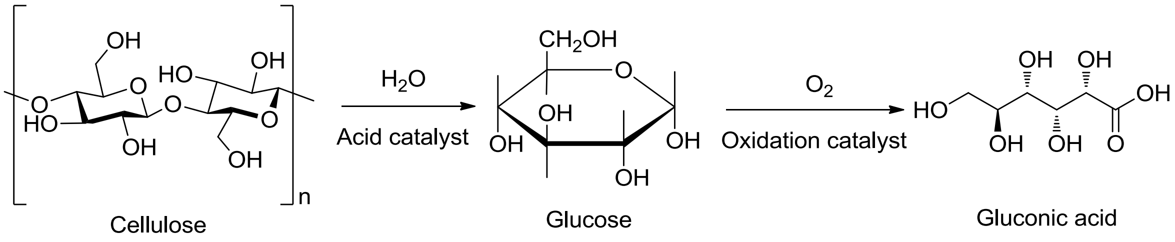


Figure 11. Conversion of cellulose into gluconic acid.

Previously, a Au/Cs_2PW system was used as catalyst for gluconic acid preparation by Zhang and coworkers. They achieved complete conversion of cellobiose into gluconic acid in water with excellent selectivity values working at 418 K for 3 h. The authors concluded that the Cs_2PW support provides solid acid sites for hydrolysis and also modulates Au redox sites for selective oxidation. The Cs_2PW support also works as a heterogeneous supporting material for Au nanoparticles, which allows the catalytic material to be easily recycled and reused[75].

1.2.1.5. Glucuronic acid and its esters production

Glucuronic acid derivatives have several known applications, such as their ability to act as surface-active compounds and bioactive molecules[76].

Glucuronic acid may be obtained as a reaction product from the catalytic oxidation of cellobiose in the presence of molecular oxygen. Thus, Shatalov *et al.*[77] obtained glucuronic acid, among many other products, by employing several molybdophosphate heteropolyanions, whose general formula corresponds to $[PMo_{12-n}V_nO_{40}]^{-(3+n)}$, as catalysts. By working with $[PMo_7V_5O_{40}]^{-8}$ at 263 K in the presence of O_2 for 2 h, a glucuronic acid yield of 41.7% was achieved, while the glucuronic acid lactone yield was 11.4%. The preparation glucuronic acid esters was performed by Bosco *et al.*[76]**¡Error! Marcador no definido.** starting from 2,3,4-tri-O-acetyl-D-glucopyranurono-6,1-lactone, and using $[\alpha_1\text{-}M(H_2O)_4P_2W_{17}O_{61}]^{-n}$ (M= Yb^{III}, n= 7, Hf^{IV} and Zr^{IV}, n= 6) Dawson-type as catalysts under microwave irradiation. It was found that while reactions carried out with glucuronic acid usually give esterified-glucosylated derivatives, when starting from 6,1-lactone derivatives, esterified products with a free anomeric hydroxyl group were selectively produced (Figure 12).

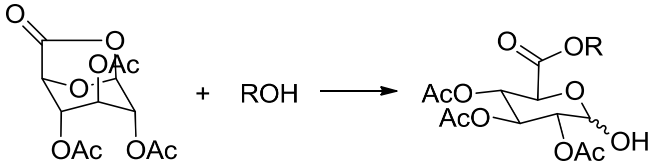


Figure 12. Glucuronic acid esters from 2,3,4-tri-O-acetyl-D-glucopyranurono-6,1-lactone.

1.2.1.6. Levulinic acid and derivatives production

Levulinic acid (LA) is useful as a solvent, food flavoring agent, and it is also considered a promising source of organic intermediates with high reactive carbonyl and carboxyl groups that can be transformed into value-added chemicals. LA has been reported as a platform chemical for the production of potential resins, plasticizers, animal feed, coating materials, antifreeze chemicals[30], pharmaceuticals products, fuels, herbicides, polymers, food, flavouring and fragrance components and solvents[78].

As it was done before for other compounds heteropolyacid-ionic liquids of general formula $[MIMPSH]_nH_{3-n}PW_{12}O_{40}$ (n= 1, 2, 3), have also been tested as catalysts for the one-pot depolymerization of cellulose and starch into LA in a water-MIBK biphasic system (Figure 13). The best results were obtained with $[MIMPSH]H_2PW_{12}O_{40}$, achieving yields of 63.1% and 48.7% after 12 and 5 h, respectively. The catalyst could be completely separated and recovered from the reaction mixture [23,79].

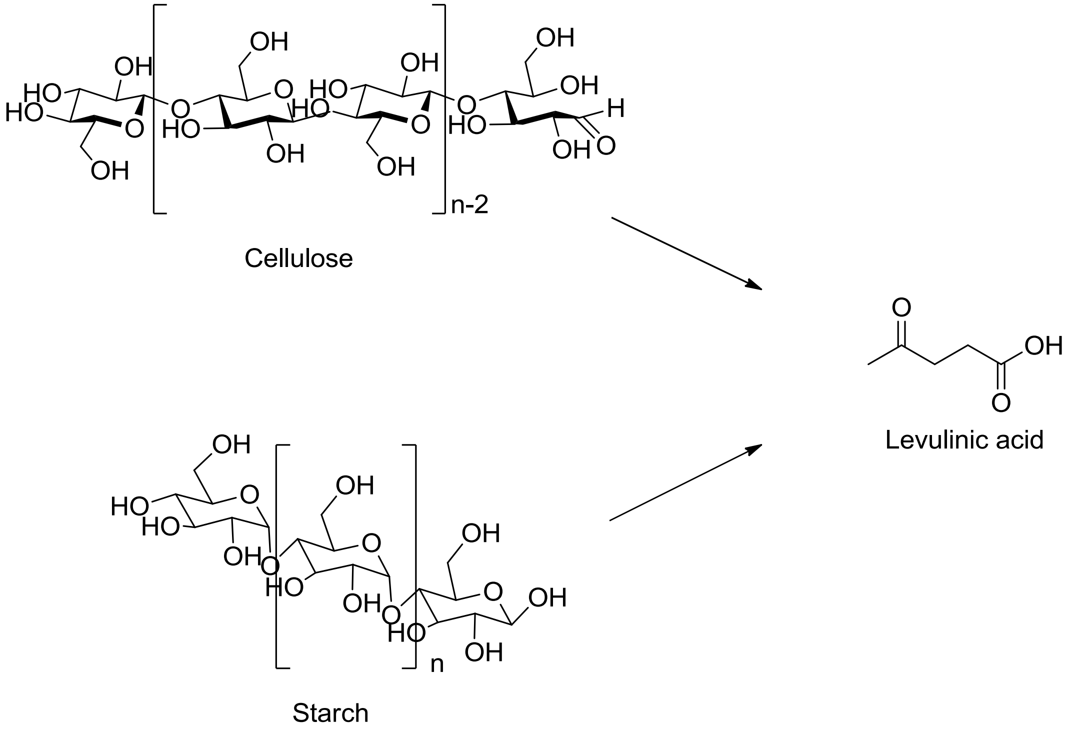


Figure 13. One-pot depolymerization of cellulose and starch into LA.

The process should be easier starting from glucose, and a series of metal-modified salt catalysts $M_xH_{3-2x}PW_{12}O_{40}$ (M_xPW, M= Zn, Cu, Cs, Ag) were prepared to study the production of LA from glucose. The best results were obtained employing Ag_3PW as catalyst with a yield of 81.61% under the optimal reaction conditions (temperature, 473 K; reaction time, 2 h; catalyst dosage, 0.9 g; and glucose concentration, 40g/L)[80,81].

Taking into account the good results obtained using ionic liquids, ionic solid nanomaterials have also been prepared and used for LA production from glucose[82]. They were prepared by using butylmethylimidazolium bromide ([BMIM][Br]) ionic liquid as cation, and three heteropolyacids, PW, PMo and SiW, as anion. The three materials were: $[BMIM]_3PW$, $[BMIM]_3PMo$ and $[BMIM]_4SiW$. Reactions took place in water at 443 K, and results showed that the best results were achieved using $[BMIM]_3PMo$ with glucose conversion, LA and HMF yield values were 60.5%, 22.4% and 5.8%, respectively, values that are much lower than those presented before using heteropolyacid-ionic liquid in a biphasic water-MIBK system.

Levulinate esters

By acid treatment of lignocellulosic biomass, it is possible to obtain LA and, from it, several levulinic esters may be prepared. Various levulinic esters may be used as gasoline and biodiesel additives because of the nontoxicity, high lubricity, flashpoint stability, and superior flow properties under cold conditions[83]. There is also one example of a levulinic ester (*n*-butyl-levulinate) used as plasticizing agent, solvent and odorous substance[84].

The one-pot dissolution-conversion of microcrystalline cellulose into methyl-levulinate has been attempted by working in supercritical methanol and methanol-H_2O (90/10) mixtures[85,86]. Under supercritical conditions (573 K/10 MPa/1 min) and in the absence of catalyst, relative low amounts of value-added chemicals were obtained. However, by working at the same reaction conditions and in the presence of solid acid catalysts such as $Cs_{2.5}PW$ and $Cs_{2.0}PW$, the formation of methyl-levulinate took place giving yields close to 20%. Other products such as methyl-lactate, methyl-acetate, HMF and succinic acid dimethyl ester were also produced in low amounts. The performance of $Cs_{2.5}PW$ for the desired product formation was slightly higher than that of $Cs_{2.0}PW$. The key factors for levulinate production from cellulose are the strength and the accessibility of soluble oligosaccharides to strong acid sites. Therefore the solubilization of cellulose in supercritical methanol-H_2O (90/10) was critical in this case for a successful process.

Furfuryl alcohol was also used as starting material for the preparation of alkyl levulinates using an organic-inorganic hybrid solid acid catalyst, $[MIMBS]_3PW$, where the synthesis is briefly summarized in Figure 14. The reaction of furfuryl alcohol with *n*-butanol in the presence of the selected catalyst at 383 K, gave *n*-butyl levulinate with yields greater than 93%[87].

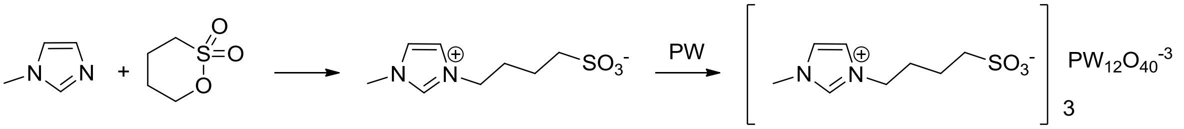


Figure 14. Preparation of $[MIMBS]_3PW$.

Supported PW heteropolyacids can be an alternative for more robust and recyclable catalysts. Thus, several zeolites have been used as support for PW heteropolyacid to achieve the direct production of ethyl levulinate from carbohydrates. Six zeolites (β, Sn-β, H-Y, H-ZSM-5, USY and ReUSY), and one structured mesoporous material (SBA-15, an acronym for Santa Barbara Amorphous) supported PW materials were prepared by the impregnation method, obtaining: PW/β, PW/Sn-β, PW/H-Y, PW/H-ZSM-5, PW/USY, PW/ReUSY, and PW/SBA-15[88]. The authors tested the alcoholysis of fructose to ethyl levulinate in ethanol, and found that the highest catalytic activity was obtained using the PW/H-ZSM-5 material. Fructose, inulin, sucrose, glucose, and cellulose were used as starting reagents. Working at 433 K for 2 h, the ethyl levulinate yields were 43.1%, 37.4%, 27.3%, 19.1%, and 8.7 %, respectively. The catalyst was reused three times showing no significant loss of activity. It is interesting to notice that with the medium pore zeolite ZSM-5 as support, only the external surface area, which is normally small, can be available for dispersing the PW. This indicates that large crystals of PW should be the active phase.

Liu and coworkers prepared methyl levulinate through the alcoholysis of fructose in methanol using iron-modified PW (Fe-PW) catalysts, in which H^+ where replaced by Fe^{+3}. The authors prepared three different catalytic materials by varying the iron content: 0.38%, 0.62% and 0.98 % of Fe. Results showed that the catalyst containing 0.38 % of Fe offers the best catalytic performance, achieving a 100% fructose conversion with a methyl levulinate yield of 73.7% under the optimal reaction conditions (at 403 K and 2 MPa, for 2 h). Then, other raw materials were used as reactants: glucose, sucrose, inulin and cellulose achieve methyl levulinate yield values of 13.8, 44.3, 92.3 and 13.7%, respectively. The reusability of the catalytic material was also evaluated: the Fe-PW catalyst could be reused at least five times without notable loss of activity[89].

In another example and instead of zeolites, acid treated clays were used as support of PW heteropolyacids[83].The catalyst with 20% w/w PW supported on K-10 was used for the esterification of LA with *n*-butanol at 393 K (Figure 15). After 4 h, 97% LA conversion and 100% selectivity towards the desired product were obtained. The authors found that the catalyst could be used without any post-treatment for two recycles.

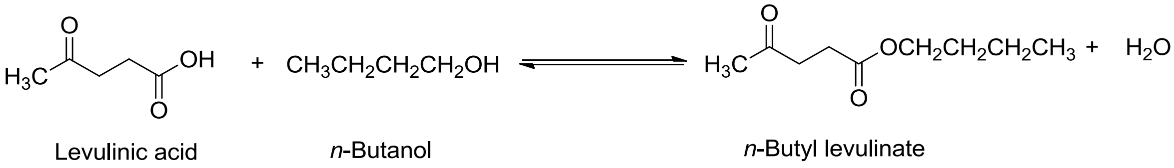


Figure 15. Esterification of levulinic acid to *n*-butyl-levulinate.

Methyl and ethyl levulinate have been prepared from LA using mesoporous silica-supported SiW catalysts[84]. These catalysts with tunable compositions were successfully prepared through a one-step method in the presence of a Brij 30 surfactant. Five materials were tested: four consisting of different loadings of SiW on SiO_2 (10, 20, 30 and 40 wt%) and SiO_2. In a typical run, LA was dissolved in methanol or ethanol, followed by the addition of the SiW/SiO_2 catalyst and cyclohexane as solvent. The system was heated at 338 and at 348 K for 6 h for methyl and ethyl levulinate preparation, respectively. In both cases, the best catalytic results were obtained with the 20 wt% SiW/SiO_2 catalyst. Thus, 73% yield for methyl levulinate (at a 79% conversion), and 67% yield for ethyl levulinate (at a 75% conversion) could be produced while the resultant catalysts maintained their catalytic activities stable.

Since a way of achieving good dispersion of the heteropolyacid in a silica matrix could be done by a co-condensation process, a Wells-Dawson heteropolyacid ($H_6P_2W_{18}O_{62}$, WD) was incorporated in the silica structure for the esterification reaction (in heterogeneous conditions) of LA with absolute ethanol at 351 K[86,90].

The catalyst was prepared by the direct incorporation of WD during the synthesis of silica by the sol-gel technique, in acidic media, using tetraethyl orthosilicate. The two materials prepared were: 20WD/SiO_2 (2.7 g of pure WD in 14.7 g of pure silica) and 40WD/SiO_2 (5 g of pure WD in 14.7 g of pure silica). In order to compare the catalyst activities, commercial PMo was also added to silica by the same technique (40PMo/SiO_2). Table 1 shows the catalytic performance of different heteropolyacids in levulinic acid esterification at 351 K. It can be seen there that the catalytic activity decreases from bulk to the added materials. The authors attributed this fact to the acidity of the involved catalysts. There is no significant difference in the results obtained by using 100 to 1000 mg of the catalytic material, and after four catalytic cycles it was observed that the activity was almost constant.

Table 1. Catalytic performance of different heteropolyacids in LA esterification.

Catalyst type	**Catalyst**	**Ethyl levulinate yield (%)**
SiO_2	None	-
	Support	-
Keggin heteropolyacid	PMo-bulk	92
	$40PMo/SiO_2$	38
Dawson heteropolyacid	WD-bulk	93
	$40WD/SiO_2$	76
	$40WD/SiO_2$[a]	-
	$40WD/SiO_2$[b]	72
	$40WD/SiO_2$[c]	70
	$40WD/SiO_2$[d]	79

Experimental conditions: 2 mmol of LA, 7.5 mL of absolute ethanol, 10 h, 351 K.

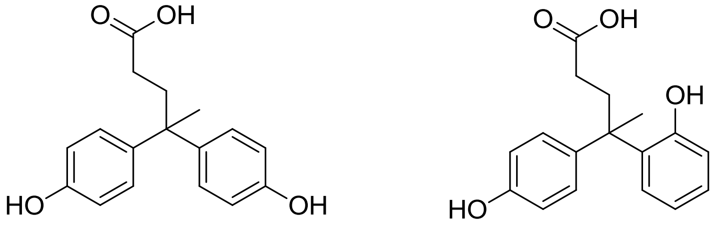
[a,b,c,d]Using 20, 100, 500 and 1000 mg of catalyst.

A 2D hexagonal mesostructured ZrO_2-based material, functionalized by benzene-bridged organosilica groups and PW (PW/ZrO_2–Si(Ph)Si), was prepared by Su *et al.*[91] using a single co-condensation-hydrothermal treatment step. The material was used for methyl levulinate synthesis through LA esterification. Working at 338 K for 3 h under a LA: MeOH molar ratio 1:7, a methyl levulinate yield of 100% was obtained. The excellent result obtained with the hybrid catalyst was attributed to their strong Brönsted acidity, well-defined ordered mesostructure, homogenous dispersion of the active sites, and enhanced surface hydrophobicity. Similar materials consisting in ZrO_2-based organic-inorganic materials functionalized by both the PW heteropolyacid and the hydrophobic alkyl groups (*i.e.*, benzene-terminally bonded organic moieties and ethane- or benzene-bridged organosilica moieties)(PW/ZrO_2–Si(Ph), PW/ZrO_2–Si(Et)Si and PW/ZrO_2–Si(Ph)Si) were prepared by Su *et al.*[92] The authors found that by tuning the initial Si/Zr molar ratios and using different organosilica precursors, the prepared materials, PW/ZrO_2–Si(Et/Ph)Si or PW/ZrO_2– Si(Ph) hybrid catalysts, possess controllable structural orderings and pore geometries. These materials were employed for methyl levulinate synthesis using LA as starting material. Results showed that 3D interconnected wormhole-like PW/ZrO_2–Si(Et)Si or PW/ZrO_2–Si(Ph) exhibits much lower catalytic activity than ordered 2D hexagonal mesostructured PW/ZrO_2–Si(Ph)Si-1.0. This fact was attributed to the decreased mass transfer limitations of the starting materials and obtained products owing to the ordered mesoporous structure.

Diphenolic acid

Diphenolic acid (DPA) is a structural analog of bisphenol A (BPA), a reactant commonly used in the polymer industry.

Mesoporous SiO_2-supported PW composites were used for DPA preparation through LA condensation with phenol. The catalytic materials were prepared with different loadings of PW and in the presence of a triblock copolymer surfactant, Pluronic P123 (P123, $EO_{20}PO_{70}EO_{20}$; EO, ethylene oxide; PO, propylene oxide), which was further eliminated through calcination or extraction treatments. When PW loadings were increased from 4.0% to 17.5% for both the extracted and the calcined materials, it was observed that LA conversion and also TOF increased significantly. The LA maximum conversions, 80.1% and 80.3%, were achieved using the extracted material 17.5 wt% PW/SiO_2 and the calcined material 15.7 wt% PW/SiO_2, respectively. However when the PW loading was increased to 58.2% and 65.1%, the catalytic activity decreased. This fact was attributed to the materials with lower loadings (from 4.0% to 17.5%) presented a largest number of available active sites, larger pore diameters, and an ordered mesostructure. Moreover, when calcination at 693 K is applied to remove the surfactant, a few acid sites are lost compared with the extracted catalyst, which results in a lower catalytic activity for the first material mentioned above. In Figure 16 the two possible DPA isomers are shown[93].



DPA (p, p') isomer

DPA (o, p') isomer

Figure 16. DPA isomers.

1.2.1.7. Sugar alcohol and derivatives production

Hexitols, sugar alcohols such as sorbitol and mannitol, and their dehydration product sorbitan, are important platform molecules that can be used as precursors to renewable chemicals and fuels (Figure 17)[94,95]. The one-pot production of hexitols starting directly from cellulose requires a bifunctional acid-metal catalytic system able to produce in a first step the hydrolysis of the cellulose into glucose (catalyzed by the acid sites), while the hydrogenation of glucose into hexitols takes place on metallic sites. Thus, Geboers and coworkers[96] reported the catalytic conversion of cellulose into hexitols by combining SiW and Ru on carbon (Ru/C). The authors determined that the rate-limiting step corresponds to cellulose hydrolysis. Using 10 wt% ball-milled cellulose as starting material, 92% yield of hexitols was obtained (yields: 65% of sugar alcohols, 27% of sorbitan, and less than 0.5 % of glucose) after 20 min reaction time.

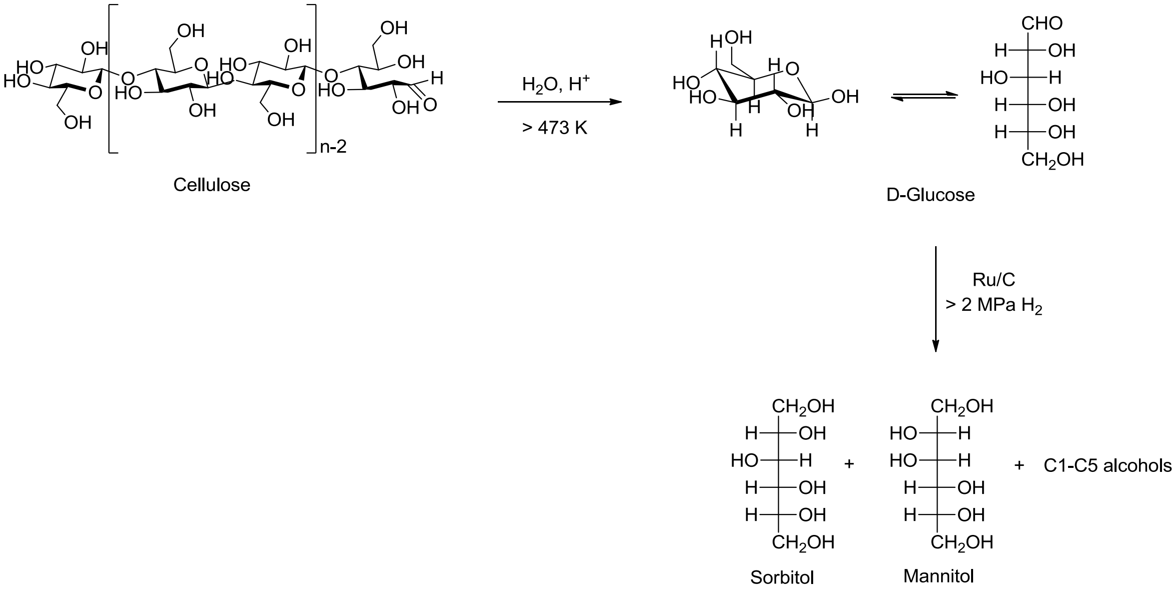


Figure 17. Polyols preparation from cellulose.

A similar protocol for the hydrolytic hydrogenation of cellulose using heteropolyacid cesium salts has been reported by the same authors[97]. They evaluated the catalytic activities of $Cs_{3.5}H_{0.5}SiW_{12}O_{40}$ ($Cs_{3.5}SiW$) and $Cs_{2.5}PW$, in combination with Ru/C, for the aqueous reductive splitting of cellulose into hexitols. Working in a water medium, at 443 K and 50 bar of H_2 for 24 h, with a hydrothermally pretreated $Cs_{3.5}SiW$ catalyst (at 463 K for 8 h), yields up to 90% of hexitols (70% of sorbitol, 20% of sorbitan, less than 0.5% of glucose) were obtained. They assumed that the applied pretreatment removes the more soluble species from the material, leaving a more stable catalyst for the desired reaction.

Palkovits *et al.*[98] also used heteropolyacids (PW and SiW) in combination with supported Ru catalysts (Ru/C) for the conversion of cellulose into sugar alcohols in a one pot process. Sorbitol and xylitol were obtained from cellulose and hemicellulose, respectively, working at 433 K in water medium, under an atmosphere of 50 bar H_2 after 7h. Additionally, further dehydration and hydrogenolysis may yield sorbitan and isosorbide, and in a parallel way other alcohols were also obtained. Using PW as catalyst cellulose conversion greater than 93% and yields in C4-C6 alcohols of 66% were obtained. These values were 98% and 80%, respectively, in the case of catalysis by SiW. The authors extended the study using wood based feedstocks as starting material, obtaining yields of sugar alcohols of 65% from spruce (Table 2).

Another bifunctional catalytic system such as PW-MOF-hybrid-supported Ru catalysts has been prepared and used for the production of sorbitol from cellulose and cellobiose under aqueous hydrogenation[99,100]. Under the optimal reaction conditions, a complete conversion of cellulose was achieved after 8h, corresponding to a sorbitol yield of 57.9%. In the case of using cellobiose as starting material, 95.1% yield of sorbitol was obtained after 10 h at 423 K.

Table 2. Sugar alcohols from spruce using heteropolyacids in combination with Ru/C as catalysts.

Catalyst	**Conversion (%)[a]**	**Yield C4-C6 (%)[a]**	**Yield C1-C3 (%)[a]**
PW	100	64.9	7.7
SiW	87	42.0	5.2

Reaction conditions: 500 mg spruce chips without pretreatment: 10 ml water, 100 mg 5%Ru/C, 500 mg HPA, 433 K, 50 bar H2 (298 K), 5 h [a]Conversion and yields were calculated assuming 45% cellulose and 30% hemicellulose, calculated as 75% cellulose.

