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Conversion of glucose into levulinic acid with solid metal(IV) phosphate catalysts

Ronen Weingarten [a], Yong Tae Kim [a], Geoffrey A. Tompsett [b], Alejandro Fernández [b], Kee Sung Han [c], Edward W. Hagaman [c], Wm. Curt Conner Jr. [b], James A. Dumesic [a], George W. Huber [a,*]

[a] Univeirsty of Wisconsin–Madison, Department of Chemical and Biological Engineering, 1415 Engineering Dr., Madison, WI 53706, USA
[b] University of Massachusetts–Amherst, Department of Chemical Engineering, 159 Goessmann Lab, 686 North Pleasant St., Amherst, MA 01003, USA
[c] Oak Ridge National Laboratory, Chemical Sciences Division, Building 4100, Room A123, 1 Bethel Valley Rd., Oak Ridge, TN 37831, USA

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ABSTRACT

We have prepared a series of well-characterized solid acid metal(IV) phosphate catalysts and tested them for the two-step dehydration/rehydration reaction to produce levulinic acid from glucose. The catalysts include zirconium (ZrP) and tin (SnP) phosphates with varying ratios of phosphorus to metal(IV). The structural, surface and bulk properties have been investigated using XRD, BET, XPS and ^{31}P solid-state MAS NMR spectroscopy. ZrP is distinguished by a high concentration of polyphosphate species in the bulk phase, as well as increased hydroxyl groups on the surface. ZrP also shows a higher concentration of total acid sites and Brønsted acid sites compared to SnP, as determined by TPD measurements using gas-phase NH_3 and isopropylamine. The catalyst selectivity is a function of the Brønsted to Lewis acid site ratio using either heterogeneous or homogeneous catalysts. Catalytic activity increases with increased Lewis acid sites. The Lewis sites mainly produce fructose *via* isomerization reactions and undesired degradation products (humins). HMF is produced on both Brønsted and Lewis sites, whereas levulinic acid is exclusively produced on Brønsted sites. Zirconium phosphate with a P/Zr molar ratio of 2 is favorable for levulinic acid production due to its inherently high surface area and enhanced Brønsted acidity. This study lays the grounds for further design of improved solid acid catalysts for aqueous phase production of HMF and levulinic from carbohydrates.

1. Introduction

Decline of petroleum supplies and increased levels of greenhouse gases in the atmosphere have stimulated a worldwide initiative to develop clean technologies that utilize a sustainably produced feedstock. Lignocellulosic biomass is a renewable feedstock that has received considerable attention as a sustainable alternative for the production of fuels and chemicals [1–10]. In contrast to other renewable energies, biomass is the only renewable source of fixed carbon, which is essential for the production of liquid hydrocarbon fuels and chemicals [11–13]. One of the key sugar-based building blocks that can be obtained from lignocellulosic biomass is levulinic acid, which has been identified by the US Department of Energy as a top platform chemical [14,15]. Levulinic acid is a five carbon molecule with carboxylic acid and ketone functionalities, and the existence of these two functional groups provides this compound with interesting reactivity pathways.

As a top platform chemical, levulinic acid is the building block to produce a great number of bio-chemicals such as succinic acid, resins, polymers, herbicides, pharmaceuticals, flavoring agents, solvents, plasticizers, and anti-freeze agents. In particular, some levulinic acid derivatives can be used for fuels and oxygenated fuel additives. Esterification of levulinic acid with C_1–C_2 alcohols produces levulinic esters which can be used as diesel additives [16]. Elliott and Frye have also shown that levulinic acid can be hydrogenated in the presence of a bifunctional catalyst to produce methyl-tetrahydrofuran (MTHF) [17], which can directly serve as a gasoline blendstock [18]. Levulinic acid can also undergo hydrogenation to produce γ-valerolactone (GVL) [19–21], which has been shown to be a sustainable liquid transportation fuel suitable of replacing ethanol in gasoline–ethanol blends [22]. Lange et al. have shown that continued hydrogenation of GVL produces valeric acid which can be esterified with alcohols to produce a new class of cellulosic transportation fuels, "valeric biofuels" [23]. Bond et al. developed an integrated catalytic process to convert GVL to liquid alkenes (ranging from C_8 to C_{24}) which could be blended with gasoline, diesel or jet fuels [24].