Besides, a direct one-pot synthesis of sorbitol (yield, 54%) from pretreated cellulose has been reported by using SiW combined with Pt and H_2 as catalyst. Sequential reactions include saccharification followed by hydrogenation (Figure 18)[27,101].

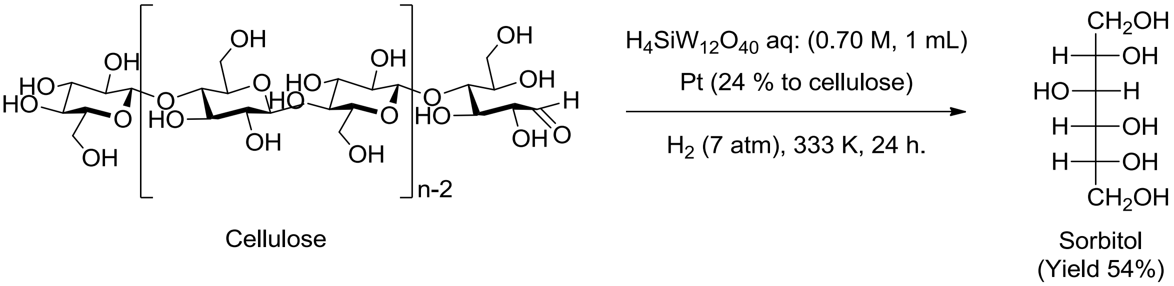


Figure 18. Sorbitol production from cellulose.

Microcrystalline cellulose was converted to hexitols by using a combined catalyst consisting of dispersed Ru on an ionic liquid ($BMIMPF_6$)–heteropolyacid ($Ru/[BMIM]_3PW$). The catalytic material presented Ru sites useful for hydrogenation, and both Lewis and Brønsted acid sites useful for hydrolysis. By working at 433 K and 5 MPa of H_2 for 24 h, a sorbitol selectivity of 70.3% with a microcrystalline cellulose conversion of 63.7% was achieved[102]. Ru was also employed to prepare Ru nanoparticles loaded on a Keggin-type polyoxometalate (Ru/Cs_xPW). These materials were used to catalyze the conversion of both cellobiose and cellulose into sorbitol in a water medium under H_2 pressure. In the case of cellobiose, by working with Ru/Cs_3PW at 413 K and after 6 h, a sorbitol yield of 86% was obtained. If ball-milled cellulose is used as starting material, sorbitol yield can reach 43% at 433 K after 24 h[103].

Trovao *et al.*[104] reported a simple method to obtain the three different possible polymorphs of D-mannitol (α, β and κ D-mannitol). Solid D-mannitol was precipitated by the addition of acetone to an aqueous solution on it and a heteropolycompound at room temperature. The α-form was obtained using SiW or $K_4SiW_{12}O_{40}.7H_2O$, the β-form was obtained in the absence of the heteropolycompound, and the κ-form was generated employing PW.

Isosorbide

Isosorbide is an anhydrous sugar alcohol useful in therapeutics, food additives, surfactants and polymer industries[105–107].

For isosorbide preparation from sorbitol, several supports were impregnated with PW: SiO_2, Al_2O_3, TiO_2, ZrO_2, and CeO_2. The highest conversion of sorbitol and selectivity towards isosorbide (96% and 46%, respectively) were obtained employing 30 wt% PW/ SiO_2 (Figure 19)[108].

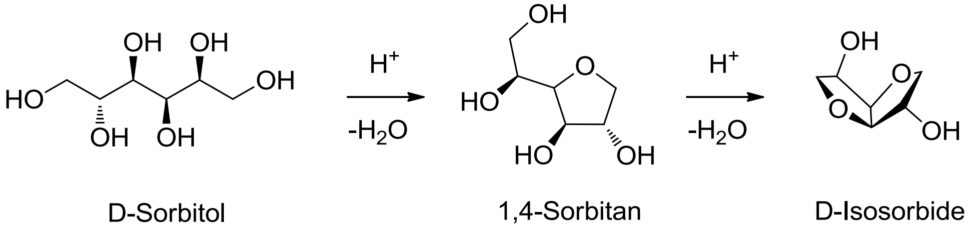


Figure 19. Isosorbide preparation from D-sorbitol.

In order to obtain isosorbide from cellulose, a combination of SiW and Ru/C was also employed as catalytic system. Researchers achieved an isosorbide yield of 50% using microcrystalline cellulose as starting material. Other lignocellulosic biomass feedstocks were employed to prepare isosorbide, and from the obtained results the authors concluded that the developed reaction system was a robust one[109].

1.2.2. Pentose derivatives

1.2.2.1. Furfural and derivatives production

Furfural is an important chemical produced on an industrial scale for the manufacture of furfuryl alcohol (for furan resin production), pesticides and tetrahydrofuran, among many other known chemical products[110]. Furfural is usually prepared by dehydration of D-xylose (Figure 20)[111].

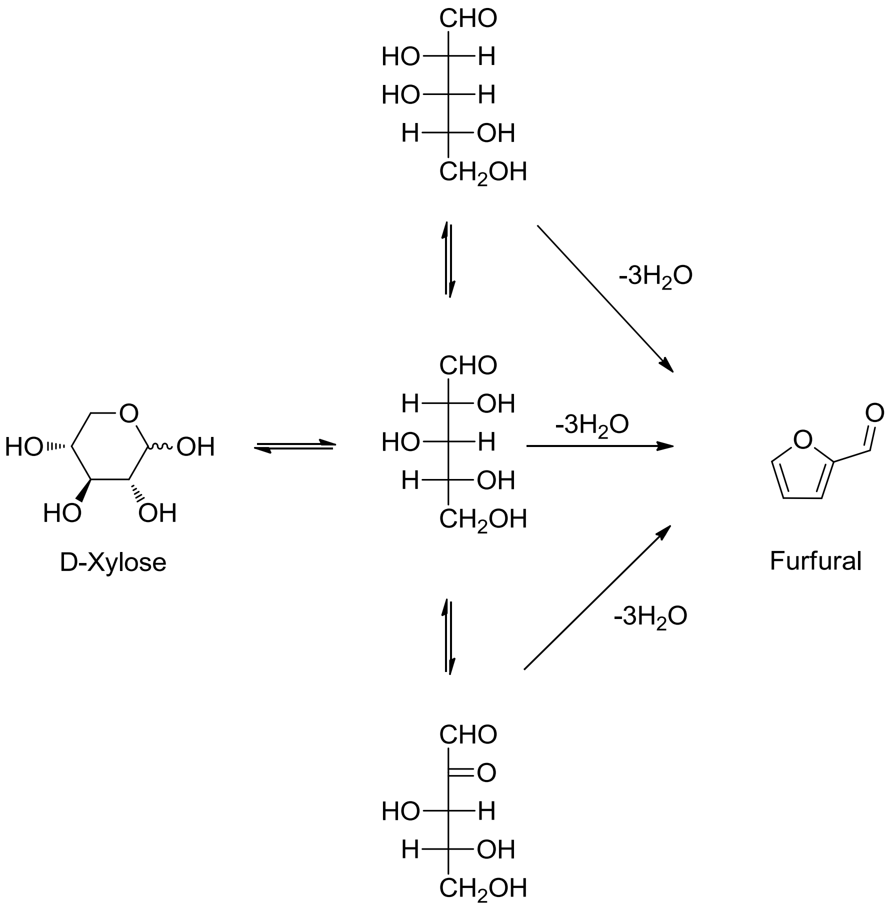


Figure 20. Furfural preparation by dehydration of D-xylose.

Dias *et al.*[112] studied the cyclodehydration of D-xylose into furfural using PW, SiW and PMo with DMSO as the reaction solvent, working at 413 K. The tungsten-based HPAs are comparable to H_2SO_4 and *p*-toluenesulfonic acid catalysts in terms of the furfural yield achieved after 4 h (58–67%), whereas by using PMo it yields less than half this amount of furfural. The same reaction was studied with PW immobilized on MCM-41[113], and also with some Cs_xPW compounds and cesium salts of PW immobilized on medium-pore or large-pore micelle-templated silica materials as catalysts[114]. Catalytic results were comparable to those obtained using sulfuric acid. In the case of Cs-modified heteropolycompounds, conversions were 65–70%, achieving 24–26% of furfural yield, working under the following reaction conditions: D-xylose (30 mg, 0.20 mmol), powdered catalyst (30 mg), and DMSO (1 mL) or, when a solvent mixture was used, water (0.3 mL) and toluene (0.7 mL), at 413/433 K for 4 h. In any case, the yields of furfural were quite low and polymerization can readily occur when increasing conversion.

Maleic acid and maleic anhydride

Maleic acid, maleic anhydride or maleic esters are widely used as starting material for resins, surface coatings, lubricant additives, plasticizers, copolymers, and agricultural chemicals production. They are usually obtained from n-butane as starting material[115]. However, they can be also produced from renewable materials such as the oxidation of furfural. Nevertheless, the major challenge of this route is to avoid the polymerization of furfural to resins under oxidative conditions.

Shi *et al.*[116] showed that by using a combination of copper nitrate with PMo it was possible to achieve a maleic acid yield of 49.2% with a selectivity value of 51.7%, at 95.2% of furfural conversion (Figure 21). The authors concluded that the combination of copper nitrate with PMo improves the reaction selectivity towards maleic acid due to the existing synergism between the two components, reducing the polymerization of the reaction intermediate to resins and promoting their conversion to maleic acid. Lower conversion but higher selectivity to maleic acid was reported by Guo *et al.*[117] for the aerobic oxidation of furfural using PMo as catalyst in an aqueous/organic biphasic system. The oxidation reaction takes place in the aqueous phase, and the organic phase (tetrachloroethane) serves as the reservoir to deliver the substrate gradually through phase equilibrium. Working at 383 K under 20 atm of oxygen, a furfural conversion of 50.4% was achieved after 14h, giving maleic acid yield and selectivity of 34.5% and 68.6%, respectively. The main advantages of using a biphasic system are the possibility of an easier product separation and simpler reactant/catalyst recycling.

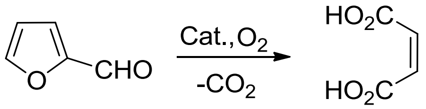


Figure 21. Maleic acid preparation from furfural through an oxidation reaction.

Lan *et al.*[118] studied the catalytic aerobic oxidation of furfural to maleic anhydride employing a combination of a Lewis acid and a heteropolyacid. With this purpose, a series of heteropolyacids were tested: PMo, PW, SiW, $H_4PVMo_{11}O_{40}$ ($PMo_{11}V$), $H_5PV_2Mo_{10}O_{40}$ ($PMo_{10}V_2$), and $H_6PV_3Mo_9O_{40}$ (PMo_9V_3). Among Lewis acids there were: $Y(CF_3SO_3)_x$ (Y= Ag, Na, Mg, Zn, Cu, Y, Yb, Sc and Al), $Pd(OAc)_2$ and $FeCl_2$. The authors found that the best catalytic results were obtained with the $Cu(CF_3SO_3)_2/PV_2Mo$ combination. Working under the optimized conditions, almost complete conversion of furfural was achieved after 14h, corresponding to a 54.0% yield of maleic anhydride and 7.5 % yield of 5-acetoxyl-2(5H)-furanone. This secondary product is a highly value-added, biologically important intermediate commonly applied in pharmaceutical synthesis. The same authors have reported recently the aerobic transformation of HMF to maleic anhydride employing just $PMo_{10}V_2$ as catalyst[119]. Reactions took place at 363 K, in an O_2 atmosphere (10 atm) with an acetonitrile/acetic acid mixture as reaction solvent. A total product yield of 64% (*i.e.*, 31.7% and 32.3% yield of maleic anhydride and maleic acid respectively) was obtained after 8 h.

1.2.3. Miscellanea

1.2.3.1. Ring-opening polymerization of tetrahydrofuran into poly(tetrahydrofuran)

This polymer family is commonly used in the chemical industry for thermoplastic manufacturing, and also to synthesize block polyether and polyurethane elastomer[120]. The ring-opening polymerization of tetrahydrofuran (THF) could be initiated by electrophilic agents such as Brönsted (*i.e.*, HCl, H_2SO_4, $HClO_4$) or Lewis acids (*i.e.*, $AlCl_3$, BF_3, OEt_2, $TiCl_4$). In several research studies, these traditional initiators were replaced by heteropolyacids[121–133]. Heteropolyacids were also used as catalysts in a number of protocols.

Bulk PW was used as catalyst in this polymerization, with acetic anhydride as initiator. The effects of acetic anhydride and catalyst amounts was studied and it was shown that an increase in the amount of both led to a decrease in the viscosity of the obtained polymer, while in the absence of acetic anhydride, THF did not polymerize[134]. The reaction system was also studied introducing also PW supported on Al_2O_3. The results showed that the unsupported heteropolyacid was more active than the supported independently of the amounts of catalysts tested. This could be expected not only on the bases of possible mass transfer limitations[135] but also because in alumina-supported catalyst a certain number of protons are trapped through a heteropolyacid-support interaction, and the number of available Brønsted-acidic sites decreases[136]. Silica is a preferred support for PW[137]. In fact, a PW immobilized on the surface of a SiO_2-carrier modified by the amino groups of organosilane γ-aminopropyl triethoxysilane (APTES) has been prepared, and tested it as catalyst for the tetrahydrofuran polymerization. The authors found that polytetramethylene ether glycol yield was 63.7%, and the catalyst could be reused at least four times, exhibiting a good maintenance of its activity[120].

The heteropolyacid PW was also supported on a high surface area structured SBA-15 silica material[138]. By investigating the effects of the mass fraction of PW, the mass ratio of APTES to SBA-15, and the pore diameter of SBA-15 on catalytic performance and on the conversion of THF, the best catalytic results were obtained using the material whose PW loading was 40 wt%, with a mass ratio of APTES/SBA-15= 0.0712. The authors concluded that the desired product presented higher molecular weight when the support had larger specific surface area, or larger pore sizes. Indeed, polytetrahydrofuran (PTHF) could be prepared by using different supported heteropolycompounds[139–142]: PW supported on neutral alumina prepared by assistance of ultrasound and plasma treatment, and several mesoporous silica-supported $Cs_{2.5}PW$ catalysts. PTHF was prepared with good results employing PW/Al_2O_3, but there were some leaching problems. In the case of the $Cs_{2.5}PW$ catalysts, good performances were observed with those silica supports with large pore diameters, and the materials resulted more active and stable than PW-based catalysts. The use of some other heteropolycompound-based catalysts was reported for the ring-open polymerization of THF: heteropolyacid-acetic anhydride[143] and PW supported on hydrous zirconia[144].

1.2.3.2. 1,4-Diacetoxybutane from tetrahydrofuran

1,4-Diacetoxybutane could be prepared through acetolysis of THF. Izumi *et al.* [145] tested PW, SiW, PMo, SiMo, $H_4GeW_{12}O_{40}$ and $H_4GeMo_{12}O_{40}$, among other compounds, as catalysts for the above-mentioned preparation. The authors found that when THF reacted with acetic acid, 1,4-diacetoxybutane was selectively obtained and when THF reacted with acetic anhydride, the major product was di(4-acetobutyl) ether. In both cases PW and SiW were the most active heteropolyacids. Working with PW, SiW and PMo as catalysts, and a mixture of acetic acid and acetic anhydride as nucleophiles at 333 K, the acetolysis of other cyclic ethers, such as 1,4-dioxane, furan and 2-methylfuran could be carried out and, a single product could be obtained in all cases[146].

1.2.3.3. Carbohydrates oxidation to formic acid

Formic acid (FA) is a commodity chemical that is widely used in the chemical, agricultural, textile, leather, pharmaceutical, and rubber industries[147]. Wölfel and coworkers affirm that ‘it has to be considered that nature converts solar energy into chemical energy *via* photosynthesis during the growth of biomass. Therefore, converting biomass into FA and using it as hydrogen carrier will *de facto* open a new route for the indirect exploitation of sun energy to produce hydrogen’ (Figure 22)[148]. Consequently, there is an increasingly interest to convert lignocellulosic biomass into formic acid through environmental friendly catalytic processes. Thus, FA has been prepared from cellulose using different HPA catalysts: PW, PMo, $H_5PV_2W_{10}O_{40}$ ($PW_{10}V_2$), $PMo_{11}V$, $PMo_{10}V_2$, and PMo_9V_3. Among all the catalysts tested, $PMo_{11}V$ was the most efficient for this reaction, giving the highest FA yield (67.8%), acetic acid being the only by-product, working at 453 K for 3 h, under 0.5 MPa O_2[149].

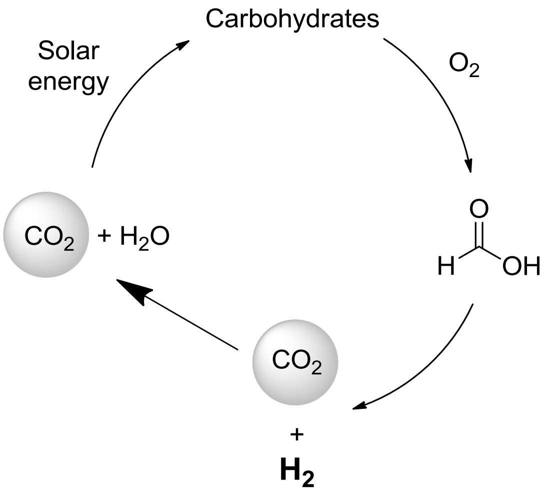


Figure 22. Indirect exploitation of sun energy to produce hydrogen.

A method that uses ball-milled cellulose hydrolytic oxidation was designed by Gromov *et al.*[150] using different heteropolyacis bearing acidic and oxidative catalytic centers such as $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$, $PMo_{10}V_2$, $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$, $Li_{2.4}H_{4.6}PMo_8V_4O_{40}$, $H_{11}P_3Mo_{16}V_6O_{76}$, and $H_{17}P_3Mo_{16}V_{10}O_{89}$. Since the concentration of both catalytic centers can influence the overall kinetics, they studied the system in two different conditions: at constant concentration of vanadium atoms having different acidities according to the catalyst used, and at constant pH (1.50) with different contents of vanadium using $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$. According to the obtained results, the authors concluded that the rate-determining step of the one-pot process is the cellulose hydrolysis. Furthermore, Wölfel *et al.*[148] studied a reaction system for the direct oxidation of several biogenic carbohydrate substrates: glucose, sorbitol, cellobiose, xylose, sucrose, glycerol, cellulose, xylan (hemicellulose), lignin, and poplar sawdust, among others. The authors obtained good results. For example, by using oxygen (30 bar) as the only oxidant and glucose as substrate, $PMo_{10}V_2$ as the homogeneously dissolved in H_2O catalyst at 353 K and after 26 h, FA yield was 49 ± 2%, corresponding to full conversion of the selected substrate. Also different heteropolyacids of the general type $H_{3+n}[PV_nMo_{12-n}O_{40}]$ (n = 0-6) have been tested as homogeneous catalysts in the selective oxidation of biomass to formic acid[151]. The higher V-substituted complexes (n= 2-6) showed considerably better activities in the oxidation of glucose than the lower V-substituted complexes (n = 0-1). Spectroelectrochemical studies comparing the complexes with n= 5 and n= 2 showed that only the complex with n= 5 had pervanadyl species, which are supposed to be responsible for the enhanced catalytic activity observed. The main results obtained are summarized in Table 3.

Table 3. Oxidative conversion of glucose into formic acid.

Catalyst	**Combined yield (%) FA +CO_2**	**Selectivity (%) FA +CO_2**
PMo	10	40:60
$PMo_{11}V$	12	50:50
$PMo_{10}V_2$	91	52:48
PMo_9V_3	100	56:44
$H_7PV_4Mo_8O_{40}$	97	54:46
$H_8PV_5Mo_7O_{40}$	94	61:39
$H_9PV_6Mo_6O_{40}$	97	58:42

Reaction conditions: 5.0 g (27.8 mmol) of glucose, 0.8 mmol of catalyst, 100 mL H_2O, 30 bar O_2, 263 K, 8 h, 1000 RPM.

Li *et al.*[152] used $PMo_{10}V_2$ for glucose oxidation into FA, achieving 55% yield of FA when oxidized by oxygen and 52% when oxidized by air. Based on X-ray photoelectron spectra and reactions of possible intermediates, they proposed a possible pathway (Figure 23). The same catalyst was also used as a bifunctional catalyst, for acid hydrolysis and oxidation, for the conversion of cellulose into FA, giving 35% yield using air as oxidant.

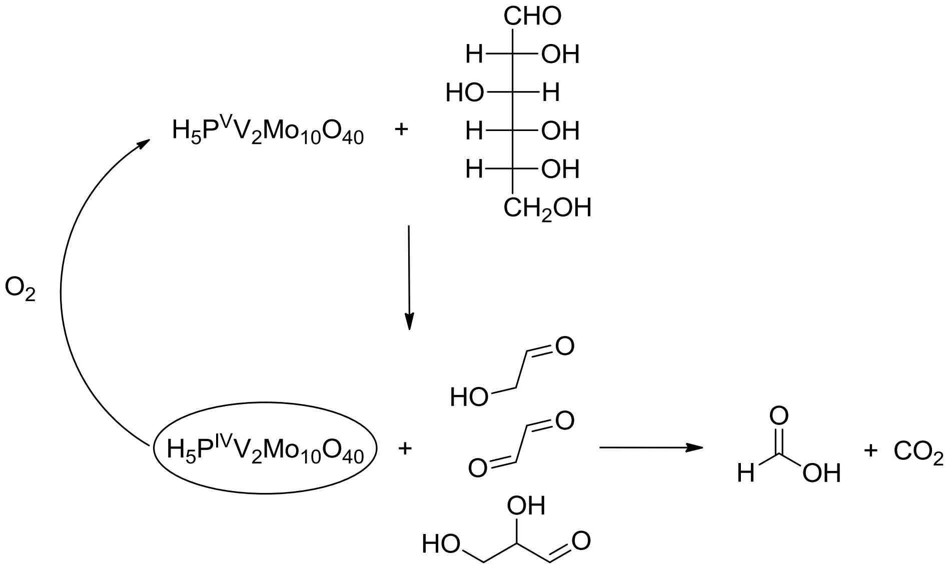


Figure 23. Possible pathway for glucose oxidation catalyzed by $PMo_{10}V_2$.

1.2.3.4. Acid lactic polymerization

Lactic acid (2-hydroxypropionic acid) is available in nature thanks to the fermentation of different carbohydrates such as glucose (from starch), maltose (produced by specific enzymatic starch conversion), sucrose (from syrups, juices, and molasses), lactose (from whey), among many others. It is a bifunctional compound amenable to numerous chemical conversions to useful products due to its hydroxyl group and acid functions.

Polylactic acid polymers are biodegradable materials currently considered as an environmentally friendly alternative to plastics derived from petrochemical materials. Researchers observed that lactic acid monomers do not polymerize directly to a large extent, due to a competing depolymerization reaction in which the cyclic dimer of the lactic acid, lactide, is generated. Several research papers are focused on controlling the molecular weight of the resulting polymer, since it is of critical importance depending on the biomedical application[30].

Choubisa *et al.*[153] presented the polycondensation of lactic acid to produce polylactic acid using silica sulfuric acid (SSA), cellulose sulfuric acid (CSA) and PW catalysts in *m*-xylene as solvent. Although the use of PW as catalyst for polylactic acid preparation had already been reported and patented[154], they conducted a new research work employing it. Reactions took place at 433 K in a time range of 12–48 h. In all cases, the highest molecular weight values were achieved employing long reaction times, and the highest molecular weight obtained with PW acting as catalyst was 36381 after 48 h.

1.2.3.5. α-Acyloxyacrylate ester production

α-Acyloxyacrylate esters have similar structures to methacrylate esters, and polymers of α-acyloxyacrylate esters show higher thermal durability than poly methyl methacrylate ones (PMMA). A variety of heteropolyacids has been used as acid catalysts to produce α-acyloxyacrylate esters by acylation of pyruvate esters. Thus, Ninomiya *et al.*[155] performed the acylation of pyruvate esters using carboxylic anhydrides, in carboxylic acid as solvent at 343 K for 1 h (Figure 24). As a result, not only α-acyloxyacrylate esters were obtained as products, but also 2,2-diacyloxypropionate esters were generated. To catalyze this reaction, several Keggin catalysts were tested: PW, SiW, PMo, $PMo_{11}V$ and SiMo. The best results were obtained with the W-based materials, and among them, the most efficient catalyst was PW, achieving an acylation selectivity (sum of the two products) of 100% and with a high formation of the corresponding α-acyloxyacrylate esters. One year later, these authors also compared the catalytic activity of $Cs_xH_{3-x}PW$ with that of the above-mentioned catalysts, paying special attention to PW[156]. They found that as the amount of Cs content increased, the yield of α-Acyloxyacrylate ester gradually decreased. Since the mass balance remained almost constant it was observed that the by-product quantity in the system was increased.

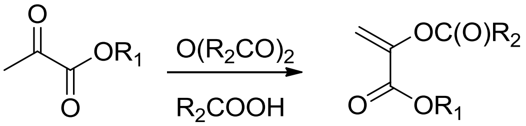


Figure 24. α-Acyloxyacrylate ester preparation from pyruvate esters.

Besides Keggin-type heteropolyacids, also Dawson-type and Preyssler-type heteropolyacids have been employed with the same purpose. Ninomiya *et al.*[157] compared the catalytic activity of PW, WD and $H_{14}[NaP_5W_{30}O_{110}]$ in the preparation of ethyl α-acetoxyacrylate from ethyl pyruvate with acetic anhydride in liquid phase. Results showed that the catalytic activity was as follows: $H_{14}[NaP_5W_{30}O_{110}] > PW > WD$. Furthermore, $Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$ ($x < 10$) was also tested: the authors found that this catalytic material could also act as an effective solid acid catalyst for the acylation reaction under heterogeneous conditions.

1.2.3.6. *N-Sulfonyl pyrrolidine-2,5-diones production*

Pyrrolidine-2,5-diones, commonly named succinimides, could have sulfonamide moieties by treating them with an acylating agent. The sulfonamide group, present in a number of biologically active molecules, is considered as a pharmacophore due to its antibacterial, antitumor, anticarbonic anhydrase, anticonvulsant and protease inhibitory activities, among many others. It has been demonstrated that sulfonamide moieties can also largely enhance the activity of antibacterial agents.

Bougheloum *et al.*[158] developed a procedure for the synthesis of N-sulfonyl pyrrolidine-2,5-diones derivatives from sulfamides and succinic anhydride (Figure 25). Succinic anhydride, acid and its esters could be prepared from the salts of succinic acid present in nature thanks to the fermentation of glucose made by some microorganisms[30]. The authors tested PW and the Wells-Dawson heteropolyacid WD as catalysts, and selected the latter as the most convenient material. By working under nitrogen atmosphere in acetonitrile at reflux for 1 h, a conversion value of 90% was obtained for the selected model reaction.

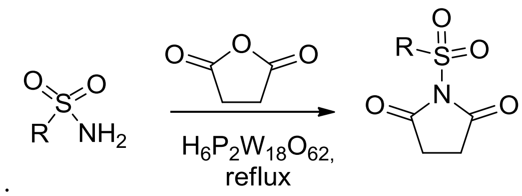


Figure 25. Synthesis of N-sulfonyl pyrrolidine-2,5-diones derivatives from sulfamides and succinic anhydride.

2. Oils and Fats

Fats and oils form another important group of biomass resources. They are principally obtained from vegetable and animal sources, mainly formed by mixed triglycerides having fatty acid moieties. While a large proportion of vegetable oils come from countries with tropical climates, animal fats are obtained from the meat industry[30].

2.1.Esterification and transesterification reactions

2.1.1.Phytosteryl ester production

Phytosterols are nontoxic natural products and inexpensive by-products of food processing. The use of plant sterols as therapeutic dietary options before resorting to drug treatment to lower the plasma cholesterol concentration is very common: a consumption of 0.5–3.0 g/day of plant sterols could produce a 30–80% lowering of cholesterol absorption, and a corresponding 10–15% lowering of LDL cholesterol[159–161]. As a food additive to be used broadly, phytosterols should/may also be conveniently incorporated into food, without the adverse organoleptic effects. Based not only on previous studies but also on the finding that phytosteryl esters are much more soluble in the oil phase than the free phytosterols, the use of phytosteryl esters in oil to lower cholesterol absorption has been proposed. In this context, heteropolyacids appear as a good catalyst alternative since they are often used as catalysts for esterification reactions in the food and chemical industries[162].

Meng *et al.*[163] tested four SiO_2 supported heteropolyacids (PW, SiW, PMo and SiMo) for phytosteryl ester preparation from some fatty acids (butyric, caprylic, stearic, lauric, palmitic, oleic, linoleic and α-linolenic acid) and phytosterols. As is shown in Table 4, the best catalytic results were obtained by using PW/SiO_2 working at 423 K for 3 h. When researchers prepared phytosteryl esters from butyric, caprylic, lauric, palmitic, oleic, linoleic, alphalinolenic and stearic acid, yields over 90% were obtained in all cases regardless of the fatty acid chain length or identity of the sterol reactant.

Table 4. Synthesis of phytosteryl oleate with SiO_2-supported heteropolyacids[a].

Catalyst	**Phytosteryl oleate (%)**
SiW/SiO_2	69.8
PW/SiO_2	60.4
$SiMo/SiO_2$	42.7
PMo/SiO_2	53.6

[a] *Reaction conditions*: 0.1% catalyst, 423 K, substrate molar ratio (oleic acid vs. phytosterol) 1:1, nitrogen flow rate 1.5 mL/min, moderate agitation.

2.1.2. Biodiesel production

The excessive demand for world petroleum reserves for the transportation and industrial sectors, and the increased environmental concerns have stimulated the search for alternative renewable fuels that are capable of fulfilling an increasing energy need. In this sense, biodiesel fuel (fatty acid methyl esters), having similar physical properties to petrochemical diesel, is considered the best alternative fuel candidate for use in diesel engines[164].

Almost all vegetable oils and animal fats can be used to prepare biodiesel. Currently, biodiesel is mostly produced from edible and nonedible vegetable oils obtained from soybean, oil palm, coconut and sunflower, among many others. The use of oils from andiroba, babassu, camelina, cumaru, *Cynara cardunculus*, groundnut, karanja, algae, poppy seed, rice bran, rubber seed, sesame, tobacco seed, palm kernel and fish was also reported[165].

A variety of heteropolyacids have been used as homogeneous and heterogeneous acid catalysts for the biodiesel production, *via* esterification of fatty acids with methanol or by transesterification of triglycerides with methanol. For instance, bulk PW has been used as homogeneous catalyst for the efficient esterification of a number of saturated and unsaturated fatty acids (myristic, palmitic, stearic, olei, linoleic,)[166,167]. In all cases, by working in an ethanol medium at reflux temperature, conversion values were higher than 85%, while selectivities were greater than 90%. A kinetic study utilizing ^{1}H-NMR spectroscopy *in situ* was done to evaluate the effects of temperature on the reaction rate, and also to determine the activation energy along with thermodynamic constants including ΔG, ΔS and ΔH. The order of reaction with respect to both substrate and catalyst concentrations was also determined[168].

Srilatha *et al.* employed CsPW as catalytic material for biodiesel preparation from rice bran fatty acids. Under optimized conditions, about 92% conversion of the starting material was obtained. The authors demonstrated that the catalyst could be reused five times maintaining its original activity[169]. $Cs_{2.5}PW$ was also used by Kiss and collaborators to achieve the esterification of dodecanoic acid at 413 K with 2-ethylhexanol[170,171].

PW, SiW and PMo immobilized on silica as catalysts were used for the esterification of palmitic, oleic and stearic acid with methanol at 333 K. The researchers observed that the catalytic activity for the esterification of palmitic acid decreases in the series: PW/ SiO_2 > SiW/ SiO_2 > PMo/ SiO_2. Then, the same reaction was also carried out over a series of PW immobilized on silica with different PW loading values: from 2.5 wt% to 8.4 wt%. It was observed that the PW-silica material with a PW content of 4.2 wt% shows the highest catalytic activity (100% conversion after 30 h), and in its reuse over four catalytic cycles it presented almost constant activity. This catalytic material was used in the esterification of oleic and stearic acid with methanol, and it also showed a good performance[172,173].

The heteropolyacid PW was supported on SiO_2, Nb_2O_5 and ZrO_2, which were then tested as catalysts for oleic acid esterification with ethanol at 333 K. Da Silva *et al.*[174] conducted this investigation, and they observed that high conversion values (> 90%) were obtained. The authors established a catalytic activity order: $PW/Nb_2O_5 > PW/ZrO_2 > PW/SiO_2$. It was concluded that after three catalytic cycles, catalyst activity is almost constant. Oleic acid esterification with ethanol was also studied by Oliveira *et al.*[175]employing PW impregnated on ZrO_2. A conversion value of 88% was achieved after 4 h of working at the optimum reaction conditions: 20 wt% PW/ ZrO_2, 373 K, a molar ratio acid: ethanol (1:6).

SiO_2-supported PW was also used by Chuayplod *et al.*[176] for the esterification of treated rice bran oil, whose conversion was almost complete at 343 K in a methanol medium for 4 h. Nb_2O_5-supported PW was employed for biodiesel production from palmitic acid and sunflower oil. The esterification activity depended on the PW loading on niobium pentoxide: it was found that the best catalytic results were obtained with 25 wt% PW/Nb_2O_5. In both cases, conversion values greater than 97% were obtained working at 338 K for 4 h. The authors also calculated the activation energies involved: 13.68 and 15.49 Kcal/ mol for the esterification of palmitic acid and sunflower oil, respectively[177].

A series of borotungstic acids and borotungstates were prepared in order to combine them with a surfactant (hexadecyltrimethylammonium bromide, CTAB) and then the whole system obtained was applied to the esterification of palmitic acid [178]. It was found that not only highly negatively charged BW, but also the (CTA)BW material could efficiently promote the esterification reaction. Using BW the conversion reached 98.6% after 3 h of working at 338 K in a methanol medium, and employing the heterogeneous catalyst (CTA)BW the conversion value was 98.7% after 5 h at the same reaction temperature. By employing the same surfactant, CTAB, Zhao and coworkers[179] prepared a Brönsted-Lewis-surfactant-combined heteropolyacid. The (CTA)$H_4TiPW_{11}O_{40}$ catalyst was used for the esterification of free fatty acid, achieving a high conversion (94.7%) and excellent efficiency (91.8% yield) after 6 h at 338 K.

SBA-15 was also employed as support: SiW was anchored on it at different loadings and then tested for the esterification of oleic acid with methanol at 333 K. After 8 h of working under the above-mentioned reaction conditions, it was observed that the 30 wt% SiW/SBA-15 material presented the best catalytic activity: a methyl oleate yield of 89.7% was achieved[180].

Some nontraditional catalysts were prepared by Ezebor *et al.* [181] using oil palm trunk (OPT) and sugarcane bagasse (SCB) combined with Keggin anions. These materials were evaluated in the esterification of palmitic acid with methanol and, under optimum conditions, the OPT and SCB catalysts afforded excellent methyl palmitate yields, respectively. Then, ethyl and butyl palmitate were also prepared, achieving good results.

Other atypical catalysts are picolinic acid-modified PW (PA-PW). Gong and coworkers[182] prepared three different PA-PW materials by varying the molar ratio PA: PW from 1:1 to 1:3. The authors found that modification of picolinic acid not only improved the stability of PW in esterification mixtures, but also maintained high acidity. In the esterification reaction of oleic acid with methanol, a total conversion was achieved at 353 K using the PA-PW material with a molar ratio PA: PW of 1:1.

A heteropolyacid-ionic liquid system $[(CH_3)_3NCH_2CH_2OH]PW$ was synthesized by Duan *et al.*[183] using choline chloride and PW as precursors. This material exhibited a particular switchable property based on temperature. It could be used as a homogeneous catalyst at relatively high temperature and, when temperature decreased, it precipitated and could be recycled. So, this catalyst combines the advantages of homogeneous and heterogeneous catalysis. The catalytic activity of this material was tested in the esterification of palmitic acid with methanol at 338 K under microwave irradiation. Results indicated that excellent conversion values were obtained at short reaction times (a conversion of 97% was achieved after less than 1 h under the optimal reaction conditions).

On the other hand, some other supported heteropolyacids have also been used as heterogeneous acid catalysts for the esterification of fatty acids with methanol. For instance, supported PMo and PW on commercial activated carbon fibers (A10, A15 and A20)[184] were used for the esterification of palmitic acid. The most appropriate catalyst was 44 wt% PMo/A20 which allowed to achieve a conversion greater than 75% at 313 K after 6 h. Moreover, it was possible to reuse the catalytic material several times without significant loss of activity if it is washed with ethanol acidified with H_2SO_4. Also insoluble heteropolytungstate materials, Cs_xPW (x = 0.9-3), were active for the esterification of palmitic acid and the transesterification of tributyrin (Figure 26). These steps are especially important in fatty acid and ester processing for biodiesel synthesis. They found that optimum performance occurs for Cs loadings of x = 2.0–2.3, while it is possible to reuse these catalytic materials maintaining both conversion and selectivity values almost constant[164].

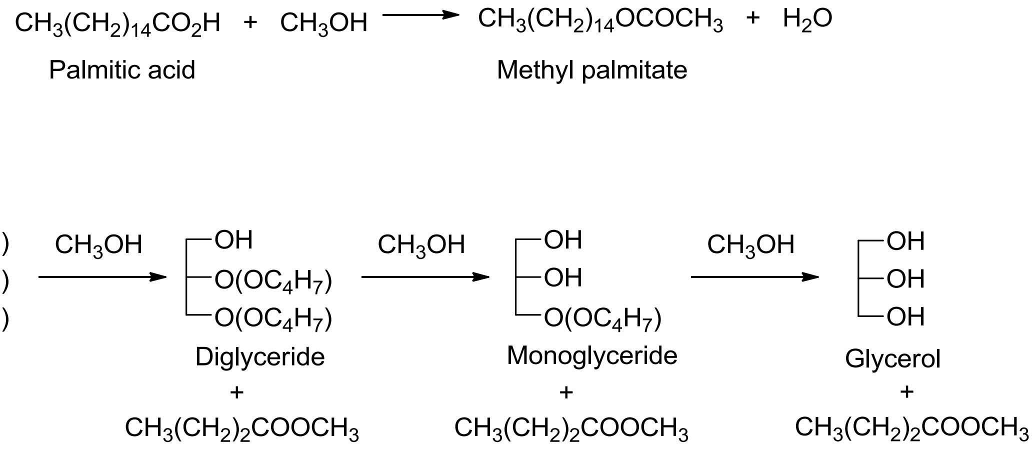


Figure 26. Esterification of palmitic acid and transesterification of tributyrin.

Cesium heteropolytungstate materials have been also used with excellent success to produce biodiesel through the transesterification of oils with methanol. Thus, Chai *et al.*[185] performed the production of biodiesel from Eruca Sativa Gars oils (ESG oils) catalyzed by Cs2.5PW, achieving high yields (99%) at 333 K for 0.75 h. In addition it was found that the properties of biodiesel from ESG were comparable to those of conventional diesel fuel, and using ESG biodiesel instead of conventional diesel fuel it is possible to reduce emission levels[186]. Microwave-assisted biodiesel production has also been used to enhance the transesterification rate. Starting from yellow horn (*Xanthoceras sorbifolia Bunge*) oils and using Cs2.5PW as catalyst[187], a conversion higher than 96% in only 0.16 h at 333 K was achieved. Rapeseed oil was used as staring material for biodiesel production through the transesterification reaction in an ethanol medium, using Cs_2PW and both bulk and SiO_2-

supported PW as catalysts[188].The authors found that the catalytic activity did not show a relationship with the measured acid strength of solid catalysts. In fact, comparable TOF were determined on PW and PW/SiO_2 while lower TOF was found for Cs_2PW. In the case of PW/SiO_2 the TOF values were explained in terms of leaching of the active phase, while reduced acid sites accessibility could explain the lower TOF exhibited by Cs_2PW. Magnetic Cs_xPW/Fe-SiO_2 materials were prepared by Feyzi *et al.*[189] and employed in the sunflower oil transesterification with methanol. The authors then determined some thermodynamic parameters such as the entropy and enthalpy variation of reaction, activation energy, the reaction order, and also the effects of temperature on the reaction rate. Besides, Cs exchanged silicotungstic acid catalysts of general formula Cs_xSiW (Cs_xSiW, x= 0.8-4) were also employed in the triglyceride transesterification, and palmitic acid esterification with methanol[190]. The authors found that for loadings of less than or equal to 0.8 Cs per Keggin unit, (trans) esterification activity arises from homogeneous contributions. However, higher degrees of substitution resulted in entirely heterogeneous catalysis. To optimize the heterogeneous catalytic activity, it was necessary to find a balance between the retention of acidic protons and the generation of stable mesopores in the prepared material.

Bimodal Cs_xSiW materials with mesopores interconnected with micropores were synthesized by Iwase and coworkers[191]. They tested their catalytic activity (after being treated with sulfuric acid) in the transesterification of glycerol tributyrate with methanol. $Cs_{2.5}$SiW-bimodal treated with sulfuric acid showed high activity towards the desired reaction due to its strong acid strength and mesoporosity.

Methanolysis of castor oil to methyl esters was made by Zieba and coworkers employing K and Cs salts of PW: the authors observed that potassium salts presented higher catalytic activity than their corresponding analogs. The material in which two protons were replaced by two potassium atoms ($K_2HPW_{12}O_{40}$) was found to be the most active salt[192].

K-10 montmorillonite was used as support for PW Keggin heteropolyacid, and this catalyst was used for the transesterification of edible (sunflower, soybean, palm, sunflower (cooked)) and nonedible (karanja and jatropha) vegetable oils with lower and higher alcohols to prepare lower alkyl esters (biodiesel) and higher esters (biolubricant). Bokade and Yadav studied these transformations looking for their optimization by adjusting different process parameters, such as catalyst loading, speed of agitation, molar ratio of oil to alcohol, catalyst reusability, and reaction temperature[193].

Another heteropolyacid was supported on niobia: $H_4PNbW_{11}O_{40}/WO_3\text{-}Nb_2O_5$, and was used for the transesterification between triolein and ethanol into ethyl oleate. This catalyst showed lower activity than two other conventional solid acid catalysts such as $H_4PNbW_{11}O_{40}$ and PW, however they were dissolved into the reaction medium. On the contrary, $H_4PNbW_{11}O_{40}/WO_3$ on Nb_2O_5 was insoluble and presented good ethyl oleate yields working in batch reactions at 373 K for 8 h[194].

The transesterification of crude jatropha oil with methanol was performed in the presence of an activated carbon-supported heteropolyacid catalyst (PW/C) under ultrasonic energy at 338 K. The experimental data obtained were used both to generate a historical design and to identify the optimum conditions by means of a response surface methodology (RSM) approach. A comparison between the predicted and the experimental results at the optimal conditions is presented in Table 5[195]. The same authors performed the same reaction by using different loadings in the activated carbon-supported heteropolyacid catalysts (PW/C): 15, 20 and 25% w/w. The 20% w/w PW/C catalyst achieved the best methyl ester yield: 87.33% after 0.66 h[196].

Table 5. Comparison between predicted and experimental results at the optimal conditions in the transesterification of crude jatropha oil with methanol.

Run	Reaction conditions			Yield (%)		Error (%)
	Time (min)	**Molar ratio[a]**	**Catalyst amount (w/w)[b]**	**Predicted**	**Experimental**	
1	40.38	24.90	3.8	94.61	90.67	4.21
2	41.27	24.36	4.42	95.76	91.97	3.86
3	37.51	25.00	4.23	96.26	91.34	5.11

[a]Molar ratio between methanol and crude jatropha oil.

Another surfactant, P123, a triblock copolymer, was used by Xu *et al.* to prepare a mesoporous polyoxometalate-tantalum pentoxide composite catalyst, PW/Ta_2O_5, with different PW loadings[197,198]. The catalytic performance of the obtained materials was evaluated in the esterification of lauric and myristic acid, and also in the transesterification of tripalmitin as well as in the direct biodiesel production from soybean oil. Results showed that 10.8 wt% PW/Ta_2O_5 was the most active catalyst among all tested materials for the esterification of lauric acid and transesterification of tripalmitin, reaching yields of 65.6% and 66.2% of the desired products at 351 K in ethanol, respectively. The authors also tested the simultaneous esterification of myristic acid and transesterification of tripalmitin. This reaction took place at 338 K with a molar ratio of myristic acid: tripalmitin: methanol of 1: 1: 90. After 6 h under these conditions, methyl myristate yield was 100%, while methyl palmitate yield was 50.7% when 10.8 wt% PW/Ta_2O_5 was used. As a final test, direct biodiesel conversion from soybean oil was made. Soybean oil consists of three kinds of triglyceride: oleic, palmitic and linoleic triglycerides. By working at 338 K in a methanol medium, an esterification yield greater than 99% was obtained after 24 h. Methyl palmitin, oleate and linoleate yields were 24.9%, 20.5% and 30.4%, respectively.

Xu and coworkers[199] also presented other Ta_2O_5-based catalysts prepared using the surfactant P123, consisting of hybrid catalysts functionalized by both alkyl-bridged organosilica fragments and PW, Ta_2O_5/ Si(R)Si-PW (R= CH_2CH_2- (Et), or C_6H_4- (Ph)). The most active catalysts for the transterification of soybean oil were Ta_2O_5/ Si(Et)Si-PW with 12.3 wt% of PW and 20 mol % of Si, and Ta_2O_5/ Si(Ph)Si-PW with 13.0 wt% of PW and 20 mol % of Si. Among them, the ethane-bridged material exhibited a slightly higher catalytic activity than the other one at similar PW loadings.

In a similar approach, Xu *et al.*[200] also prepared, by a single step sol-gel co-condensation method followed by a hydrothermal treatment in the presence of the P123 surfactant, some mesoporous Ta_2O_5 materials functionalized with both alkyl group and a Keggin-type heteropolyacid, Ta_2O_5/SiO_2-[PW/R] (R = Me or Ph). The as-prepared materials were tested for biodiesel production using soybean oil directly, in the presence of 20 wt% myristic acid under atmosphere refluxing. Reaction conditions included the use of a molar ratio of oil: methanol of 1:90 at 338 K and, after 24 h, methyl oleate, palmitin and linoleate yields were higher than 50%, 60%, and 80%, respectively.

Some other similar ethane-bridged materials were employed for biodiesel production: mesostructured ZrO_2-based hybrid catalysts, functionalized by both an ethane-bridged organosilica group and PW, PW–ZrO_2–Si(Et)Si, were prepared by Su and coworkers[201]. Catalyst preparation was achieved through a one-step sol-gel-hydrothermal method in the presence of a triblock copolymer surfactant (F127). ESG oil was transesterified with methanol to produce the corresponding fatty acid methyl esters. The PW–ZrO_2–Si(Et)Si material exhibited higher catalytic activity than the alkyl-free PW–ZrO_2 material. The authors attributed the observed difference to the improvement of the surface hydrophobicity of PW–ZrO_2 due to the introduction of the ethane-bridged organosilica groups. The best catalytic results were obtained using the PW–ZrO_2–Si(Et)Si material with 60 mol % of ethane-bridged silica groups in its structure.

Morin *et al.*[202] performed the transesterification of rapeseed oil using PW, SiW, PMo and SiMo as catalysts. The obtained results are shown in Table 6. As can be seen, Mo-based heteropolyacids presented a higher catalytic activity. The authors attributed this difference to the ability of Mo samples to lose hydration water at lower pretreatment temperatures.

Table 6. Transesterification of rapeseed oil for biodiesel production.

Catalyst	Triglycerides conversion (%)[a]	Selectivity (%)[a]		
		Ethyl ester	Monoglyceride	Diglyceride
PW	27	95	4	0
PMo	55	51	36	12

SiW	20	44	17	35
SiMo	45	63	31	6

[a]*Reaction conditions:* 358 K, molar ratio EtOH:-COOR 6:1, 3 h.

SBA-16 with different supported loadings of PMo was employed for the single-step esterification of crude karanja oil to fatty acid methyl esters. Experimental results revealed that 15 wt% PMo/SBA-16 was the most active catalyst, achieving a fatty acid methyl ester yield of 81.8% working with a molar ratio of crude karanja oil: methanol 1:8, at 413 K for 5 h[203].

Silver salts of PW were also used for the transesterification of triglycerides with methanol. Zieba *et al.*[204] presented a study in which Ag_xPW salts with a Ag content from X=0.5 to 3 were used to catalyze the above-mentioned reaction. As the protons in PW are replaced by Ag^+ cations, the conversion of triglycerides gradually decreases, so $Ag_{0.5}$PW was found to be the most convenient catalytic material.

Waste oils are low-cost feedstocks for the biodiesel production; however, these feedstocks contain a high amount of free fatty acids, which limits their use for the production of biodiesel using conventional homogeneous bases for the transesterification process. Therefore, the use of strong acid catalysts such as homogeneous or heterogeneous heteropolyacids able to produce the esterification of free fatty acids and the transesterification of triglycerides is an interesting alternative to produce biodiesel from these feedstocks. Thus, waste cooking oil has been transesterified with methanol in the presence of PW[205,206]. A conversion of 88 % was obtained at 338 K after 14 h of reaction.

The catalyst did not show loss of activity after four catalytic cycles under the optimal reaction conditions. Noshadi *et al.*[207] developed a continuous process to produce biodiesel from waste cooking oil in a reactive distillation column using PW as catalyst; the authors highlighted that the introduction of this reaction system reduced the alcohol demand, achieving a desired product yield value of 93.98%.

A solid acid catalyst based on a supported heteropolyacid catalyst was evaluated by Baig and Ng[208,209] for the production of biodiesel from soybean oil containing up to 25 wt % palmitic acid. The authors found that by working for 10 h at 473 K with molar ratio oil: alcohol (1:2), a high quality biodiesel with an ester content of 93.95% was produced

A solid zirconiumdodecatungstophosphate $Zr_{0.7}H_{0.2}PW_{12}O_{40}$ with nanotube structure was synthesized by Zhang *et al.*[210] using natural cellulose fiber as a template. This particular material was employed to catalyze the esterification of free fatty acids from waste cooking oil. Results showed that the free fatty acid content decreased from 26.89 to 0.3 wt%, and the transesterification of triglycerides was achieved with a conversion value of 98.5% under mild conditions. Other PW-based nanotubes with double acid sites were prepared and used for the production of biodiesel from waste cooking oil by simultaneous esterification and transesterification. $Zn_{1.2}H_{0.6}PW_{12}O_{40}$ materials were prepared using cellulose fibers as templates. This catalyst exhibited higher catalytic activities for the esterification of palmitic acid than the parent acid catalyst PW. Moreover, the prepared PW-based nanotubes containing Zn atoms led to markedly enhanced yields of methyl esters in the preparation of biodiesel from waste cooking oil, working at 338 K in a methanol medium[211]. Also $Al_{0.9}H_{0.3}PW_{12}O_{40}$ catalysts were prepared by employing a natural cellulose fiber template. These materials, combining both Brönsted and Lewis acid sites, were used as nanoheterogeneous catalysts for the above-mentioned biodiesel preparation from waste cooking oil[212].