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* Corresponding author. Address: 4631 Engineering Hall, 1415 Engineering Dr., Madison, WI 53706, USA. Fax: +1 608 262 5434.

E-mail addresses: rweingarten@wisc.edu (R. Weingarten), exkimyt@gmail.com (Y.T. Kim), tompsett@ecs.umass.edu (G.A. Tompsett), jandro.fs@hotmail.com (A. Fernández), hanks@ornl.gov (K.S. Han), hagamanew@ornl.gov (E.W. Hagaman), wconner@ecs.umass.edu (W.C. Conner Jr.), dumesic@engr.wisc.edu (J.A. Dumesic), huber@engr.wisc.edu (G.W. Huber).

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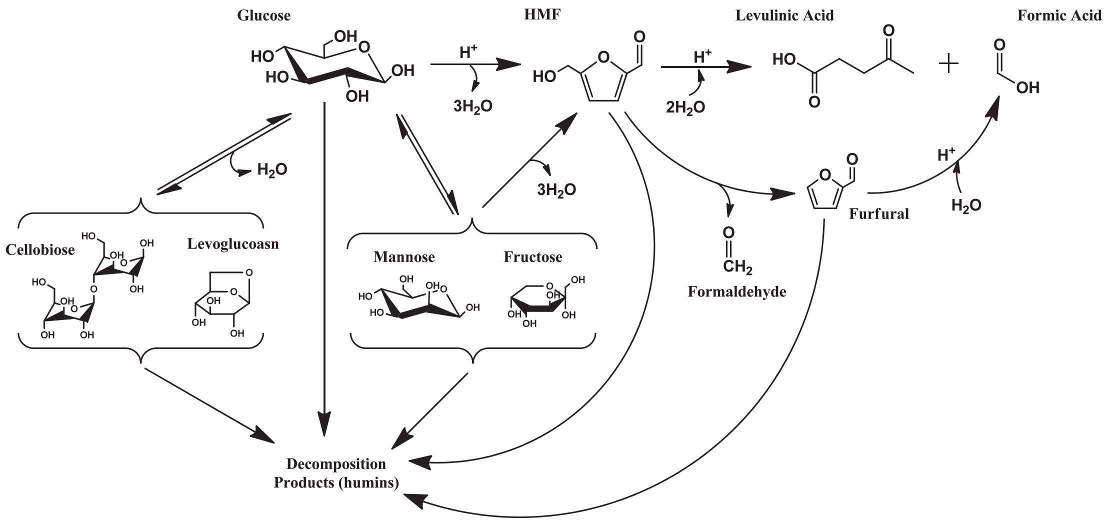

Fig. 1. Reaction pathway scheme for the conversion of glucose to levulinic acid.

Levulinic acid is produced through acid-catalyzed dehydration of hexose sugars. Among these, glucose is the most abundant in nature, available in the polysaccharide form as starch or cellulose in biomass [25]. Levulinic acid is produced from glucose by way of a two-step acid-catalyzed reaction (Fig. 1). We have studied the kinetics of levulinic acid production from aqueous glucose solutions with a homogeneous acid catalyst in a continuous regime [26]. Overall, there are four parallel pathways in which glucose can react: (1) Reversion reactions can lead to the formation of cellobiose and levoglucosan [27–29]; (2) degradation reactions to form highly polymerized carbonaceous species (i.e. humins); (3) epimerization reactions to form fructose and mannose [28], and (4) dehydration to produce 5-hydroxymethylfurfural (HMF). It has been reported that reversion and epimerization products can also decompose to form humins [30]. The humins are both water soluble and water insoluble. Water-soluble humins polymerize with time to form water-insoluble compounds. The isomerization of glucose into fructose has been reported to be favored by the presence of Lewis acid sites [31–33]. Recent studies have reported the efficient conversion of glucose to HMF using a combination of Lewis and Brønsted acid catalysts in a biphasic reactor system with 2-s-butylphenol as the extracting solvent [34,35]. The reaction proceeds through a tandem pathway including isomerization of glucose to fructose followed by dehydration of fructose to HMF. Subsequently, HMF can rehydrate to produce levulinic acid and formic acid. HMF can also decompose to produce humins and produce furfural *via* loss of formaldehyde [36–39]. Furfural can also undergo degradation reactions to form humins [40]. Formic acid is also a by-product of furfural degradation by way of hydrolytic fission of the furfural aldehyde group [41,42].

Attempts have been made to utilize recyclable solid acid catalysts to produce levulinic acid from biomass feedstocks. These range from zeolites and novel metal oxides to acidic ion-exchange polymer resins [43]. In particular, metal(IV) phosphate catalysts have shown to be selective and active for aqueous phase acid-catalyzed dehydration and isomerization reactions [44–47]. Extensive investigations have been carried out to determine the physicochemical and acidic properties of these catalysts [48,49]. Studies have shown that the amorphous form of these catalysts demonstrate higher activity due to increased overall acidity and surface area compared to their crystalline analog [50,51]. In addition, metal(IV) phosphates are beneficial as catalyst supports for metal oxides due to their textural and acid properties [52–54].

In the field of biomass conversion, various studies have been reported on the selective production of HMF from carbohydrates in the aqueous phase using metal phosphates as solid acid catalysts [55–58]. More recently, we found that amorphous zirconium phosphate containing a high Brønsted to Lewis acid site ratio exhibits high selectivity for furfural production from xylose [40]. The activity and selectivity for furfural production of the zirconium phosphate were comparable to those obtained from dehydration reactions with HCl. The dehydration of sorbitol to produce isosorbide with metal(IV) phosphates has also been reported [59]. Li et al. have found that platinum supported on zirconium phosphate serves as a stable, selective, and active catalyst for aqueous phase hydrodeoxygenation of aqueous sugar solutions to produce high-octane gasoline [60,61]. They found the catalyst to be stable in aqueous media at high temperatures (245 °C), and no deactivation occurred after 200 h time-on-stream. ICP studies confirmed that no leaching occurred. This coincides with a study by Asghari et al. who also found zirconium phosphate to be stable under subcritical water conditions [62]. Niobium-based catalysts have also received much consideration as solid acid catalysts due to their hydrothermal stability and high activity for aqueous phase dehydration of alcohols to olefins [63,64].

Zirconium phosphate has unique properties as a solid acid catalyst in that it is compatible in aqueous media. Various studies have investigated the source of the active sites on this class of catalysts. In their study of crystalline zirconium phosphate, Hattori et al. concluded that the catalyst possesses weak and strong acid sites, both of which are derived from P(OH) groups [65]. Clearfield and Thakur observed a decrease in the activity of zirconium phosphate after poisoning the catalyst with quinoline or following proton exchange with Cs^+ on the catalyst surface [44,48]. They correlated the active sites to surface hydroxyl groups but also associated some of the activity to Lewis-type sites. La Ginestra et al. used a similar surface poisoning technique to conclude that the catalytic activity of zirconium phosphate was solely from Brønsted acid sites on the surface of the catalyst [45]. Sinhamahapatra et al. observed both Brønsted and Lewis acid sites in their study on mesoporous zirconium phosphate [66]. They postulated that the Brønsted acid sites possibly arise from geminal P(OH) groups. The Lewis acid centers could be attributed to Zr^{4+}, as suggested by Spielbauer et al. [67].

The objective of this study is to characterize the different catalytic sites on supported metal(IV) phosphate solid acid catalysts and identify their roles in catalyzing the aqueous phase conversion