Shin *et al.*[213] employed $Cs_{2.5}PW$ for the transesterification of some used vegetable oils in supercritical methanol. The content of fatty acid methyl esters reached 92% working at 533 K for 0.66 h. SBA-15-supported CsPW was also used as catalytic material for biodiesel production from waste cooking oil. The maximum yield achieved a yield value of 90.5% from waste cooking oil after 1 h at 333 K with the composite loaded catalyst system of 0.03% concentration, and a methanol: oil molar ratio of 6.6: 1[214].

Solid sludge from wastewater treatment plants is another low-cost feed-stock for biodiesel production. Mesoporous ordered silica, SBA-15, was impregnated with PW and tested in the above-mentioned transformation[215]. By employing 15 wt% PW/SBA-15 a biodiesel yield of 30.14 wt% after 3 h at 408 K and a pressure of 135 psi was obtained.

2.2. Glycerol Derivatives

2.2.1. 1,2-Propanediol, 1,3-propanediol and their derivatives production

Glycerol is a by-product of the biodiesel industry, formed during the transesterification of oils and fats. Using glycerol as starting materials, it is possible to obtain, through different treatments, mono, di- and triesters, glycidol, oligoglycerol esters, hyperbranched polyglycerols, fuel additives, alkenyl ethers, epoxy resins, dihydroxyacetone, glyceraldehyde, hydroxyl carboxylic acids, acrolein and acrylic acid, and methanol, among many other substances. The hydrogenolysis of glycerol leads to the formation of 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO) as main products, ethylene glycol as a degradation product, and 1-propanol, 2-propanol as over-hydrogenolysis products (Figure 27)[216].

1,2-PDO, the three-carbon diol with a stereogenic center at the central carbon atom, is an important medium-value commodity chemical commonly used in the preparation of polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavors and fragrances, personal care products, paints, animal feed, antifreeze, etc. It can also be used as an alternative to toxic ethylene glycol-based deicing agents[217–221]. On the other hand, 1,3-PDO is an important monomer to produce high performance biodegradable polyesters[222].

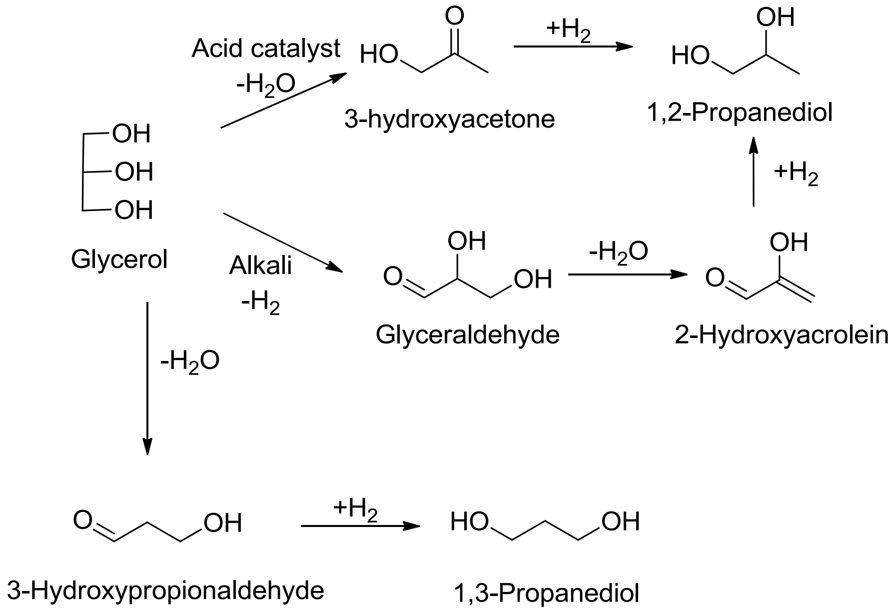


Figure 27. Glycerol hydrogenolysis.

Alhanash *et al.* [216] investigated the catalytic activity of Ru supported on $Cs_{2.5}PW$ for 1,2-PDO preparation. They found that this is an active bifunctional catalyst for the hydrogenolysis of glycerol, providing 1,2-PDO with a selectivity value of 96% at 21% of conversion, working at 423 K and 5 bar of H_2.

A 1,2-PDO derivative, 3-(1-phenylethoxy)propane-1,2-diol, is an important biologically active compound that could act as antibacterial, anti-inflammatory, antifungal and antitumor agent. Yadav *et al.*[223] employed several supported heteropolyacid materials for its synthesis: PW supported on hexagonal mesoporous silica (PW/HMS), on montmorillonite clay (PW/K-10), PMo supported on HMS (PMo/HMS), on montmorillonite clay (PMo/K-10), CsPW and CsPMo supported on montmorillonite clay (CsPW/K-10 and CsPMo/K-10, respectively). Among all tested catalytic materials, 20 wt% PW/HMS gave the highest conversion value of about 94% after 2 h, with selectivity of 75% to the desired monoether product.

The catalytic hydrogenolysis of glycerol to value-added 1,3-PDO was investigated by Zhu *et al.*[224] They employed a series of alkaline metals (Li, K, Rb and Cs) to modify Pt–SiW/ZrO_2 catalysts, and used them in a continuous process. Results showed that Li-exchanged SiW exhibited superior activity and maximum 1,3-PDO selectivity, attaining 43.5% glycerol conversion with 53.6% 1,3-PDO selectivity, and also achieving 120 h long-term stability. Previous to this research, these authors used Pt-SiW/SiO_2 to catalyze the hydrogenolysis of glycerol to 1,3-PDO in aqueous phase. They found that the optimized catalytic material, Pt-SiW/SiO_2 with a Pt content of 2 wt% (as in all tested materials) and 15 wt% of SiW allowed achieving a desired product yield value of 31.4%, corresponding to a glycerol conversion of 81.2%, working at 473 K and 6 MPa[225]. A variety of ZrO_2-

supported bifunctional catalysts, containing Pt and a heteropolyacid (SiW, PW or PMo) have been also used for this transformation[226]. For comparison purposes, Pt/ZrO_2 was also included. The best performance was shown by Pt-SiW/ZrO_2, and it was observed that the addition of the heteropolyacid increased the catalytic activity. As a conclusion, the 1,3-PDO yield was proportional to the concentration of Brönsted acid sites in the catalytic material, while the Lewis acid sites concentration determined the 1,2-PDO yield.

Long alkyl chain ether

Propylene and ethylene glycols are easily produced from biomass via fermentation, thermochemical and catalytic processes. Many derivatives of these compounds have found numerous important applications as building blocks for the synthesis of various valuable chemicals, such as oxygenated fuel additives, pharmaceutical and agrochemical products, nonionic surfactants, antimicrobial and antiseptic agents, and precursors of polymers, among many other examples[227].

Yadav *et al.*[227] studied the etherification of ethylene glycol with 1-octene to 2-(octan-2-yloxy) ethanol (C8 ether) and 1,2-bis(octan-2-yloxy) ethane (C16 ether), employing several heterogeneous solid acid catalysts supported on K10 clay (Figure 28). PW and $Cs_{2.5}$PW were supported on K10 clay, while PW was supported on ZrO_2. The most efficient catalyst was 20 wt% PW/K10, achieving an ethylene glycol conversion of 72% after 5 h working at 413 K, with 80 % selectivity to a 2-(octan-2-yloxy) ethanol (C8 ether).

Then, the authors also employed glycerol and 1,2-propylene glycol as starting materials, obtaining good results.

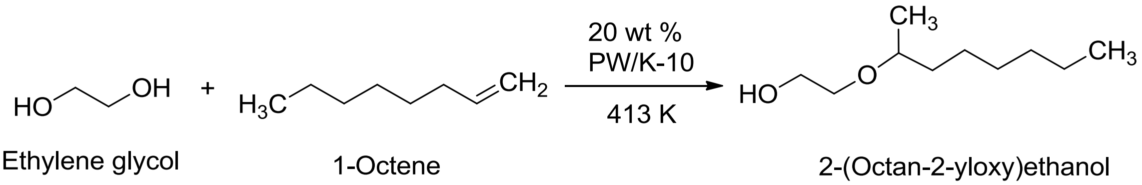


Figure 28. Etherification of ethylene glycol with 1-octene.

2.2.2. Acrolein and derivatives production

Acrolein, one of the products in the dehydration of glycerol, is used as a raw material for acrylic acid, medicines, fiber treatment, among others (Figure 29)[228]. Acrolein could also polymerize and form polyacrolein, a material highly cross-linked through intermolecular acetal linkages. In a recent research work acrolein polymerization was catalyzed by porous materials based on PW-functionalized aluminum 2-aminoterefthalate metal-organic frameworks[229].

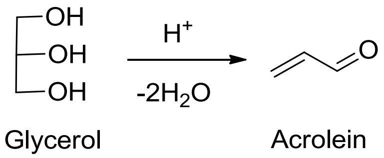


Figure 29. Acrolein production.

Tsukuda *et al.*[228] studied acrolein production from glycerol with high selectivity over silica-supported acid catalysts (PW, SiW and PMo) at 598 K for 5 h. The authors concluded that the size of the mesopores in the silica support affected the catalytic activity: the SiW/SiO_2 material with mesopores of 10 nm showed stable catalytic activity with the highest acrolein selectivity above 85 mol %, for conversions of 98%; whereas the silica support with small mesopores (3 nm) induces steep deactivation. The SiW heteropolyacid supported on activated carbon at different loadings (0%, 5, 10, 20 and 30%), was used to produce acrolein from glycerol over the gas phase reaction. The best catalytic results were obtained with 10% SiW supported on activated carbon: conversion and selectivity values were 92.6% and 75.1%, respectively[230].

PMo, PW, SiW, and $(NH_4)_3PMo_{12}O_{40}$ supported on silica, alumina, and aluminosilicates supported heteropolyacid catalysts (supports denoted as Al_2O_3, SiO_2, AS4, A12 and S11) were also used to produce acrolein from glycerol. The authors found that, generally, all tungsten-containing catalysts showed outstanding performance with regard to activity and selectivity compared to Mo- and P-containing materials. The best results include a selectivity value of 75% at complete conversion, which was achieved using SiW supported on aluminosilicate at 548 K[231,232]

The dehydration of glycerol using ZrO_2-supported PW catalysts at 588 K gave acrolein with conversion and yield values of 76 and 54% respectively[233,234], while using ZrO_2-supported SiW catalysts at 573 K higher conversion of glycerol was achieved (92 %), however the selectivity to acrolein was similar[235]. $PMo_{11}V$ supported on ZrO_2 resulted in a more selective catalyst for the dehydration of glycerol into acrolein. Thus, by employing 40 wt% $PMo_{11}V/ZrO_2$ and working at 498 K a total conversion of glycerol with an acrolein selectivity value of 89% was achieved[236].

PMo and $PMo_{11}V$ Keggin heteropolyacids supported on SiO_2-Al_2O_3 carriers with Si/Al values from 0.21 to 0.32, as well as on Al-MCM-41 (Si/Al= 10), were employed for the dehydration of glycerol to acrolein at 553K[237]. It was found that the highest acrolein selectivity values were obtained with PMo and $PMo_{11}V$ supported on Al–MCM-41. It was concluded that the presence of both V in the catalytic materials and molecular oxygen in the feed helped to suppress catalyst deactivation by keeping the metal ions in a more oxidized state, and the carbon deposits in a less condensed state. Al–MCM-41 with the highest surface area, lowest surface acidity and smallest mean pore diameter showed the highest molybdate dispersion. Kang and coworkers[238] also employed PW supported on silica-alumina, but they tested different SiO_2 contents in the support system: 0, 15, 30, 50, 85 and 100 mol%. They found that, among all tested catalytic materials, 85 mol% PW/SiO_2-Al_2O_3 showed the largest Brönsted acidity and also the highest yield of acrolein.

Haider *et al.*[239] reported the dehydration of glycerol using Rb- and Cs-doped SiW (Rb_xSiW and Cs_xSiW, respectively) as acid catalysts. Several catalysts were prepared by varying the concentration of the dopant metal cations while keeping the concentration of the Keggin material unchanged. Since high acrolein selectivity (94–96%) was observed with unsupported Cs_xSiW and Rb_xSiW with a dilute glycerol feed (0.5 wt% in water), these catalysts were then supported on both alpha-alumina and an alumina comprising a theta-delta mixture. The maximum selectivity values (90% at total conversion of glycerol) for 90-h time on stream, with a 10 wt% glycerol solution, were achieved with the Cs_xSiW material supported on theta-delta alumina ($Cs_xSiW/\delta,\theta$-Al_2O_3). The authors concluded that the binding strength of the partially doped silicotungstic acid on the alumina was found to be crucial to sustain the supported Keggin structure and hence the acidity of the active sites, resulting in a high acrolein yield.

Nb_2O_5 was used as support to impregnate PW with different loadings between 10 and 40%. This material was highly active in the glycerol dehydration, showing higher activity than PW supported on TiO_2 and ZrO_2[240]. Nb_2O_5 was also employed as support for $Cs_{2.5}PW$ catalyst at different loadings lower than 20 wt%. The catalyst was tested for acrolein production by gas-phase dehydration of glycerol at 573 K. The $Cs_{2.5}PW/Nb_2O_5$ material gave glycerol conversion and acrolein selectivity values of 96 and 80%, respectively[241].

Not only supported $Cs_{2.5}PW$ was used, but also bulk $Cs_{2.5}PW$ was employed as catalyst to prepare acrolein from glycerol at 548 K[242,243].

Cs modified SBA-15 (Cs-SBA-15) material was used as support for the PW Keggin heteropolyacid. This catalytic system was tested for glycerol dehydration and it was found that the best catalyst, including a PW loading of 50%, had the largest fraction of medium acid sites (71%) and gave 85% acrolein yield at 573 K[244]. PW was also supported on W modified SBA-15 (PW/W-SBA-15) which showed an acrolein selectivity of 75%, corresponding to total conversion of glycerol working at 498 K[245].

Several rutile TiO_2-supported heteropolyacid catalysts were prepared through the incipient wetness impregnation method using SiW, PW, and PMo acids as active compounds. Results showed that the 20 wt% PW/ TiO_2 (rutile) catalyst presented the highest catalytic activity: at almost total conversion of glycerol (99%) the selectivity towards acrolein was 80%[246].

Acid catalysts that catalyze the dehydration of glycerol into acrolein tend to form carbonaceous species on their surface, which leads to their deactivation. Katryniok *et al.*[247] studied the regeneration of different supported heteropolyacids by performing the reaction in a tubular fixed-bed reactor. Results showed that the support has a strong impact on the thermal stability of the active phase. They found that Zirconia stabilizes SiW, thus enabling the desired nondestructive regeneration of the catalyst (SiW/ZrO_2-SBA-15).

An extensive study on the gas-phase dehydration of glycerol to acrolein employing a variety of 10 wt% SiW catalysts supported on different materials including γ-Al_2O_3, SiO_2-Al_2O_3, TiO_2, ZrO_2, SiO_2, C, CeO_2 and MgO, showed that each supported SiW catalyst showed higher catalytic activity than the corresponding support alone. According to the results obtained in the initial 2 h of the experiment, the selectivity order towards acrolein was: SiW/ZrO_2 ~ SiW/SiO_2-Al_2O_3 > SiW/γ-Al_2O_3 > SiW/TiO_2 > SiW/C > SiW/SiO_2 > SiW/MgO > SiW/CeO_2[248,249]. In some other research papers α-Al_2O_3 was employed as support for PW[250] while Al_2O_3 was used for SiW[251], and these catalytic materials were also tested for the catalytic gas-phase glycerol dehydration to acrolein.

1,4-Butanediol

1,4-Butanediol is an important precursor for polybutylene terephthalate (PBT) production, a high-performance engineering plastic. 1,4-Butanediol was prepared from acrolein and 2-methyl 1,3-propanediol through a multistep process (Figure 30) by using a bifunctional catalyst consisting in 5 wt% Ru and 5 wt% SiW supported. It was found that this catalytic material was active and could also be used in four catalytic cycles, being in each reuse a little more active than in the preceding one, achieving 1,4-butanediol yield values greater than 96%[252].

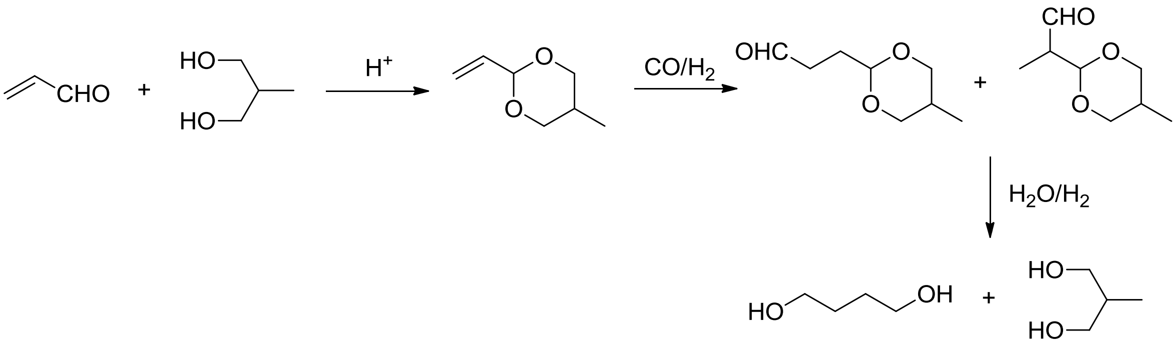


Figure 30. 1,4-Butanediol preparation from acrolein.

2.2.3. Acrylic and methacrylic acid production

Acrylic acid and some of its derivatives are used in the polymer industry for the production of superabsorbers, adhesives and paints, among other products.

Liu and collaborators employed a series of $Mo_3VO_x/SiW/Al_2O_3$ materials for the one-step oxydehydration of glycerol to acrylic acid. SiW acted as the dehydration component, while Mo_3VO_x was the oxidation component. The authors carried out a very complete study on the evolution of reactive phases with calcination temperature, and its correlation with the catalytic property changes[253].

Acrylic acid was also prepared from acrolein oxidation using $K_xH_{3-x}PMo_{12}O_{40}$ of different compositions as catalysts[254–256]. Andrushkevich *et al.*[257] studied the thermolysis of PMo and the catalytic properties of the thermal decomposition products in the oxidation of acrolein. Results showed that the $(PMo_{12}O_{38.5})_n$ phase and the $(MoO_2)_2P_2O_7$ compound presented higher selectivity to acrylic acid than PMo. Then, these authors studied the redox mechanism of oxygen insertion into acrolein upon its oxidation by molecular oxygen on $PMo_{12}O_{38.5}$ catalyst[258]. Kuznetsova *et al.*[259] also studied the acrolein oxidation using as a catalytic system the product obtained from decomposition of the ammonium salt of vanadium-molybdenum/silicon heteropolyacid. PMo was also used for methacrolein oxidation to methacrylic acid at 573 K[260].

2.2.4. Solketal production

Solketal, 2,2-dimethyl-1,3-dioxolane-4-methanol, is an excellent compound to be used as gasoline, diesel and biodiesel fuel additive since it reduces gum formation and increases the octane number[261,262]. Other uses of solketal include its application as cleaning metallic, electrical and plastic substrates, as water miscible solvent for pharmaceutical injections, as an additive in ointments in the cosmetic industry, and in low transfer fluids in the chemical industry[263–265].

Solketal is prepared by acid catalyzed ketalization of acetone with glycerol, and usually a mixture of isomers, the dioxolane (solketal) and dioxane isomers are obtained (Figure 31). Bulk PW, PMo and SiW were used as catalyst for the ketalization of acetone with glycerol at room temperature under solvent-free conditions. Under these conditions, it was found that PW was the most active catalyst, achieving a solketal selectivity of 97% at a conversion of 90%. Other ketal derivatives were prepared by using cyclic and acyclic ketones[266].

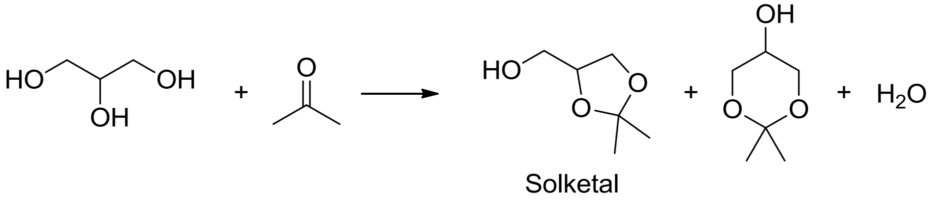


Figure 31. Solketal preparation from glycerol and ketone.

Supported heteropolyacids have been used as catalysts for this transformation. Ferreira *et al.*[267] studied the ketalization of acetone with glycerol using PW, SiW, PMo and SiMo immobilized on silica. Reactions were carried out at 343 K, and results showed that all tested catalysts exhibited excellent solketal selectivity values at almost complete conversion. Solketal was also prepared using different loadings of PW immobilized on SBA-15, at 343 K. The most active material was 10.8 wt% PW/SBA-15: a 99% solketal selectivity was achieved at complete conversion[268].

Sandesh *et al.*[265] reported the preparation of several organic-inorganic hybrid catalysts, and among them, they selected tetrapropylammonium salt of PW $[(CH_3CH_2CH_2)_4N)_3PW_{12}O_{40}]$ as the most efficient heterogeneous catalyst for solketal synthesis from glycerol and acetone at room temperature. Results showed that after 2 h, a high glycerol conversion of 94% was obtained with 98% of solketal selectivity.

2.2.5. Esters of glycerol production

Monoacetin, diacetin and triacetin are the products of glycerol acetylation (Figure 32). Monoacetin and diacetin are used in cryogenics and also as raw material for the production of biodegradable polyesters, while triacetin could be used from cosmetics to fuel additive industries[269].

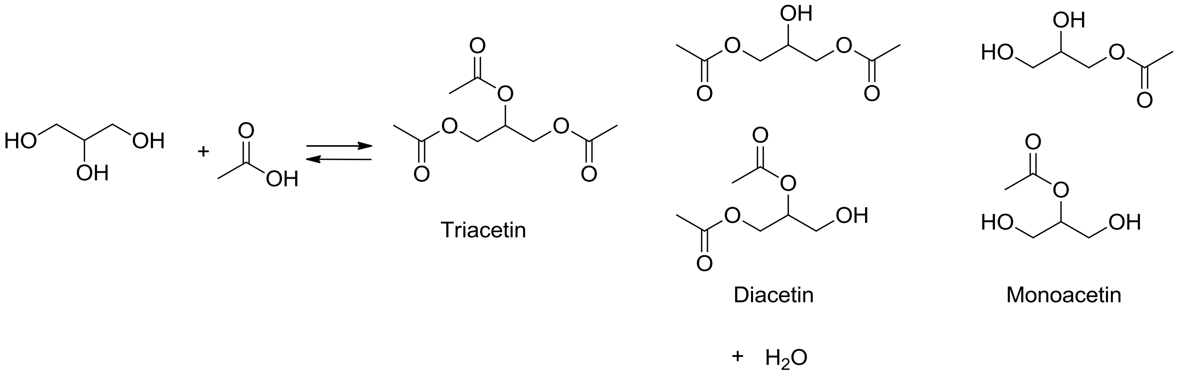


Figure 32. Glycerol acetylation.

Monoacetin was selectively prepared using PW supported on Cs-containing ZrO_2 (PW/Cs-ZrO_2) at 333 K, while that the selectivity to diacetin and triacetin increased when the temperature increased from 333 to 393 K[270]. Ferreira *et al.*[271] prepared diacetin with high selectivity using PW immobilized in a silica matrix, prepared by two different techniques (sol-gel and impregnation), as catalytic materials[269]. Diacetin was also obtained as the main reaction product when PW immobilized on activated carbon was employed as catalyst, working at 393 K. Moreover, monoacetin and diacetin were obtained as the main products when reactions were carried out with PW/Nb_2O_5 as catalysts at 393 K. After 0.5 h of reaction time, the conversion value was about 90%[272].

2.2.6. Dichloropropanol production

Dichloropropanol (DCP) is mainly used for the production of epichlorohydrin (ECH)[273]. Several modified heteropolyacids that include $H_3PMo_{12-X}W_XO_{40}$ (X= 0-12), $H_4SiMo_{12-X}W_XO_{40}$ (X= 0-12), $H_{3+X}PW_{12-X}V_XO_{40}$ (X= 0-3), and $H_{3+X}PMo_{12-X}V_XO_{40}$ (X= 0-3) were used as catalysts for DCP preparation from glycerol and HCl. The best catalytic performance was shown by PW, achieving DCP selectivity values greater than 30%[274,275]. After testing the catalytic activity of $H_3PMo_{12-X}W_XO_{40}$ (X = 0, 3, 6, 9, and 12), SiW, and SiMo heteropolyacid catalysts, Song and collaborators also found that PW was the most convenient option[276]. Since it was observed that the water formed during the reaction retarded the formation of the desired product, the effect of including a water absorbent in the reaction system was evaluated. Results showed that using silica gel blue, the formation of DCP was greatly enhanced[277,278].

Lee and collaborators studied the effect of several reaction conditions when PW was employed as catalyst for the direct preparation of DCP from glycerol (Figure 33). Selectivity to DCP was higher with increased reaction time and catalyst amount. The maximum selectivity value was achieved at 10 bar and at 403 K[273]. The study to determine an appropriate treatment for PW regeneration after this reaction was also done. Three different methods were tested: (I) evaporation of a homogeneous liquid phase product solution, (II) oxidative calcination of the solid product recovered by method I, and (III) subsequent oxidative calcination of the solid product recovered by method II. Among them, method III was found to be the most efficient one for the regeneration of PW[279].

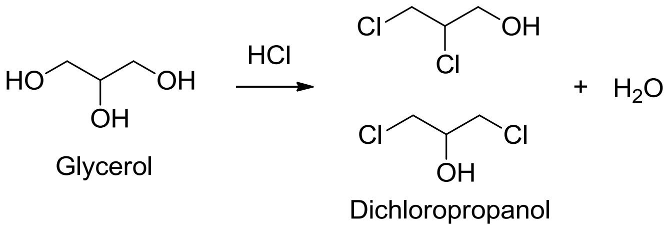


Figure 33. Dichloropropanol preparation from glycerol.

Several Wells-Dawson heteropolyacids were also employed to catalyze DCP preparation from glycerol. Lee *et al.*[280] tested a Keggin $H_3PMo_{12-X}W_XO_{40}$ (X= 0-12) and a Wells-Dawson $H_6P_2Mo_{18-X}W_XO_{62}$ (X= 0-18) heteropolyacid at 383 K under a N_2 atmosphere, and found that PW was the catalytic material that showed the best catalytic performance.

3. Terpenes

Terpenes are composed of units of five carbons, called isoprene, usually ordered in a regular pattern. They are found in essential oils that are components of resins, steroids, and rubber, and as by-products of the pulp, paper and citric juice industries[281]. Terpenes are widely distributed in the plant kingdom. The most widespread compounds are limonene, α-pinene and β-pinene, which constitute real building blocks for the synthesis of new important chemicals for use as fragrances, flavors, pharmaceuticals, solvents, and also chiral intermediates[30]. α-Pinene could be isomerized to camphene, terpinenes, limonene, *p*-cymene and terpinolenes, employing encapsulated PW in the mesopores of MCM-41 molecular sieves[282]. Several specific isomerization studies were conducted, as shown below.

3.1. Oxidation reactions

3.1.1. Epoxymonoterpene production

Epoxides of monoterpenes constitute important starting materials for the preparation of fragrances, flavors and therapeutically active substances[283].

Composite materials incorporating a trivacant Keggin-type polyoxometalate ($[A\text{-}PW_9O_{34}]^{-9}$) impregnated in the three-dimensional porous metal-organic framework MIL-

101 (Cr) were employed to oxidize various monoterpenes. In this work, geraniol and R-(+)-limonene were used as starting materials, and experiments were done in air (at atmospheric pressure) in an acetonitrile medium employing H_2O_2 as oxidant. In the oxidation of geraniol, made at room temperature and protected from light, after 0.5 h complete conversion was achieved with a 2,3-epoxygeraniol selectivity of 100%. In the case of R-(+)-limonene, notably lower selectivity was obtained and three products were detected: 1,2-epoxide, diepoxide and 1,2-diol (Figure 34)[284].

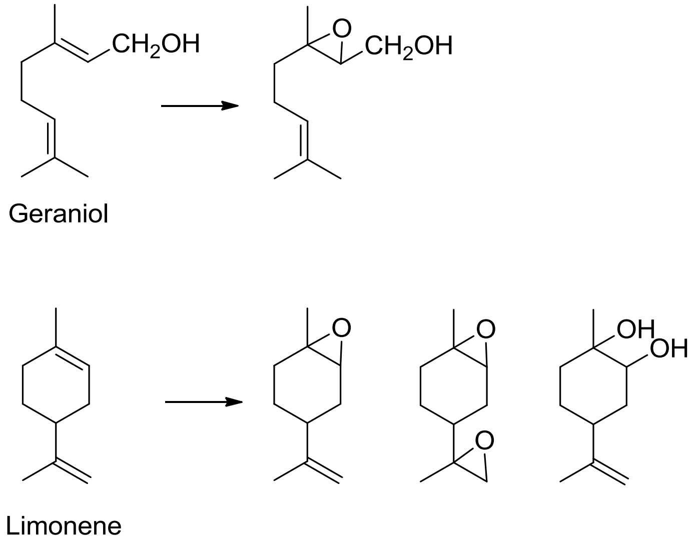


Figure 34. Oxidation of geraniol and R-(+)-limonene.

The same authors reported the use of potassium salts of the monovacant polyoxotungstates $[PW_{11}O_{39}]^{-7}$ and $[SiW_{11}O_{39}]^{-8}$ in the porous MIL-101 (Cr) for the oxidation of both geraniol and R-(+)-limonene. Working under similar reaction conditions, they obtained 2,3-epoxygeraniol from geraniol with a selectivity of 100%, and 1,2-epoxide, bis(epoxide) and 1,2-diol when R-(+)-limonene was employed as starting material[285].

Geraniol and R-(+)-limonene were also oxidized by another sandwich-type polyoxometalate: $(TBA)_7H_3[Co_4(H_2O)_2(PW_9O_{34})_2]$ (TBA: tetrabutylammonium) immobilized in MIL-101. Reactions were carried out in acetonitrile under air atmosphere at atmospheric pressure with H_2O_2 as oxidant. After 4 h of reaction, 1,2-epoxygeraniol was the only product formed with 100% conversion of geraniol. When R-(+)-limonene was used as reactant, 1,2-epoxide was the first product obtained, which was subsequently converted into 1,2-diol as the main product, whereas the corresponding bis(epoxide) was also produced[286].

Several uncommon heteropolycompounds containing tetrabutylammonium where prepared by Balula and coworkers. The activity of two sandwich-type $[M_4(H_2O)_2(PW_9O_{34})_2]^{-n}$ (M= Fe^{III} and Co^{II}) materials in the oxidation of both geraniol and R-(+)-limonene with H_2O_2 in acetonitrile was compared with the corresponding activities of the lacunary $[PW_{11}O_{39}]^{-7}$, and the monosubstituted $[M(H_2O)PW_{11}O_{39}]^{-m}$ (M= Fe^{III} and Co^{II}). Results showed that all tested catalysts are active in the two selected oxidation reactions. The lacunary and the cobalt-containing catalysts demonstrated to be more active than the iron compounds. Then, the lacunary and the monosubstituted materials were more selective catalysts than the sandwich ones[287].

Silica nanoparticles supporting potassium salts of both α-$[Fe^{III}(H_2O)PW_{11}O_{39}]^{-4}$ and a sandwich-type tungstophosphate of formula B-α-$[(PW_9O_{39})_2Fe^{III}_4(H_2O)_2]^{-6}$ were also employed for geraniol oxidation using H_2O_2 as oxygen donor. The results showed that the α-$[Fe^{III}(H_2O)PW_{11}O_{39}]^{-4}/SiO_2$ nanocomposite material was the most efficient catalyst, achieving conversion and 2,3-epoxygeraniol selectivity values of 96 and 88%, respectively[288].

Several compounds based on the association of polyoxometalates and cationic porphyrins or metalloporphyrins were prepared by Santos *et al.*[289]. These compounds presented the general formula (porphyrin)$_x$H$_y$[XM$_{12}$O$_{40}$]·(x = 0.75 or 1, X= P or Si and M=W or Mo). Some other compounds with metal-substituted Keggin anions ([PW$_{11}$Y(H$_2$O)O$_{39}$]$^{n-}$, Y= Mn, Fe, Ni and Zn) were also prepared. The catalytic materials were tested in the oxidation of geraniol and (+)-3-carene in acetonitrile in the presence of H_2O_2, using ammonium acetate as the co-catalyst. It was observed that the association [(MnClTDCPPyP)H]H$_2$[PW$_{12}$O$_{40}$]·4H$_2$O·3CH$_3$OH (Figure 35) showed the best performance, affording conversions significantly higher than those obtained with the corresponding porphyrin alone, without significant change in the regio-, chemo- and stereoselectivity of the desired oxidation reactions: geraniol gave 6,7-epoxygeraniol as the major product, and (+)-3-carene was preferably oxidized to the (+)-3,4-epoxycarane (Figure 36).

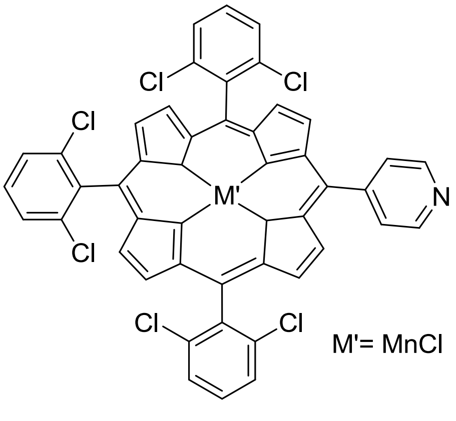


Figure 35. MnClTDCPPyP structure.

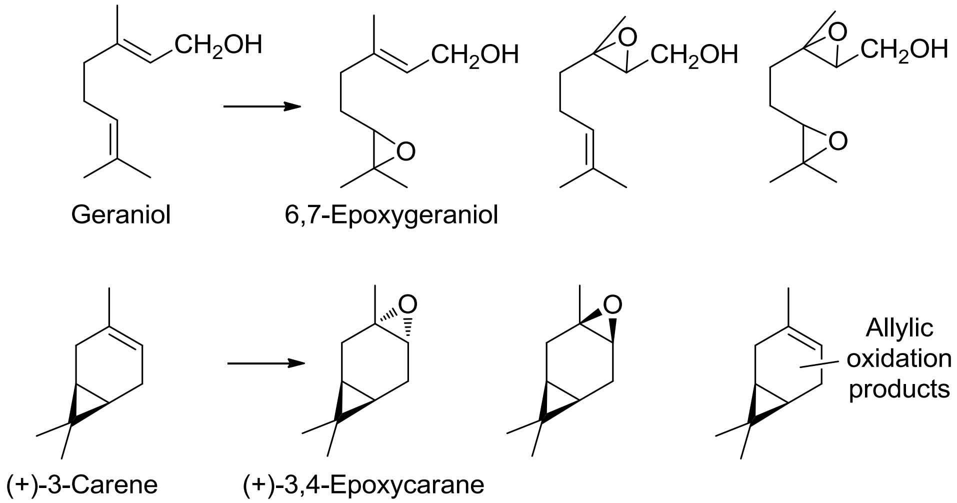


Figure 36. Oxidation of geraniol and (+)-3-carene.

A variety of Keggin-type tungstoborates of formula $(TBA)_4H_2[Mn(H_2O)BW_{11}O_{39}]\cdot H_2O$, $(CTA)_4H_2[Mn(H_2O)BW_{11}O_{39}]\cdot 10H_2O$ and $(TBA)_4H[BW_{12}O_{40}]\cdot 7H_2O$ were used for the oxidation of monoterpenes in an acetonitrile medium employing H_2O_2 as oxidant agent. The studied monoterpenes include geraniol, nerol, (+)-3-carene, thymol, and carvacrol. When geraniol and nerol were used as starting materials, reactions took place at room temperature, while reflux temperature was used for (+)-3-carene, thymol and carvacrol. Geraniol and nerol gave products preferentially epoxidized at the C2–C3 double bond, whereas the (+)-3-carene could afford only the α-epoxide. Results also showed that the oxidation of thymol and carvacrol yielded a mixture of benzoquinones[290].

α-Pinene oxide was obtained from α-pinene through an oxidation reaction with H_2O_2 that took place employing $Na_5PV_2Mo_{10}O_{40}$ supported on mesoporous molecular sieves MCM-41 and MCM-41 modified with amino groups as catalysts. Results showed that with all catalytic materials tested, the major product was α-pinene oxide, while verbenone and verbenol were produced as minor products (Figure 37)[291].

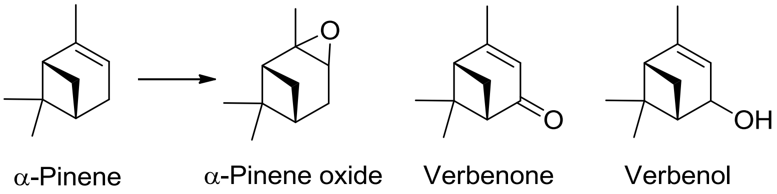


Figure 37. α-Pinene oxidation: α-pinene oxide, verbenone and verbenol preparation.

Other catalytic materials employed for α-pinene oxide preparation from α-pinene include: $(TBA)_4H[PW_{11}Co(H_2O)O_{39}]$ supported on SiO_2, APTES-modified SBA-15 and mesoporous cellular foams (MCF) (with $(TBA)_4H[PW_{11}Co(H_2O)O_{39}]/NH_2$-MCF the selectivity to *α*-pinene epoxide reached 94% at 96% conversion after 2 h)[292,293] and a heterogeneous catalyst obtained by exchange of a commercial macroreticular Amberlite IRA-900 with the Venturello anion $\{PO_4[WO(O_2)_2]_4\}^{-3}$. With this catalyst limonene, geraniol, nerol and 3-carene were efficiently converted to their corresponding epoxides in an acetonitrile medium at low reaction temperatures[294].

3.1.2. Verbenol and verbenone production

Verbenol and verbenone are commonly employed in the pharmaceutical industry[295]. Verbenol and verbenone were prepared from α-pinene oxidation using three catalytic materials: $(TBA)_7H[\{PW_{11}O_{39}Zr(\textit{í}\text{-}OH)\}_2]$ (1), $(TBA)_8[\{PW_{11}O_{39}\text{-}Zr(\textit{í}\text{-}OH)\}_2]$ (2), and $(TBA)_9[\{PW_{11}O_{39}Zr\}_2(\textit{í}\text{-}OH)(\textit{í}\text{-}O)]$ (3). Results are listed in Table 7. As can be seen, the catalyst (3) is almost inactive for the selected reaction, and the authors concluded that acid protons are crucial for the catalytic activity of these Zr-containing heteropolycompounds[296].

Table 7. Verbenol and verbenone production from α-pinene[a].

Catalyst	α-pinene conversion (%)	Yield (%)	
		Verbenol (%)	Verbenone (%)
1	40	21	18
2	25	35	40
3	7	Nd	Nd

[a] *Reaction conditions:* α-pinene, 0.1 M, H_2O_2, 0.12 M, Zr, 0.0025, acetonitrile, 1 h.

Catalysts consisting of titanium- and cobalt-monosubstituted Keggin heteropolyanions, $[PW_{11}CoO_{39}]^{-5}$ and $[PW_{11}TiO_{40}]^{-5}$, which were electrostatically bound to the chromium terephthalate polymer matrix MIL-101, were also employed for verbenol and verbenone production. Results showed that the MIL-supported Ti-containing polyoxometalate demonstrated fairly good catalytic activity and selectivity in α-pinene allylic oxidation with hydrogen peroxide, whereas the MIL-supported Co-containing polyoxometalate catalyzed α-pinene allylic oxidation by molecular oxygen (Figure 38)[297].

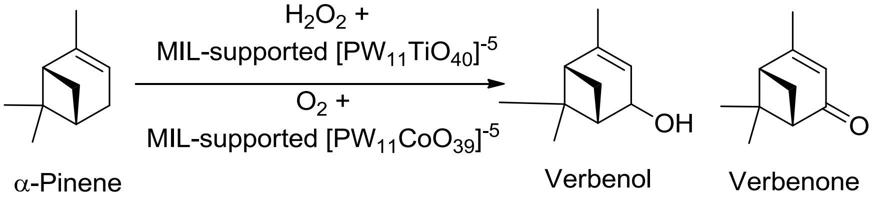


Figure 38. Verbenol and verbenone production from α-pinene.

Maksimchuk and coworkers prepared $H_5PW_{11}TiO_{40}/SiO_2$ by a sol-gel method. By using this material at 303 K in an acetonitrile medium, the selectivity towards verbenol/verbenone attained 80–82% at 8–15% conversion of α-pinene and, 68% selectivity at a conversion value of 28%[298].

The use of a Co-containing polyoxometalate $(TBA)_4H[PW_{11}Co\text{-}(H_2O)O_{39}]$ electrostatically bound to various NH_2-modified silica matrixes, including SiO_2-xerogels, MCF, and SBA-15, was also reported. The authors found that α-pinene autoxidation in the presence of the supported Co-containing polyoxometalates leads to the formation of the allylic oxidation products verbenol and verbenone, with selectivity values in the range of 60–70% at a conversion of about 20%[292].

3.2. Isomerization reactions

3.2.1. Campholenic aldehyde production

Campholenic aldehyde is a constituent of the East Indian sandalwood oil, and is an intermediate in the manufacture of sandalwood-like fragrances, such as Sandalor® (Givaudan), Bacdanol® (IFF), Brahmanol® (Dragoso) and Polysantol® (Firmenich).

PW supported on SiO_2 has been used for α-pinene oxide isomerization to campholenic aldehyde working at 288-313 K in a cyclohexane medium (Figure 39). After 5 min the conversion was total with a selectivity to campholenic aldehyde of 70%[299].

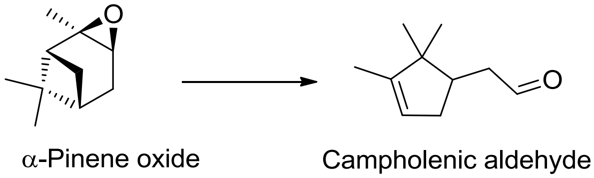


Figure 39. α-Pinene oxide isomerization to campholenic aldehyde.

3.2.2. trans-Carveol production

trans-Carveol is a constituent of the Valencia orange essence oil, and is an expensive ingredient in both the perfume and the flavor industries.

The isomerization of α-pinene to *trans*-carveol (Figure 40) was performed using PW as catalyst at different reaction temperatures (from 373 to 393 K). Conversion and selectivity greater than 80% for reaction times of less than 2 h were achieved[300].

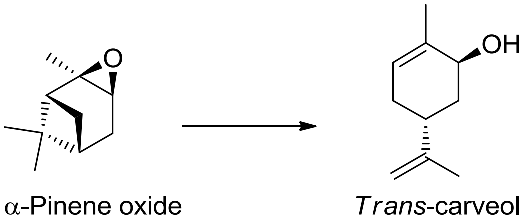


Figure 40. α-Pinene isomerization to trans-carveol.

3.2.3. Camphene production

Camphene is commonly used in the flavor industry, and also as a synthesis intermediate. Moreover, camphene can be variously functionalized[30] to enlarge its possible applications.

The α-pinene isomerization to camphene was performed using SiO_2-supported PW as catalyst. Working at 373 K for 1 h, a conversion of 90% was achieved, whereas camphene and limonene (the main by-products) selectivity values were 50 and 28% respectively. After reaction, the catalyst was separated by centrifugation and reused three times showing no significant loss of activity and selectivity. The authors proposed that the transformation of α-pinene is likely to occur *via* a carbenium-ion mechanism (Figure 41)[301].

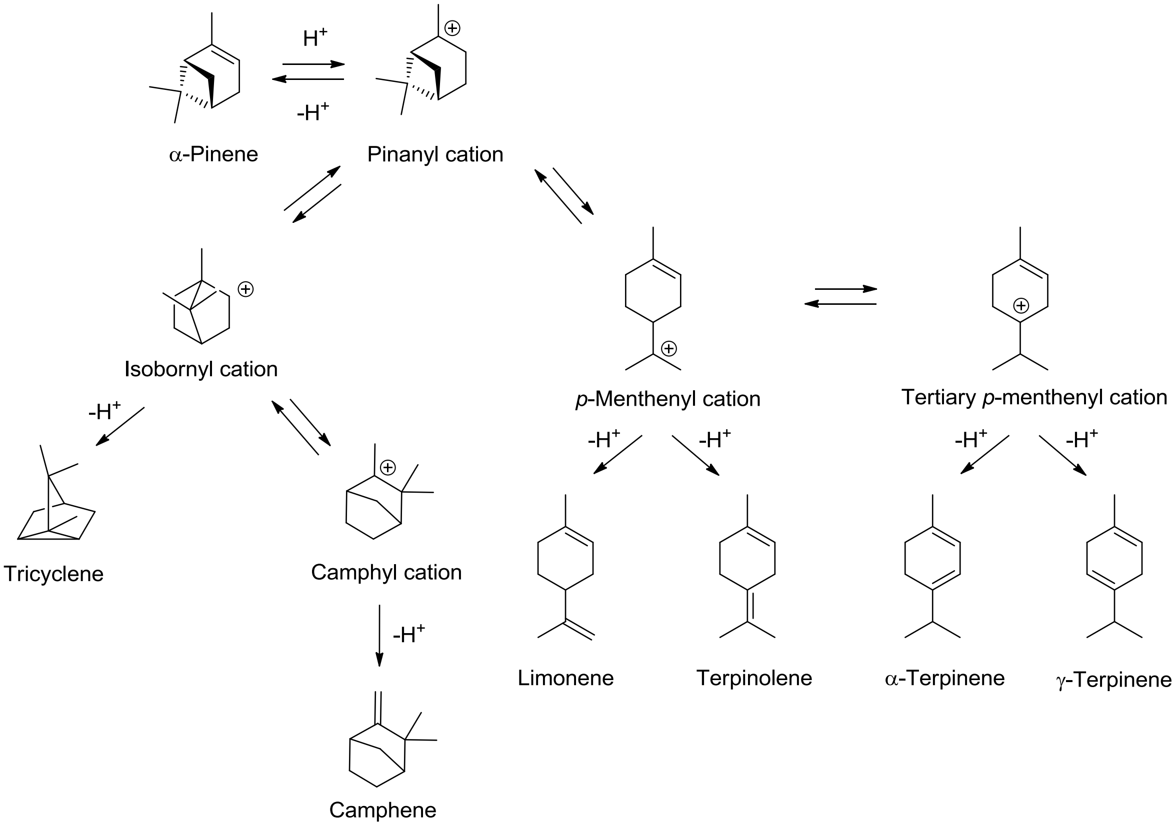


Figure 41. Possible pathways in the isomerization of α-pinene *via* a carbenium-ion mechanism.

PW supported on SiO_2 was used for camphene preparation through α-pinene isomerization by working at 373 K for 1 h[302] obtaining both camphene and terpinene as the main products. When working at lower temperature (333 K), the conversion of α-pinene was lower than 20% whereas the selectivity to camphene was greater than 50%[303].

Another support for PW consisted of natural zeolite rich in clinoptilolite, which is a zeolite mineral series having the distinctive framework topology of heulandite and the ratio

Si/Al>4[304]. By employing this material a camphene selectivity of about 40% was obtained[305]. PW supported on several carriers that include SiO_2, TiO_2 and ZrO_2, were used as catalysts in the α-pinene isomerization to camphene. The authors established the following activity order according to the support employed: $SiO_2 > TiO_2 > ZrO_2$. They correlated the activity order with the number and strength of acid sites. Using PW/SiO_2, conversion and selectivity values were 93 and 37% working at 353 K, after 2h whereas those values were 20 and 52% working at 318 K[306].

3.2.4. Dihydrocarvone production

Dihydrocarvone is a valuable synthetic intermediate compound, and is widely used as ingredient in the flavor industry.

Dihydrocarvone has been produced from limonene oxide, which can be obtained from limonene epoxidation or extracted from citric essential oils. The reaction was catalyzed by $Cs_{2.5}$PW and both bulk and silica-supported PW in liquid phase using a range of aprotic solvents. When limonene oxide isomerization occurred in the presence of PW, dihydrocarvone was obtained in a 50–60% yield along with only one or two minor products: an aldehyde, or carveol and exo-carveol, which are also valuable fragrance compounds (Figure 42). The best selectivity values were obtained in oxygenated solvents (such as 1,4-dioxane), which dissolve PW. $Cs_{2.5}$PW was also tested as heterogeneous catalyst using different solvents. It was observed that dihydrocarvone was the major reaction product in all the solvents, achieving the highest dihydrocarvone yield (82%) when using 1,4-dioxane at room temperature[307].

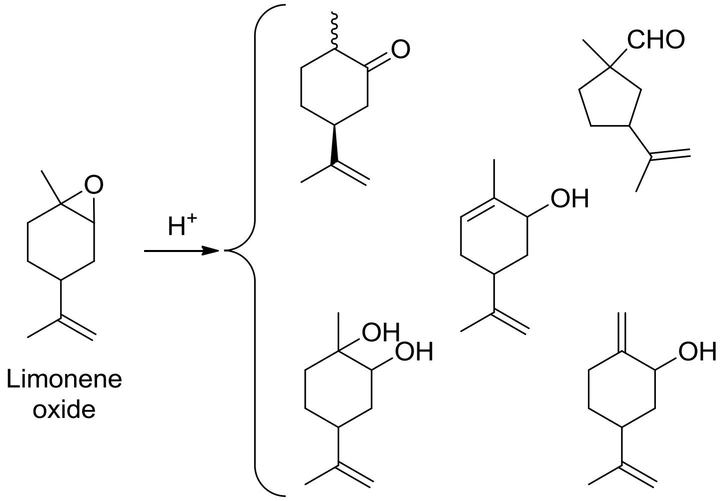


Figure 42. Main products obtained in the acid-catalyzed transformation of limonene oxide.

3.2.5. Isolongifolene production

Isolongifolene is commonly used as an intermediate in the perfumery industry: their oxygenated derivatives have extremely rich woody and floral odor, occupying a vintage place in this industry.

Da Silva and coworkers studied isolongifolene preparation from longifolene using SiO_2-supported PW as catalyst (Figure 43). After 70 min at 373 K, longifolene conversion reached 96% with an isolongifolene selectivity of 98%. After reaction, the catalyst was separated by centrifugation and reused twice showing no significant loss of activity and selectivity[301].

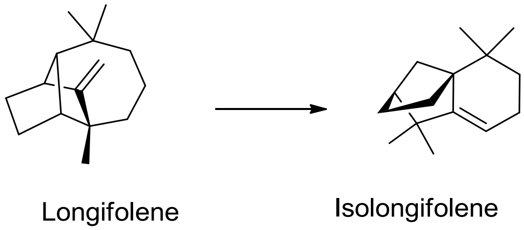


Figure 43. Longifolene isomerization to isolongifolene.

3.2.6. 1,4-Cineole and 1,8-cineole production

The cineoles, symmetrical monoterpenic cyclic ethers, are commonly found as components of essential oils from aromatic plants. 1,8-Cineole (1,8-epoxy-*p*-menthane also known as Eucalyptol) has a characteristic fresh and camphoraceous fragrance, and pungent taste. A 1,8-cineole isomer, the 1,4-cineole (1,4-epoxy-*p*-menthane), is also a widely distributed natural oxygenated monoterpene that can be found in the same plant species, although usually in much lower concentrations than 1,8-cineole. 1,4-Cineole is a valuable intermediate for the preparation of some herbicides[308–313].

The isomerization of α-terpineol to 1,8- cineole and 1,4-cineole was performed using bulk and silica-supported PW (Figure 44). It was found that 1,8-cineole and 1,4-cineole were obtained with selectivity values of 25% and 23–27%, respectively, at 50–90% α-terpineol conversion using bulk PW in a nitrobenzene solution, at 313 K. In the case of the heterogeneous system, the selectivity values obtained were 35% and 25% for 1,8-cineole and 1,4-cineole, respectively, at 70–100% conversion in a cyclohexane solution at 333 K using SiO_2-supported PW catalyst[313].

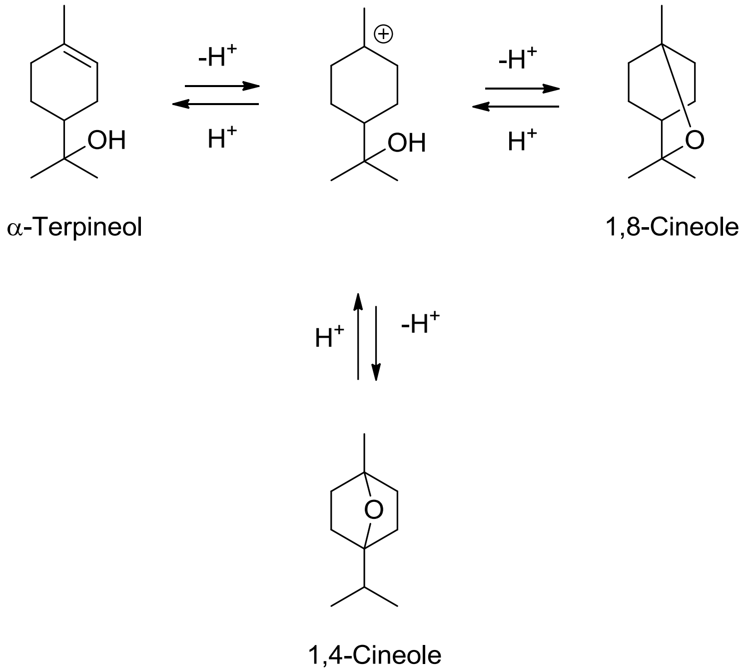


Figure 44. Isomerization of α-terpineol to 1,8-cineole and 1,4-cineole.

3.2.7. p-Cymene production

p-Cymene is an aromatic organic compound related to a monoterpene and it is a precursor of carvacrol. This substance constitutes an important intermediate commonly used for the production of drugs, fungicides and pesticides, and is also used as flavoring agent. In mice, *p*-cymene demonstrated analgesic and anti-inflammatory properties[314]. *p*-Cymene was also employed to produce some organoruthenium-containing heteropolytungstates, such as $[\{Ru\text{-}(L)\}_2(\alpha\text{-}XW_{11}O_{39})_2WO_2]^{-m}$ (L= benzene, *p*-cymene; X= Ge^{IV}, Si^{IV}, m= 10; X= B^{III}, m= 12)[315], $[\{PW_{11}O_{39}Ru(\eta^6\text{-}p\text{-cymene})\}_2\{WO_2\}]^{-8}$ [316], the monomeric species (type-m) $[\{(p\text{-cymene})Ru(H_2O)\}PW_{11}O_{39}]^{-5}$ and the dimeric species (type-d) $[(\{(p\text{-cymene})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]^{-8}$ [317].

Through the oxidation of *p*-cymene, it is possible to obtain 4-methylacetophenone, a key intermediate in the manufacture of perfumes, or 4-isopropylbenzaldehyde, commonly used as flavoring agent[318,319]. The first-mentioned oxidation transformation was carried out with aqueous H_2O_2 in acetonitrile at 353 K and was catalyzed by TBA salts of $[XW_{11}Fe^{III}(H_2O)O_{39}]^{-n}$ (X= P, B or Si)[320].

p-Cymene has been produced through a two-step procedure using PW impregnated on calcined SiO_2 as a bifunctional catalyst. In the first step, α-pinene is transformed into camphene and terpinene by isomerization on the acid sites. Almost total conversion is achieved after 1 h at 373 K. Then, products are treated in order to produce the dehydrogenation into the desired product on the acid and redox sites of the catalytic material. At 433 K, the conversion obtained was greater than 60% after 1 h, and higher conversion values could be obtained with longer reaction times, even with lower relative amounts of the catalyst. 3-*p*-Menthene and carvomenthene are by-products obtained in a low quantity by a disproportionation reaction. A complete view of each transformation is shown in Figure 45[302].

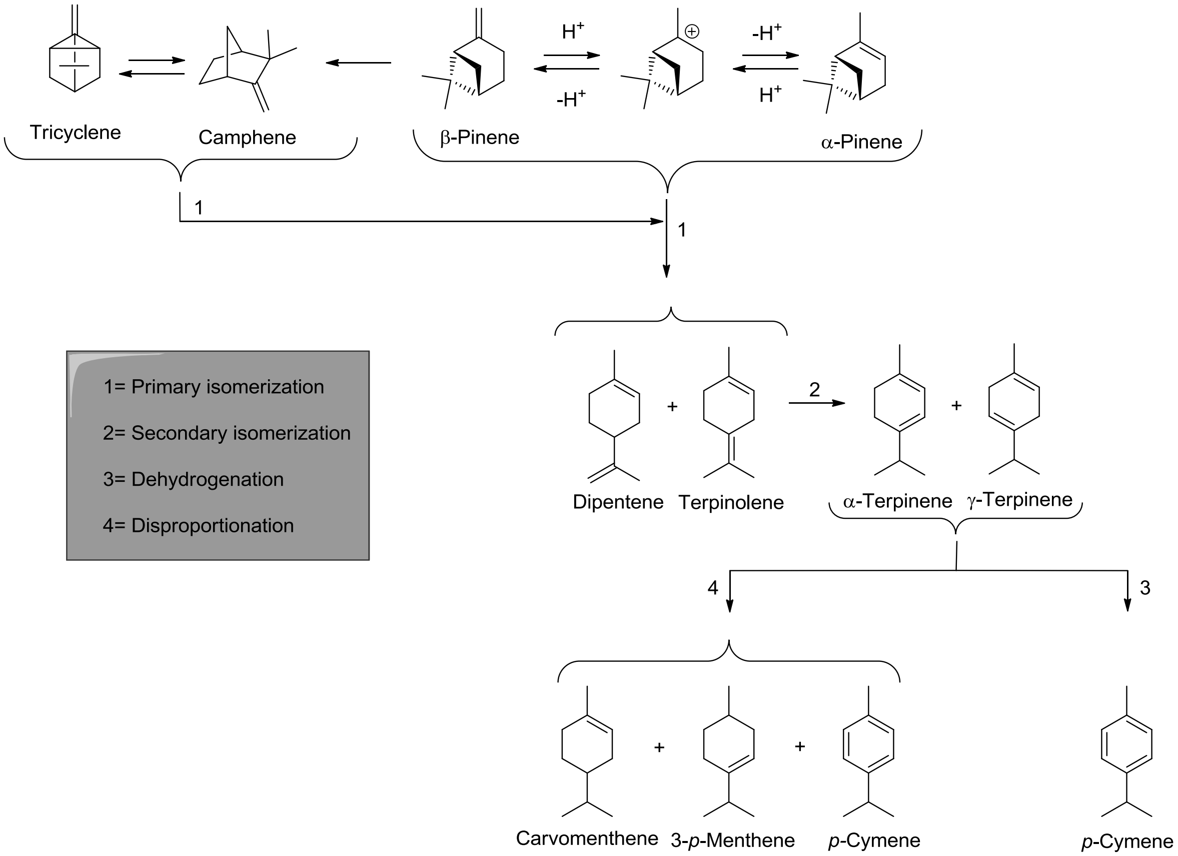


Figure 45. Transformation of α-pinene into *p*-cymene, among other products.

3.3. Cyclization reactions

3.3.1. Ionone production

Ionones, citral-derived compounds, are commonly used in the preparation of natural products (such as carotenoids, edulan derivatives and theaspiranes), and in the pharmaceutical and fragrance industries. The β-ionone isomer is a key reactant in vitamin A synthesis, while α- and γ- isomers are employed for fragrance preparation due to their intrinsic odor characteristics depending on the isomer used[321].

Ionones could be prepared by a two-step process that includes the preparation of pseudoionone from citral and acetone aldol condensation, and then the cyclization of the pseudoionone to give the corresponding ionone (Figure 46).

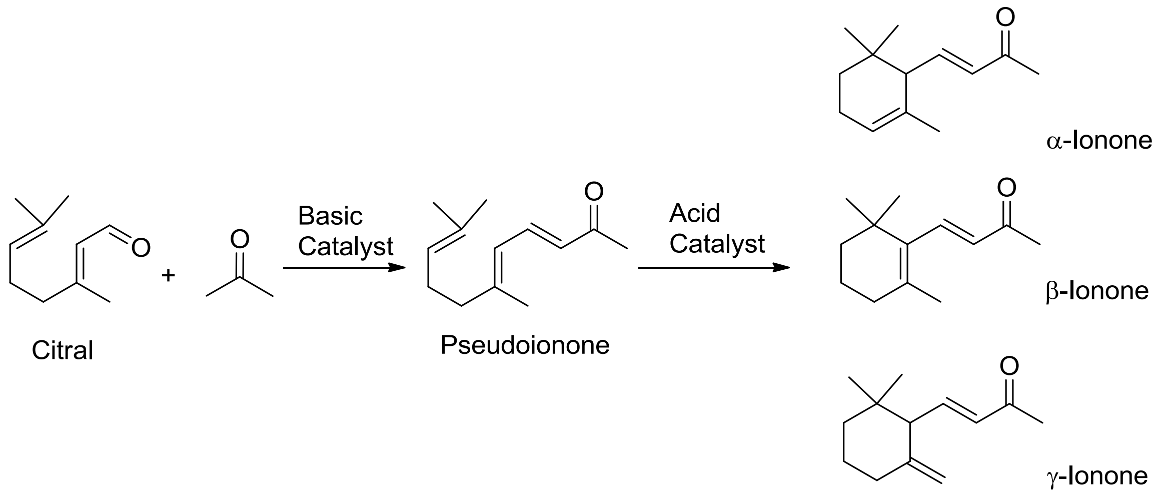


Figure 46. Ionone preparation

Diez *et al.*[322] prepared ionone isomers from pseudoionone through its cyclization employing several catalysts, which included bulk and SiO_2-supported PW, and bulk $Cs_{2.5}PW$. After 1.5 h at 383 K, an ionone yield of 79 % was obtained with 58.5 wt% PW/SiO_2 as catalyst. The authors also found that the isomer distribution can be controlled by varying both the reaction temperature and times. Then, they reported the possible reaction pathways for ionone formation from pseudoionone with a heteropolyacid catalyst[323,324].

3.3.2. Isopulegol production

Isopulegol is widely employed in the flavor and perfume industries for the production of fragrances with blossom compositions and for manufacturing menthol, which is an important ingredient of various cosmetics and pharmaceuticals.

Da Silva *et al.*[325] used SiO_2-supported PW as catalyst for the liquid-phase cyclization of citronellal into isopulegol (Figure 47). Reactions took place at 288-313 K in cyclohexane, achieving total conversion and 100% selectivity to (-)-isopulegol and (+)-neo-isopulegol, with more than 80% of stereoselectivity to the more valuable product (-)-isopulegol. The catalyst was reused six times and no appreciable loss of activity was observed.

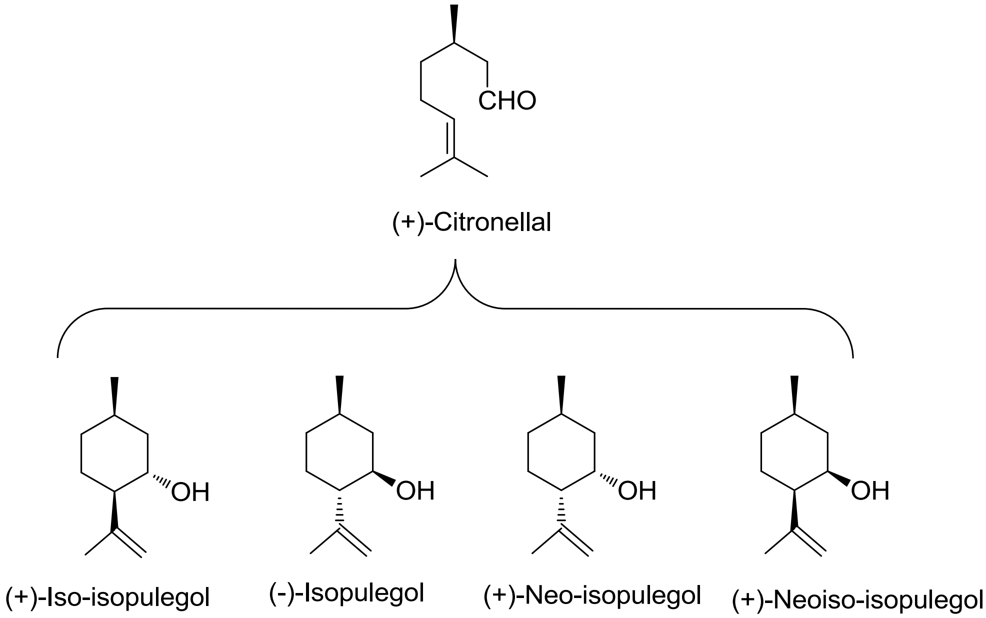


Figure 47. Citronellal cyclization.

PW was also supported on MCM-41and applied in the intramolecular cyclization of (+)-citronellal. Different heteropolyacid loadings were tested, but the 20% PW/MCM-41 sample was found to be the most active. Under 1 h of reaction, (-)-isopulegol was obtained with 65% selectivity when the system presented 96% conversion[326].

A dialuminum-substituted silicotungstate $TBA_3H[\gamma\text{-}SiW_{10}O_{36}\{Al(OH_2)\}_2(\mu\text{-}OH)_2].4H_2O$, was prepared through the reaction of the potassium salt of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with 2 equivalents of $Al(NO_3)_3$ in an acidic aqueous medium. According to the X-ray crystallographic analysis, a monomer of the γ-Keggin dialuminum-substituted silicotungstate with a $\{Al_2(\mu\text{-}OH)_2\}$ diamond core was obtained. The catalytic material was tested in the intramolecular cyclization of (+)-citronellal into (-)- isopulegol, obtaining diastereoselectivity and yield values of 87% and 93%, respectively, working at 348 K in acetonitrile for 10 h. The cyclization of 3-methylcitronellal was also evaluated under the same reaction conditions, and it was found that the total yield was greater than 99%, corresponding to an isomer ratio *trans: cis* (98:2)[327].

A series of di- and tetranuclear zirconium or hafnium-containing polyoxometalates with γ-Keggin silicotungstate units of $Cs_{10}[(\gamma\text{-}SiW_{10}\text{-}O_{36})_2\{Zr(H2O)\}_2(\mu\text{-}OH)_2]$ $18H_2O$ (Zr2), $Cs_{10}[(\gamma\text{-}SiW_{10}O_{36})_2\{Hf(H_2O)\}_2(\mu\text{-}OH)_2]\cdot 17H_2O$ (Hf2), $Cs_8[(\gamma\text{-}SiW_{10}O_{36})_2\{Zr(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]$ $26H_2O$ (Zr4), and $Cs_8[(\gamma\text{-}SiW_{10}O_{36})_2\{Hf(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]$ $23H_2O$ (Hf4) were prepared, characterized and employed for the catalytic intramolecular cyclization of (+)-citronellal. Reactions were carried out at 348 K in Ar atmosphere, and the results showed that the tetranuclear zirconium and hafnium complexes Zr4 and Hf4 presented higher catalytic activity for the desired reaction (giving conversion values greater than 90%), while the dinuclear zirconium and hafnium complexes were inactive[328].

3.3.3. Menthol production

Menthol is an important ingredient of various cosmetic, pharmaceutical and other specialty products. Among eight isomers of menthol, only (-)-menthol possesses a characteristic odor and produces a physiological cooling effect.

Da Silva Rocha *et al.*[329] used Pd-PW/SiO_2 as bifunctional catalyst for the one-pot transformation of (+)-citronellal to menthol (Figure 48). The first step involves the acid-catalyzed cyclization of (+)-citronellal, followed by Pd-catalyzed hydrogenation. The authors achieved a menthol yield of 92% at total citronellal conversion working at 343 K and 35 bar of H_2 in cyclohexane, with a 85% stereoselectivity to the desired (-)-menthol.

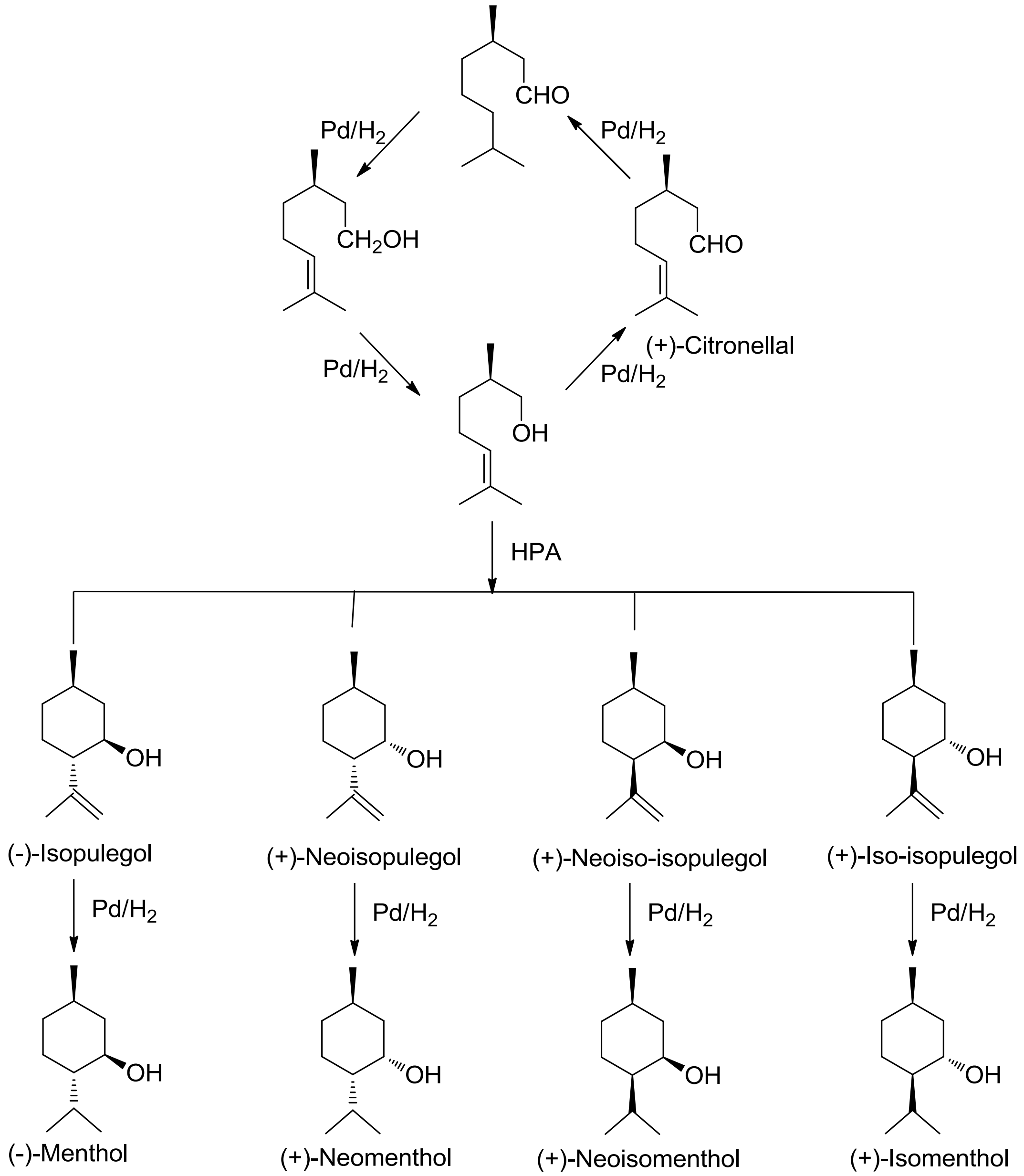


Figure 48. Transformation of (+)-citronellal to menthol.

3.4. Esterification and etherification reactions

3.4.1. α-Terpineol and α-terpinyl ether/ester production

α-Terpineol and α-terpinyl ethers and esters are widely used in the flavor industry. In particular, α-terpinyl methyl ether is a compound with grapefruit-like smell[281].

Castanheiro *et al.*[330] prepared PMo immobilized in polymeric matrixes of polyvinyl alcohol (PVA) and polydimethylsiloxane (PDMS), and used these catalytic membranes in the hydration of α-pinene. While the PMo/PVA membranes were prepared by entrapping PMo in a cross-linked PVA matrix (accomplished by heating PVA with succinic acid), the preparation of PMo/PDMS membranes by directly entrapping the HPA in the polymer matrix was not possible. The authors attributed this fact to the heteropolyacid since it could inhibit the polymer cross-linking. An alternative preparation procedure, previously reported, was used in which PMo was incorporated in the supercages of USY-zeolite. When this catalyst was used for α-pinene hydration at 323 K in aqueous acetone, a selectivity of 75% at total conversion was achieved[331]. Thus, PMo was directly synthesized inside the zeolite supercages, and then the PMo/USY catalyst was dispersed in the polymeric matrix. Working at 323 K in aqueous acetone, and in the case of PVA membranes, the best results were obtained using PMo10/PVA20 and PMo10/PVA30 (selectivity values of 70–75% at 90% conversion, the code PMo*x*/PVA*y* means a membrane prepared by adding *x*% (w/w) of PMo relative to the PVA amount, with *y*% of –OH groups esterified in each PVA chain). Using the membrane PMo-USY/PDMS under the same reaction conditions, a maximum selectivity of 65% is achieved at 80% conversion. Reuse tests revealed that in both cases, PMo/PVA and PMo-USY/PDMS, the catalyst activity increases in the subsequent uses of the same membrane. The researchers explained this in terms of the probable interaction between retained α-terpineol and the polymer matrix, promoting a better diffusion of pinene molecules to the catalyst active sites[330]. In order to improve the hydrophobic properties of PMo/PVA catalyst, the membrane material cross-linked with succinic acid was modified by treatment with acetic anhydride. Reactions were carried out in the same reaction conditions, and it was found that membrane acetylation improves the transport properties, as reflected by pinene diffusivity. The catalytic activity in the α-pinene hydration reaction increases with the acetylation degree, and the most selective catalyst to α-terpineol is the one that has the most acetylated membrane. The authors made a kinetic-diffusional model, and they finally concluded that the increment in the catalytic activity is mainly due to the improvement of the membrane transport properties for water[332].

Robles-Dutenhefner *et al.*[333] prepared α-terpineol and α-terpinyl acetate by hydration or acetoxylation of limonene, α-pinene and β-pinene using PW as catalyst in both homogeneous and heterogeneous conditions (Figure 49). The authors found that, under optimized conditions, all three substrates give the desired products with total selectivity values from 85% to 90 %, at conversions greater than 70%. Terpinolene, α-terpinene and γ-terpinene are obtained as by-products, and they could be recycled together with the unconverted substrate.

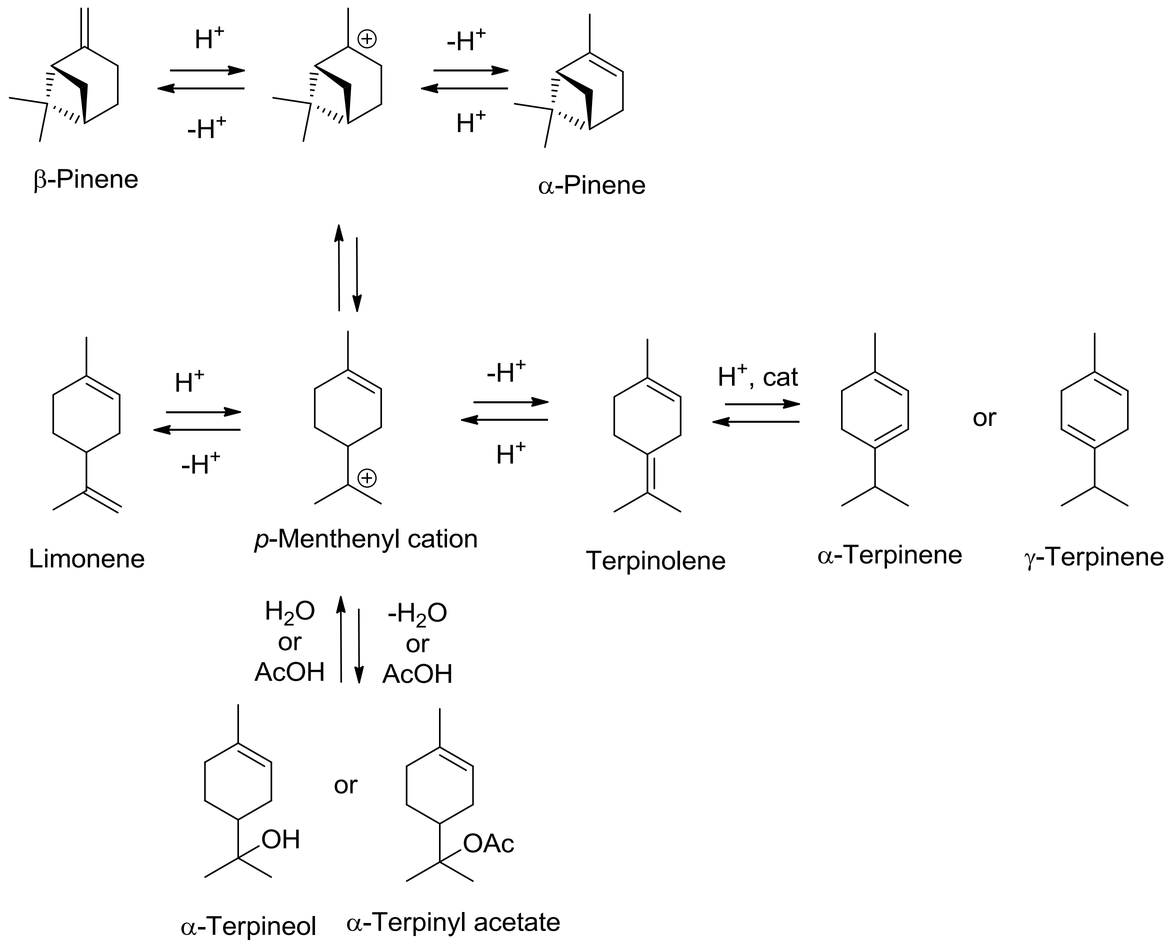


Figure 49. α-Terpineol and α-terpinyl acetate production from limonene, α-pinene and β-pinene.

The hydration and acetoxylation of limonene was also studied by Avila *et al.*[334], but they compared the catalytic activity of PW and PMo, both in bulk and supported on TiO_2 and SiO_2. Working at 313 K in an acetic glacial acid medium for 1 h, the authors found that the limonene transformation reaction begins with exocyclic carbocation formation, which leads to limonene isomers, alcohols or the corresponding acetate formation. As is shown in Table 8, the relation between the desired products (alcohols and acetates) and by-products is higher for the catalysts based on PW.

Table 8. Products obtained through hydration and acetoxylation of limonene over six different catalysts[a].

Catalyst	**Alcohols and acetates/ isomers[b]**
PW	3.5
PW/SiO_2	3.6
PW/TiO_2	3.4
PMo	1.6
PMo/SiO_2	1.8
PMo/TiO_2	2.3

[a] *Reaction conditions:* 313 K, acetic glacial acid medium, 1 h.

[b] (Percentage of hydration + Percentage of acetylation products)/ Percentage of isomerization products.

Pito *et al.*[335] used four catalysts for α-pinene methoxylation: PW, PMo, SiW and SiMo, which were immobilized on SiO_2 *via* the sol-gel method. Experiments were carried out at 333 K in a methanol medium, obtaining α-terpinyl methyl ether as the main product, and bornyl methyl ether, fenchyl methyl ether, limonene and terpinolene as by-products. The authors could establish an order of catalytic activity as follows: SiMo/ SiO_2 < PMo/ SiO_2 < SiW/ SiO_2 < PW/ SiO_2. According to this, they prepared four catalysts with different loadings of PW on SiO_2 (0.025, 0.042, 0.065 and 0.084 g PW/g SiO_2) and observed that the catalytic activity increases with the amount of PW immobilized, achieving a maximum with 0.042 g PW/g SiO_2; at higher amounts of PW on SiO_2 the catalytic activity decreases.

They also developed a kinetic model that fits the experimental data quite well. All tested catalysts achieved selectivity values close to 60%, and in many cases it corresponds to almost complete conversion.

3.4.2. Isoborneol and isobornyl ethers/ester production

Isoborneol, isobornyl ethers and esters are used in the formulations of soap, cosmetic perfumes and drugs, and they also provide popular fruit and pine smells almost identical to natural ones. Isoborneol is used in the industrial production of synthetic camphor[281].

PW and SiW were used as catalysts in the homogeneous hydration of camphene into isoborneol. Reactions were carried out in a H_2O-acetone medium at 323 K for 6 h. It was found that isoborneol was formed almost exclusively, and that PW had a slightly higher turnover number per proton than SiW[336]. PW and SiW were also used to catalyze the reaction of camphene with methyl, ethyl, isopropyl and *tert*-butanol alcohols to produce the corresponding isobornyl ethers. In all studied cases, working at 338 K for 3 h, the desired ethers were obtained as the main product. Results are presented in Table 9[337].

Table 9. Isobornyl ethers obtained from camphene.

Reagent	**Catalyst**	**Product mass (%)**[a]		
		Camphene	**Ether**	**Other**
Methanol	PW	7.5	92.5	Trace
	SiW	8.0	92.0	Trace
Ethanol	PW	13.0	87.0	-

	SiW	13.5	86.5	-
Isopropanol	PW	21.0	19.0	-
	SiW	22.0	78.0	-
Tert-butanol	PW	49.0	51.0	-
	SiW	47.5	52.5	-

[a]*Reaction conditions:* 338 K, 3 h.

The liquid phase acetoxylation and hydration of camphene in both homogeneous and heterogeneous systems for isobornyl acetate and isoborneol production was investigated by Da Silva *et al.*[338] (Figure 50). Reactions were catalyzed by both bulk and SiO_2-supported PW in AcOH/H_2O solutions. Isobornyl acetate and isoborneol were found to be the main reaction products, with total selectivity values close to 100% in both cases, achieving almost total reactant conversion in the case of the homogeneous system. The heterogeneous catalyst was reused three times, and it was found that a loss of 10% of activity took place after each run.

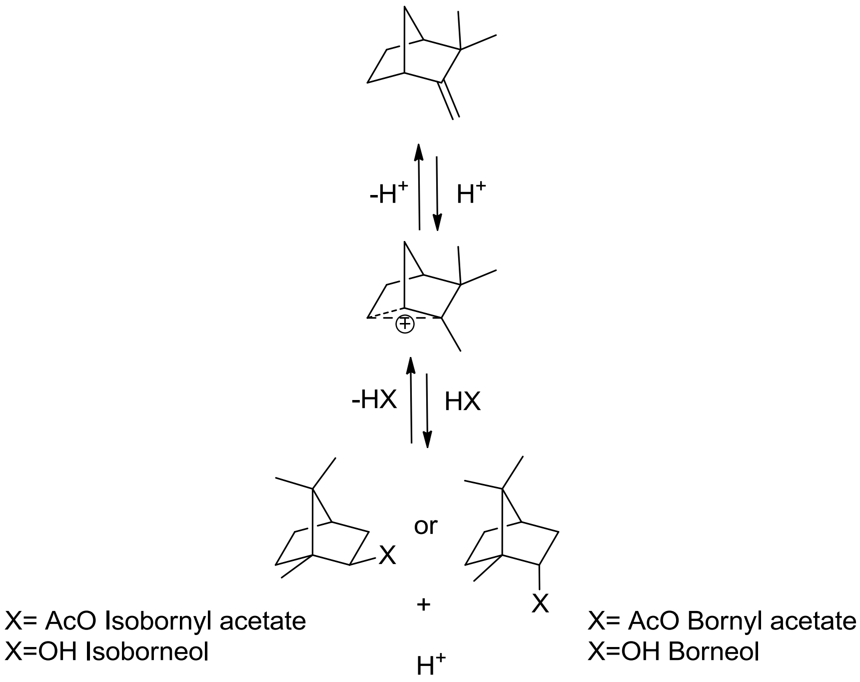


Figure 50. Acetoxylation and hydration of camphene.

Camphene has also been esterified with carboxylic acids, such as acetic, *n*-butyric and *n*-hexanoic acids, using SiO_2-supported PW at 333 K in isooctane. The desired esters were obtained in 80–90% yield, and up to 3000 catalyst turnover number[339].

3.4.3. Terpenic ester production

Many monoterpenoids present natural insecticidal properties, making them key compounds for the development of safe, effective and biodegradable insecticides. Several botanical families for pest control are described, such as *Meliaceae, Rutaceae, Asteraceae, Labiatae, and Malvaceae*. Some commercial pesticides or repellents have D-limonene, menthol and linalool in their formulas. The essential oil of *M. lucida* has insecticidal activity against *C. maculatus* (an economically important pest of several pulses making them unfit for human consumption and unviable for replanting). It was demonstrated that this essential oil is composed of many terpenic esters, such as isobornyl acetate, trans-sabinyl acetate, trans-pinocarvyl acetate, α-terpinyl acetate, cis-carvyl acetate, neryl acetate, and geranyl acetate, among many others[340]. α-Terpinyl acetate is also present in the essential oil of *Artemisia rupestris* L. aerial, whose insecticidal and repellent activity against the booklice *Liposcelis bostrychophila* Badonnel and the isolation of insecticidal and repellent constituents from the essential oil were also investigated. The essential oil, as well as its four active constituents (α-terpineol, α-terpinyl acetate, 4-terpineol and linalool), has potential for development into natural insecticides or fumigants as well as repellents for the control of insects in stored grains[341]

A variety of studies have demonstrated that the derivatization of monoterpenoids increased the activity of those compounds since they are more lipophilic than their parent compounds, which may contribute to a more rapid penetration of them. For example, this testing was done with eugenol, geraniol, linalool, L-menthol, terpineol, and its corresponding acetyl derivatives against *Ae. aegypti* mosquito (the main vector of dengue virus), comparing their activities. The authors concluded that acetylation of the hydroxyl group in general increased the activity in comparison with hydroxyl compounds, and based on LC50 values (ppm), they established and activity order: eugenyl acetate (50.2)> linalyl acetate (119.7)> terpinyl acetate (287.1)> menthyl acetate (308.4)> geranyl acetate (325.5), as compared with monoterpenoids: eugenol (82.8)> linalool (242.6)> terpineol (331.7)> L-menthol (365.8)> geraniol (415.0). From this, they suggested that eugenol acetate may be considered for the development of a formulation to control *Ae. aegypti* larvae[342].

The acetylation of many alcohols was studied by Habibi *et al.*[343] by using $K_5CoW_{12}O_{40}.3H_2O$ as catalyst, with acetic acid or ethyl acetate at reflux. Particularly, (-)-menthol was transformed into (-)-menthyl acetate, achieving yields of 70% after 4 h, using 0.01 mol equivalents of the catalyst with acetic acid, and 35% yield after 8 h, using 0.05 mol equivalents of the catalyst with ethyl acetate. However, when using acetic anhydride in acetonitrile at room temperature, a yield of 94% of (-)-menthyl acetate was achieved after 1.25 h[344]. $AlPW_{12}O_{40}$ has been also used as catalyst for alcohol acetylation with acetic anhydride at room temperature under heterogeneous conditions. Using norborneol, (-)-menthol and terpineol as starting materials, they obtained product yields greater than 90 % for reaction times of 12, 11 and 140 min, respectively[345].

3.5. Miscellanea

3.5.1. trans-Sobrerol production

Trans-Sobrerol is a component commonly used in the flavor industry. Particularly, the *trans*-sobrerol (5-hydroxy- α, α,4-trimethyl-3-cyclohexene-l-methanol) is a terpenoid-like compound that in animal and clinical studies has been shown to have bronchial mucokinetic activity. The drug is commercially available in European countries[346].

Da Silva Rocha *et al.*[300] studied the *trans*-sobrerol preparation from α-pinene catalyzed by PW. Working in an acetone medium at 298 K, a *trans*-sobrerol yield of 71% was achieved in 10 min. The authors proposed a possible reaction mechanism that is shown in Figure 51.

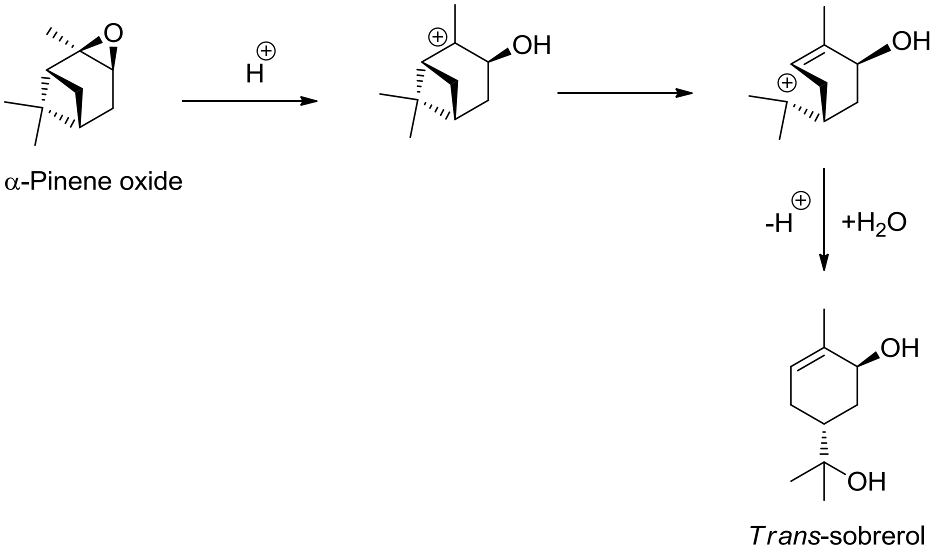


Figure 51. Possible reaction mechanism for *trans*-sobrerol formation from α-pinene.

3.5.2. Oxybicyclo[3.3.1]nonene production

Compounds containing a bicyclo[3.3.1]nonene moiety usually have amber woody odor notes and are used in fine perfumery. Specifically, oxybicyclo[3.3.1]nonene is a compound with a sweet woody smell[281].

Costa and collaborators prepared oxybicyclo[3.3.1]nonene from three different monoterpenes: α-pinene, β-pinene and limonene (Figure 52). The catalytic materials were SiO_2-supported PW and $Cs_{2.5}PW$, which were used in dichloroethane solutions containing crotonaldehyde. For all monoterpenes used, selectivity values were greater than 70%, corresponding to conversions of 85–90%. Results are shown in Table 10[347].

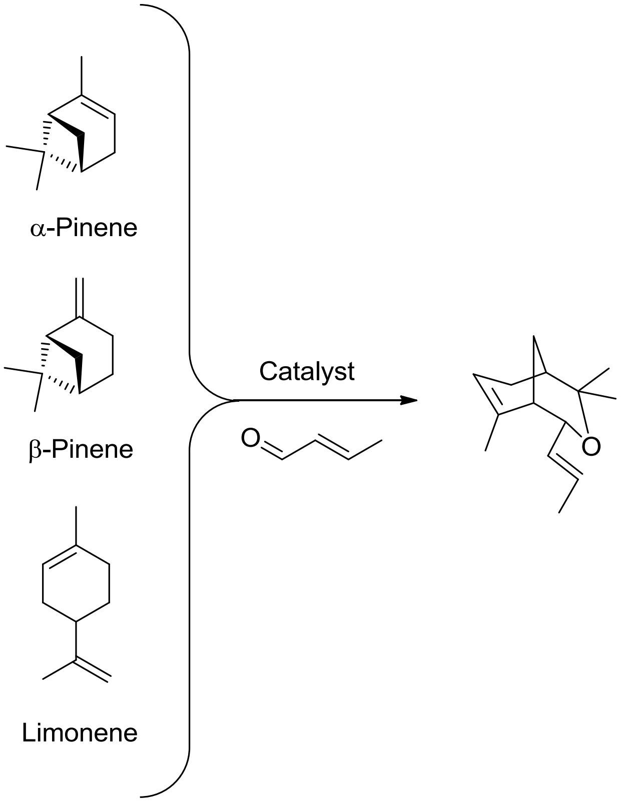


Figure 52. Oxybicyclo[3.3.1]nonene preparation from limonene, α-pinene and β-pinene.

Table 10. Oxybicyclo[3.3.1]nonene preparation from limonene, α-pinene and β-pinene using PW/SiO_2 and $Cs_{2.5}$PW/SiO_2.

Terpene	Catalyst	T (K)	t (h)	Conversion (%)	Selectivity (%)
Limonene	PW/SiO_2	323	5	94	86
		333	5	90	90
	$Cs_{2.5}$PW/SiO_2	323	10	92	94
		343	10	95	94
α-Pinene	PW/SiO_2	298	1	96	82
			3	100	90

	$Cs_{2.5}PW/SiO_2$	298	1	86	86
			3	94	85
β-Pinene	PW/SiO_2	298	1	100	83
			7	100	87
	$Cs_{2.5}PW/SiO_2$	298	1	100	86
			3	100	85

3.5.3. α-Terpinene-maleic anhydride adduct (TMA) production

α-Terpinene-maleic anhydride adduct (TMA) is produced as a result of a Diels-Alder addition reaction. This compound has several applications as intermediate in fine chemistry, and is also used as a monomer for the production of epoxy and terpene resins[281].

Nie *et al.*[348] prepared TMA through the Diels-Alder reaction of α-pinene and maleic anhydride heterogeneously catalyzed by PMo supported on carbon (Figure 53). At the optimum reaction conditions, heating at 353 K for 8 h with 15% PMo/C (load 18.8 wt%), the yield of TMA was greater than 80%. The authors tested the possibility of reuse that offers the selected catalytic material, and they found that after five catalytic cycles there was a minimal loss of activity.

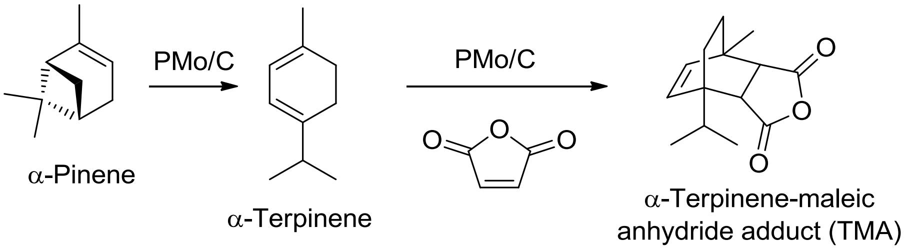


Figure 53. TMA synthesis from α-pinene.

3.5.4. Caryophyllene derivatives production

Caryophyllene is present in some essential oils, such as clove oil, and could be oxidized to caryophyllene oxide, which is a food and cosmetic stabilizer and it is also used as a flavoring substance. Furthermore, various synthetic derivatives of β-caryophyllene also find a use as aromatic additives for tobacco products, as odor fixatives, and in the pharmaceutical industry due to their known biological activities[349].

Maksimchuk *et al.*[297] reported the use of a catalyst based on MIL-101 and a Ti-monosubstituted heteropolycompound whose formula is $[PW_{11}TiO_{40}]^{-5}$. The caryophyllene epoxidation with the green oxidant H_2O_2 was achieved, giving selectivity and conversion values of 100 and 88%, respectively (Figure 54).

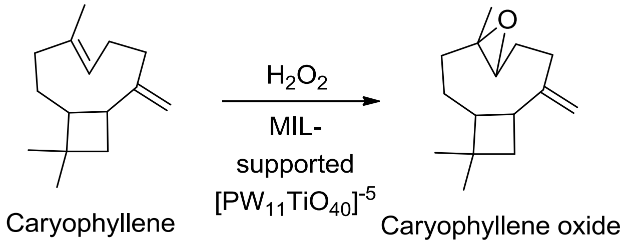


Figure 54. Caryophyllene epoxidation reaction.

The preparation of a mixture containing two stereoisomeric β-caryolanyl acetates from β-caryophyllene achieving a 100% yield was reported by Rocha and collaborators (Figure 55). The reported method used PW as a homogeneous catalyst under mild reaction conditions for 3 to 7 h[350].

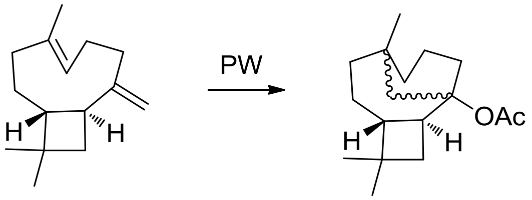


Figure 55. β-caryolanyl acetates preparation from β-caryophyllene.

3.5.5. Polymer production

Polymers formed from terpenes are called terpene resins, and can be used in many industrial applications: as pressure-sensitive adhesives, holt-melt coatings, tackifying agents and additives in rubber, among others[351]. In some cases heteropolycompounds may act as initiators, in others they are the catalysts[352], while in other cases they play the two roles: as both the initiator and the catalyst[353].

Zhu *et al.* tested the catalytic activity of three materials in the polymerization of β-pinene: PW, SiW, PMo. The best results were obtained after 22 h, working under a N_2 atmosphere with dichloromethane at 263 K using PW (pretreated at 473 K): β-pinene conversion was greater than 96.53%, and the polymer selectivity was 63.04%. The authors attributed the differences in catalytic activities to the material acidity. Results are presented in Table 11[351].

Table 11. β-Pinene polymerization.

Catalyst	**Conversion (%)**	**Polymer Selectivity (%)**	**Polymer Yield (%)**	**Mn**	**Polydispersity**
PW	96.53	63.04	60.85	815	1.29
SiW	87.64	32.80	28.75	741	1.24
PMo	64.25	15.97	10.26	682	1.30

Reaction conditions: 263 K, 5 ml of β-Pinene and 5 mL of dichloromethane, 5% of HPA (pretreated at 473 K), 22 h.

These researchers also presented an extended study in which they achieved β-pinene polymerization in the same reaction conditions as in the above-mentioned work, but using other catalytic materials: PW, SiW, PMo, PMo, PW supported on carbon (PW/C), PW supported on SiO_2 (PW/SiO_2) and $Cs_3PW_{12}O_{40}$ (Cs_3PW). As can be seen in Table 12, the best catalytic results continue being those already presented that were obtained using bulk PW[354]. Liu *et al.*[355] also employed PW/C as catalyst for β-pinene polymerization. They achieved a polymer yield greater than 73.0% and a number-average molecular weight of about 860 after 2 h, working at the optimal reaction conditions. Furthermore, PW/SiO_2 was also reported as catalytic material for β-pinene polymerization. The yield value for poly(β-pinene)s was 90.4%, while the number-average molecular weight was about 1100[356].

Table 12. β-Pinene polymerization: extended study.

Catalyst	**Conversion (%)**	**Polymer Yield (%)**
Untreated PW	52	-
PW	96	61
SiW	87	29
PMo	64	11
PW/C	54	-
PW/SiO_2	56	-
Cs_3PW	34	-

Reaction conditions: 283K, 5 mL pinene, 5 mL solvent, 5 wt % HPA, 22 h.

The β-pinene polymerization was also performed using PW, cetyltrimethylammonium phosphotungstate, *n*-butylpyridinium phosphotungstate, antimony phosphotungstate, and Cs_xPW as catalytic materials. These catalysts were tested in dichloromethane at 261 K for 9 h, and the results revealed that cetyltrimethylammonium phosphotungstate offers the highest molecular weight and polymer yield values. Then, six cetyltrimethylammonium phosphotungstates were prepared with different molar ratios of cetyltrimethylammonium to PW (C_{16}/PW): 0.1, 0.2, 0.4, 0.5, 0.7 and 0.8. The best performance was exhibited by the catalyst with the C_{16}/PW ratio equal to 0.5, achieving a polymer yield of 53.0%, molecular weight of 1437[357].

SiW was employed as catalyst for α-pinene polymerization and it was found that SiW acted as both the catalyst and the counter-anion of the growing cationic center. After 1 h under the optimized reaction conditions, the conversion of α -pinene was 90.87%, while the polymer yield value was 62.46%, with an average number of molecular weight of about 600[358].

3.5.6.Terpinyl alcohol production

Terpinyl cyclohexanols are, together with α-campholenic aldehyde derivatives, a successful commercial group of synthetic compounds used for the manufacture of sandalwood-like fragrances. Many terpinyl phenols present antioxidant properties and pharmacological activity[359].

The alkylation of phenol with camphene was performed in the presence of a number of Keggin heteropolyacids supported on zirconium and titanium oxides: PW, SiW and

$H_5PW_{11}TiO_{10}$ ($PW_{11}Ti$) (Figure 56). Reactions took place with a phenol to camphene ratio of 1:1 at 373 K during a period from 2 to 4 h. The authors could establish an activity order of heteropolyacids, valid for both supports used, as follows: PW > SiW > PWTi. Complete results are shown in Table 13[359].

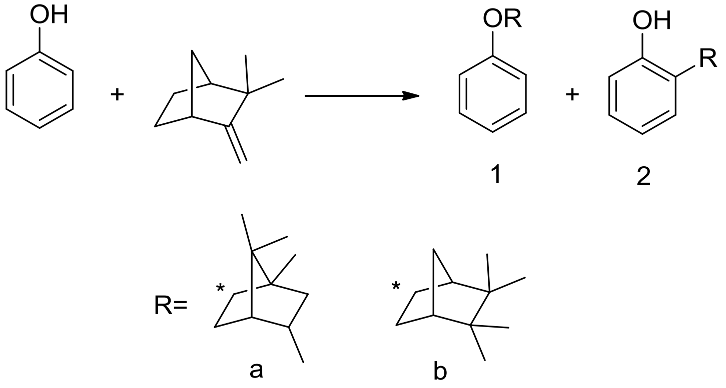


Figure 56. Products in the alkylation of phenol with camphene.

Table 13. Alkylation of phenol with camphene.

Catalyst	**t (h)**	**Conversion (%)**	**Selectivity (%)**			
			1a	1b	2a	2b
PW/ZrO_2	3	75	46	10	13	19
SiW/ZrO_2	4	66	52	15	7	15
$PW_{11}Ti/ZrO_2$	4	61	61	10	7	14
PW/TiO_2	2	64	7		28	49
SiW/TiO_2	3	61	5		28	46

Reaction conditions: Phenol: Camphene molar ratio 1:1, 2-4 h.

Conclusions

Throughout this article, we have shown shown that heteropolycompounds are promising catalysts for the transformation of biomass into valuable chemical compounds. Due to their multifunctionality as acid-base and redox catalysts, they can be used as catalysts in a wide variety of catalytic biomass transformations, including hydrolysis, esterifications, etherifications, oxidations, hydroxyalkylations, dehydrations, or isomerizations. For instance, the strong acitidy of heteropolyacids are exploited in cellulose hydrolysis or biodiesel production, where they can carry out simultaneously esterification and transesterification reactions. Additionally, their acid and redox functionality allow performing one-pot reactions such as the direct transformation of fructose into diformyl furan, while they can also be combined with a hydrogenation or oxidation catalyst to convert, for instance, directly cellulose into sugars alcohols and gluconic acid respectively. Starting with three biomass sources (carbohydrates, oils and fats, and terpenes), more than fifty different product families have been presented, and their corresponding preparations using heteropolyacid catalysts have been conveniently described.

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Catalytic materials

Heteropolycompound	**Abbreviation**	**Section**
$H_3PW_{12}O_{40}$	PW	1.1
$H_4SiW_{12}O_{40}$	SiW	
[1-(3-sulfonic acid) propyl-3-methyl imidazolium]$_{3-n}H_nPW_{12}O_{40}$	$[MIMPSH]_nH_{3-n}PW_{12}O_{40}$,	
[hexadecyltrimethylammonium]$H_2PW_{12}O_{40}$	-	
$Cs_xH_{3-x}PW_{12}O_{40}$	Cs_xPW	
$H_6CoW_{12}O_{40}$	-	
$H_5BW_{12}O_{40}$	BW	
$H_5AlW_{12}O_{40}$	-	
$H_5GaW_{12}O_{40}$	-	
$H_3PMo_{12}O_{40}$	PMo	1.2.1.2
$Ag_3PMo_{12}O_{40}$	Ag_3PMo	
$Sn_{0.75}PMo_{12}O_{40}$	-	
$H_4SiMo_{12}O_{40}$	SiMo	1.2.1.3
Cr[(dodecyl sulfate)$H_2PW_{12}O_{40}]_3$	$Cr[(DS)H_2PW_{12}O_{40}]_3$	
(hexadecyltrimethylammonium)$H_4PW_{11}TiO_{40}$	$(CTA)H_4PW_{11}TiO_{40}$	
(cetyltrimethyl ammonium)$H_3PW_{11}CrO_{39}$	$C_{16}H_3PW_{11}CrO_{39}$	
$Ag_3PW_{12}O_{40}$	Ag_3PW	
$FePW_{12}O_{40}$	-	
Poly(1-vinyl-3-propane sulfonate imidazolium)-$PW_{12}O_{40}$	poly(VMPS)-PW	

(Lysine)$_x$H$_{3-x}$PW$_{12}$O$_{40}$	Ly$_x$PW	
$H_4PMo_{11}VO_{40}$	$PMo_{11}V$	
$H_5PMo_{10}V_2O_{40}$	$PMo_{10}V_2$	
$H_4PW_{11}VO_{40}$	$PW_{11}V$	
$H_5SiMo_{11}VO_{40}$	$SiMo_{11}V$	
$Cs_xH_{3-x}PVMo_{11}O_{40}$	Cs_xPVMo	
(SO_3H-functionalized polymer)$PW_{12}O_{40}$	poly(VMPS)-PW	
$H_4SiW_{12}O_{40}$/MCM-41	SiW/MCM-41	
$H_3PW_{12}O_{40}$/K-10 clay	PW/K-10	
[methylimidazolebutylsulfate]$_3$PW$_{12}$O$_{40}$	[MIMBS]$_3$PW	
Au/$Cs_xH_{3-x}PW_{12}O_{40}$	Au/Cs_xPW	
$[PMo_7V_5O_{40}]^{-8}$	-	1.2.1.4
$[\alpha_1\text{-M}(H_2O)_4P_2W_{17}O_{61}]^{-n}$ (M= Yb^{III}, n= 7, Hf^{IV} and Zr^{IV}, n= 6)	-	1.2.1.5
$M_xH_{3-2x}PW_{12}O_{40}$ (M= Zn, Cu, Cs, Ag)	M_xPW	1.2.1.6
[butylmethylimidazolium]$_3$PW$_{12}$O$_{40}$	[BMIM]$_3$PW	
[butylmethylimidazolium]$_3$PMo$_{12}$O$_{40}$	[BMIM]$_3$PMo	
[butylmethylimidazolium]$_4$SiW$_{12}$O$_{40}$	[BMIM]$_4$SiW	
$H_3PW_{12}O_{40}$/β	PW/β	
$H_3PW_{12}O_{40}$/Sn-β	PW/Sn-β	
$H_3PW_{12}O_{40}$/H-Y	PW/H-Y	
$H_3PW_{12}O_{40}$/H-ZSM-5	PW/H-ZSM-5	

$H_3PW_{12}O_{40}/USY$	PW/USY	
$H_3PW_{12}O_{40}/ReUSY$	PW/ReUSY	
$H_3PW_{12}O_{40}/SBA\text{-}15$	PW/SBA-15	
Iron-modified $H_3PW_{12}O_{40}$	Fe-PW	
$H_4SiW_{12}O_{40}/SiO_2$	SiW/SiO_2	
$H_6P_2W_{18}O_{62}$	WD	
$H_6P_2W_{18}O_{62}/SiO_2$	WD/SiO_2	
$H_3PMo_{12}O_{40}/SiO_2$	PMo/SiO_2	
$H_3PW_{12}O_{40}/ZrO_2$–Si(Ph)Si	PW/ZrO_2–Si(Ph)Si	
$H_3PW_{12}O_{40}/ZrO_2$–Si(Ph)	PW/ZrO_2–Si(Ph)	
$H_3PW_{12}O_{40}/ZrO_2$–Si(Et)Si	PW/ZrO_2–Si(Et)Si	
$H_3PW_{12}O_{40}/ZrO_2$–Si(Ph)Si	PW/ZrO_2–Si(Ph)Si	
$H_3PW_{12}O_{40}/SiO_2$	PW/SiO_2	
$Cs_{3.5}H_{0.5}SiW_{12}O_{40}$	$Cs_{3.5}SiW$	
Ru/[butylmethylimidazolium]$_3PW_{12}O_{40}$	Ru/[BMIM]$_3$PW	
$Ru/Cs_xH_{3-x}PW_{12}O_{40}$	Ru/Cs_xPW	
$K_4SiW_{12}O_{40}.7H_2O$	-	
$H_3PW_{12}O_{40}/SiO_2$	PW/SiO_2	1.2.1.7
$H_3PW_{12}O_{40}/Al_2O_3$	PW/Al_2O_3	
$H_3PW_{12}O_{40}/TiO_2$	PW/TiO_2	
$H_3PW_{12}O_{40}/ZrO_2$	PW/ZrO_2	
$H_3PW_{12}O_{40}/CeO_2$	PW/CeO_2	

$H_3PW_{12}O_{40}$/MCM-41	SiW/MCM-41	1.2.2.1
$Cs_xH_{3-x}PW_{12}O_{40}/SiO_2$	Cs_xPW/SiO_2	
$H_6PV_3Mo_9O_{40}$	PMo_9V_3	
$H_3PW_{12}O_{40}/SiO_2$ (modified with γ-aminopropyl triethoxysilane)	PW/SiO_2(APTES)	1.2.3.1
$H_4GeW_{12}O_{40}$	-	1.2.3.2
$H_4GeMo_{12}O_{40}$	-	
$H_5PV_2W_{10}O_{40}$	$PW_{10}V_2$	1.2.3.3
$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	-	
$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	-	
$Li_{2.4}H_{4.6}PMo_8V_4O_{40}$	-	
$H_{11}P_3Mo_{16}V_6O_{76}$	-	
$H_{17}P_3Mo_{16}V_{10}O_{89}$	-	
$H_7PV_4Mo_8O_{40}$	-	
$H_8PV_5Mo_7O_{40}$	-	
$H_9PV_6Mo_6O_{40}$	-	
$H_{14}[NaP_5W_{30}O_{110}]$	-	1.2.3.5
$Cs_xH_{14-x}[NaP_5W_{30}O_{110}]$ ($x< 10$)	-	
$H_4SiMo_{12}O_{40}/SiO_2$	$SiMo/SiO_2$	2.1.1
$H_3PW_{12}O_{40}/Nb_2O_5$	PW/Nb_2O_5	
(hexadecyltrimethylammonium)$H_4BW_{12}O_{40}$	(CTA)BW	
(hexadecyltrimethylammonium)$H_4TiPW_{11}O_{40}$	(CTA)$H_4TiPW_{11}O_{40}$	

$H_4SiW_{12}O_{40}$/SBA-15	SiW/SBA-15
Picolinic acid- $H_3PW_{12}O_{40}$	PA-PW
[choline]PW	$[(CH_3)_3NCH_2CH_2OH]$PW
$H_3PMo_{12}O_{40}$/A10	PMo/A10
$H_3PMo_{12}O_{40}$/A15	PMo/A15
$H_3PMo_{12}O_{40}$/A20	PMo/A20
$H_3PW_{12}O_{40}$/A10	PW/A10
$H_3PW_{12}O_{40}$/A15	PW/A15
$H_3PW_{12}O_{40}$/A20	PW/A20
$K_2HPW_{12}O_{40}$	-
$H_4PNbW_{11}O_{40}/WO_3\text{-}Nb_2O_5$	-
$H_3PW_{12}O_{40}$/C	PW/C
$H_3PW_{12}O_{40}/Ta_2O_5$	PW/Ta_2O_5
Ta_2O_5/Si(Et)Si-$H_3PW_{12}O_{40}$	Ta_2O_5/Si(Et)Si-PW
Ta_2O_5/Si(Ph)Si-$H_3PW_{12}O_{40}$	Ta_2O_5/Si(Ph)Si-PW
$Ta_2O_5/SiO_2\text{-}[H_3PW_{12}O_{40}/CH_3]$	Ta_2O_5/SiO_2-[PW/CH_3]
Ta_2O_5/SiO_2-[$H_3PW_{12}O_{40}$/Ph]	Ta_2O_5/SiO_2-[PW/Ph]
$H_3PW_{12}O_{40}$–ZrO_2–Si(Et)Si	PW–ZrO_2–Si(Et)Si
$H_3PMo_{12}O_{40}$/SBA-16	PMo/SBA-16
$Ag_xH_{3-x}PW_{12}O_{40}$	Ag_xPW
$Zr_{0.7}H_{0.2}PW_{12}O_{40}$	-
$Zn_{1.2}H_{0.6}PW_{12}O_{40}$	-

$Al_{0.9}H_{0.3}PW_{12}O_{40}$	-	
$Cs_xH_{3-x}PW_{12}O_{40}/SiO_2$	Cs_xPW/SBA-15	
$Ru/Cs_{2.5}H_{0.5}PW_{12}O_{40}$	$Ru/Cs_{2.5}PW$	2.2.1
$H_3PW_{12}O_{40}$/Hexagonal mesoporous SiO_2	PW/HMS	
$H_3PMo_{12}O_{40}$/Hexagonal mesoporous SiO_2	PMo/HMS	
$H_3PMo_{12}O_{40}$/K-10	PMo/K-10	
$Cs_xH_{3-x}PW_{12}O_{40}$/K-10	Cs_xPW/K-10	
$Cs_xH_{3-x}PMo_{12}O_{40}$/K-10	Cs_xPMo/K-10	
$Pt\text{-}Li_xH_{4-x}SiW_{12}O_{40}/ZrO_2$	$Pt–Li_xSiW/ZrO_2$	
$Pt\text{-}K_xH_{4-x}SiW_{12}O_{40}/ZrO_2$	$Pt–K_xSiW/ZrO_2$	
$Pt\text{-}Rb_xH_{4-x}SiW_{12}O_{40}/ZrO_2$	$Pt–Rb_xSiW/ZrO_2$	
$Pt\text{-}Cs_xH_{4-x}SiW_{12}O_{40}/ZrO_2$	$Pt–Cs_xSiW/ZrO_2$	
$Pt\text{-}H_4SiW_{12}O_{40}/ZrO_2$	$Pt–SiW/ZrO_2$	
$Pt\text{-}H_3PW_{12}O_{40}/ZrO_2$	$Pt–PW/ZrO_2$	
$Pt\text{-}H_3PMo_{12}O_{40}/ZrO_2$	$Pt–PMo/ZrO_2$	
$(NH_4)_3PMo_{12}O_{40}/SiO_2$	-	2.2.2
$(NH_4)_3PMo_{12}O_{40}/Al_2O_3$	-	
$H_4SiW_{12}O_{40}/Al_2O_3$	SiW/Al_2O_3	
$H_3PMo_{12}O_{40}/Al_2O_3$	PMo/Al_2O_3	
$H_4SiW_{12}O_{40}$/AS4	SiW/AS4	
$H_4SiW_{12}O_{40}$/A12	SiW/A12	
$H_4SiW_{12}O_{40}$/S11	SiW/S11	

$H_4PMo_{11}VO_{40}$	$PMo_{11}V/ZrO_2$	
$H_3PMo_{12}O_{40}/SiO_2\text{-}Al_2O_3$	$PMo/SiO_2\text{-}Al_2O_3$	
$H_4PMo_{11}VO_{40}/SiO_2\text{-}Al_2O_3$	$PMo_{11}V/SiO_2\text{-}Al_2O_3$	
$H_3PMo_{12}O_{40}$/Al-MCM-41	PMo/Al-MCM-41	
$H_4PMo_{11}VO_{40}$/Al-MCM-41	$PMo_{11}V$/ Al-MCM-41	
$H_3PW_{12}O_{40}/SiO_2\text{-}Al_2O_3$	$PW/SiO_2\text{-}Al_2O_3$	
$Rb_xH_{4-x}SiW_{12}O_{40}/\alpha\text{-}Al_2O_3$	$Rb_xSiW/\alpha\text{-}Al_2O_3$	
$Cs_xH_{4-x}SiW_{12}O_{40}/\alpha\text{-}Al_2O_3$	$Cs_xSiW/\alpha\text{-}Al_2O_3$	
$Rb_xH_{4-x}SiW_{12}O_{40}/\delta,\theta\text{-}Al_2O_3$	$Rb_xSiW/\delta,\theta\text{-}Al_2O_3$	
$Cs_xH_{4-x}SiW_{12}O_{40}/\delta,\theta\text{-}Al_2O_3$	$Cs_xSiW/\delta,\theta\text{-}Al_2O_3$	
$Cs_xH_{3-x}PW_{12}O_{40}/Nb_2O_5$	Cs_xPW/Nb_2O_5	
$H_4SiW_{12}O_{40}/TiO_2$	SiW/TiO_2	
$H_3PMo_{12}O_{40}/TiO_2$	PMo/TiO_2	
$H_4SiW_{12}O_{40}/ZrO_2$-SBA-15	SiW/ZrO_2-SBA-15	
$H_4SiW_{12}O_{40}/ZrO_2$	SiW/ZrO_2	
$H_4SiW_{12}O_{40}/SiO_2\text{-}Al_2O_3$	$SiW/SiO_2\text{-}Al_2O_3$	
$H_4SiW_{12}O_{40}/\gamma\text{-}Al_2O_3$	$SiW/\gamma\text{-}Al_2O_3$	
$H_4SiW_{12}O_{40}/C$	SiW/C	
$H_4SiW_{12}O_{40}/MgO$	SiW/MgO	
$H_4SiW_{12}O_{40}/CeO_2$	SiW/CeO_2	
$H_3PW_{12}O_{40}/\alpha\text{-}Al_2O_3$	$PW/\alpha\text{-}Al_2O_3$	
$Mo_3VO_x/H_4SiW_{12}O_{40}/Al_2O_3$	$Mo_3VO_x/SiW/Al_2O_3$	2.2.3

$K_xH_{3-x}PMoO_{40}$	-	
$PMo_{12}O_{38.5}$	-	
$(CH_3CH_2CH_2)_4N)_3PW_{12}O_{40}$	-	2.2.4
$H_3PW_{12}O_{40}$/Cs-ZrO_2	PW/Cs-ZrO_2	2.2.5
$H_3PMo_{12-x}W_xO_{40}$ (X= 0-12)	-	2.2.6
$H_4SiMo_{12-x}W_xO_{40}$ (X= 0-12)	-	
$H_{3+x}PMo_{12-x}V_xO_{40}$ (X= 0-3)	-	
$H_{3+x}PW_{12-x}V_xO_{40}$ (X= 0-3)	-	
$H_6P_2Mo_{18-x}W_xO_{62}$ (X= 0-18)	-	
$[A\text{-}PW_9O_{34}]^{-9}$/MIL-101 (Cr)	-	3.1.1
$K_7PW_{11}O_{39}$/MIL-101 (Cr)	-	
$K_8SiW_{11}O_{39}$/MIL-101 (Cr)	-	
(tetrabutylammonium)$_7H_3[Co_4(H_2O)_2(PW_9O_{34})_2]$/MIL-101	-	
(tetrabutylammonium)$_4H_3[PW_{11}O_{39}]$	-	
(tetrabutylammonium)$_6[Fe_4(H_2O)_2(PW_9O_{34})_2]$	-	
(tetrabutylammonium)$_7H_3[Co_4(H_2O)_2(PW_9O_{34})_2]$	-	
(tetrabutylammonium)$_4[Fe(H_2O)PW_{11}O_{39}]$	-	
(tetrabutylammonium)$_4H[Co(H_2O)PW_{11}O_{39}]$	-	
$K_4\alpha\text{-}[Fe(H_2O)PW_{11}O_{39}]/SiO_2$	-	
$K_6B\text{-}\alpha\text{-}[(PW_9O_{39})_2Fe_4(H_2O)_2]/SiO_2$	-	
(porphyrin)$_xH_y[PW_{12}O_{40}]$ (x = 0.75 or 1)	-	

(porphyrin)$_x$H$_y$[PMo$_{12}$O$_{40}$] (x = 0.75 or 1)	-	
(porphyrin)$_x$H$_y$[SiW$_{12}$O$_{40}$] (x = 0.75 or 1)	-	
(porphyrin)$_x$H$_y$[SiMo$_{12}$O$_{40}$] (x = 0.75 or 1)	-	
(porphyrin)[PW$_{11}$Fe(H$_2$O)O$_{39}$]	-	
(porphyrin)H[PW$_{11}$Ni(H$_2$O)O$_{39}$]	-	
(porphyrin)H[PW$_{11}$Zn(H$_2$O)O$_{39}$]	-	
(porphyrin)[PW$_{11}$Mn(H$_2$O)O$_{39}$]	-	
(tetrabutylammonium)$_4$H$_2$[Mn(H$_2$O)BW$_{11}$O$_{39}$]	-	
(hexadecyltrimethylammonium)$_4$H$_2$[Mn(H$_2$O)BW$_{11}$O$_{39}$]·	-	
(tetrabutylammonium)$_4$H[BW$_{12}$O$_{40}$]·7H$_2$O	-	
Na$_5$PV$_2$Mo$_{10}$O$_{40}$/MCM-41	-	
Na$_5$PV$_2$Mo$_{10}$O$_{40}$/NH$_2$-MCM-41	-	
(tetrabutylammonium)$_4$H[PW$_{11}$Co(H$_2$O)O$_{39}$]/SiO$_2$	-	
(tetrabutylammonium)$_4$H[PW$_{11}$Co(H$_2$O)O$_{39}$]/NH$_2$-MCF	-	
(tetrabutylammonium)$_4$H[PW$_{11}$Co(H$_2$O)O$_{39}$]/NH$_2$-SBA-15	-	
[(C$_4$H$_9$)N]$_3$PO$_4$[WO(O$_2$)$_2$]$_4$/IRA-900	-	
(tetrabutylammonium)$_7$H[{PW$_{11}$O$_{39}$Zr(í-OH)}$_2$]	-	3.1.2
(tetrabutylammonium)$_8$[{PW$_{11}$O$_{39}$-Zr(í-OH)}$_2$]	-	
(tetrabutylammonium)$_9$[{PW$_{11}$O$_{39}$Zr}$_2$(í-OH)(í-O)]	-	

$(\text{tetrabutylammonium})_4H[PW_{11}CoO_{39}]$/MIL-101	-	
$NaH_4[PW_{11}TiO_{40}]$/MIL-101	-	
$H_5PW_{11}TiO_{40}/SiO_2$	-	
$H_3PW_{12}O_{40}$/natural zeolite rich in clinoptilolite	-	3.2.3
$[\{Ru\text{-(benzene)}\}_2(\alpha\text{-}GeW_{11}O_{39})_2WO_2]^{-10}$	-	3.2.7
$[\{Ru\text{-(benzene)}\}_2(\alpha\text{-}SiW_{11}O_{39})_2WO_2]^{-10}$	-	
$[\{Ru\text{-(}p\text{-cymene)}\}_2(\alpha\text{-}GeW_{11}O_{39})_2WO_2]^{-10}$	-	
$[\{Ru\text{-(}p\text{-cymene)}\}_2(\alpha\text{-}SiW_{11}O_{39})_2WO_2]^{-10}$	-	
$[\{Ru\text{-(benzene)}\}_2(\alpha\text{-}BW_{11}O_{39})_2WO_2]^{-12}$	-	
$[\{Ru\text{-(}p\text{-cymene)}\}_2(\alpha\text{-}BW_{11}O_{39})_2WO_2]^{-12}$	-	
$[\{PW_{11}O_{39}Ru(\eta^6\text{-}p\text{-cymene)}\}_2\{WO_2\}]^{-8}$	-	
(type-d) $[(\{(p\text{-cymene})Ru\}PW_{11}O_{39})_2(\mu\text{-}WO_2)]^{-8}$	-	
$(\text{tetrabutylammonium})_4[Fe(H_2O)BW_{11}O_{39}]$	-	
$(\text{tetrabutylammonium})_4[Fe(H_2O)SiW_{11}O_{39}]$	-	
$(\text{tetrabutylammonium})_3H[\gamma\text{-}SiW_{10}O_{36}\{Al(OH_2)\}_2(\mu\text{-}OH)_2].4H_2O$	-	3.3.2
$Cs_{10}[(\gamma\text{-}SiW_{10}\text{-}O_{36})_2\{Zr(H2O)\}_2(\mu\text{-}OH)_2]\ 18H_2O$	-	
$Cs_{10}[(\gamma\text{-}SiW_{10}O_{36})_2\{Hf(H_2O)\}_2(\mu\text{-}OH)_2]\cdot 17H_2O$	-	
$Cs_8[(\gamma\text{-}SiW_{10}O_{36})_2\{Zr(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]\ 26H_2O$	-	
$Cs_8[(\gamma\text{-}SiW_{10}O_{36})_2\{Hf(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]\ 23H_2O$	-	
PMo/polyvinyl alcohol	PMo/PVA	3.4.1
PMo/polydimethylsiloxane	PMo/PDMS	

$H_3PMo_{12}O_{40}$/USY	PMo/USY	
PMo-USY/polydimethylsiloxane	PMo-USY/PDMS	
$K_5CoW_{12}O_{40}$	-	3.4.3
$H_3PMo_{12}O_{40}$/C	PMo/C	3.5.3
(cetyltrimethyl ammonium)/$H_3PW_{12}O_{40}$	C_{16}/PW	3.5.5
$H_5PW_{11}TiO_{40}/ZrO_2$	$PW_{11}Ti/ZrO_2$	3.5.6

Acronyms

1,2-Propanediol	1,2-PDO
1,3-Propanediol	1,3-PDO
2,5-Diformylfuran	DFF
5-Ethoxymethylfurfural	EMF
5-Hydroxymethylfurfural	HMF
Bisphenol A	BPA
Cellulose sulfuric acid	CSA
Dichloropropanol	DCP
Diphenolic acid	DPA
Empty fruit bunch	EFB
Ethylene oxide	EO
Epichlorohydrin	ECH
Eruca Sativa Gars oils	ESG oils
Formic acid	FA

Hexadecyltrimethylammonium bromide	CTAB
Levulinic acid	LA
Metal-organic framework	MOF
Oil palm trunk	OPT
Propylene oxide	PO
Poly methyl methacrylate ones	PMMA
Polybutylene terephthalate	PBT
Polydimethylsiloxane	PDMS
Polytetrahydrofuran	PTHF
Polyvinyl alcohol	PVA
Silica sulfuric acid	SSA
Sugarcane bagasse	SCB
Tetrahydrofuran	THF
Total reducing sugars	TRS
Turnover frequency	TOF
Water-methyl isobutyl ketone	Water-MIBK
Xanthoceras Sorbifolia Bunge	XSB
α-Terpinene-maleic anhydride adduct	TMA
γ-Aminopropyl triethoxysilane	APTES

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