



Efficient green catalysis for the conversion of fructose to levulinic acid



Indira Thapa^a, Brian Mullen^b, Ammar Saleem^c, Cora Leibig^b, R. Tom Baker^a,
Javier B. Giorgi^{a,*}

^a Centre for Catalysis Research and Innovation, Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

^b Segetis, Inc., 680 Mendelssohn Ave N, Golden Valley, MN 55427, USA

^c Laboratory for the Analysis of Natural and Synthetic Environmental Toxins, Centre for Advanced Research in Environmental Genomics, University of Ottawa, Ottawa, Ontario, Canada

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ABSTRACT

Highly efficient and selective production of levulinic acid has been achieved from D-fructose in the presence of polystyrene-based sulphonic acid resin catalyst, Dowex 50 × 8–100, at mild reaction conditions of 120 °C, over 24 h in a 50:50 mixture of water/GVL resulting in 72 mol% yield under optimized reaction conditions. Optimization of the effect of reaction temperature, time, pressure, catalyst to substrate ratio, fructose concentration and solvent was performed. Various polystyrene-based sulfonic acid resins were also investigated for quantitative production of LA from 5-hydroxymethylfurfural (5-HMF) in pure water. Catalyst recycling was carried out up to 6 cycles. Significant mechanistic information was obtained for the formation of “humins”, which are the primary cause of catalyst fouling, by the identification of soluble by-products and polymerization precursors using Q-ToF mass spectrometry based on accurate masses.

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1. Introduction

The continuity and reconversion of the current energy supply are major challenges increasingly faced by modern civilization. The present massive exploitation of energy resources and the consequent negative impact on the environment is also a growing major concern. Fossil fuels such as coal, natural gas, and petroleum provide about 90% of the energy used today by developed countries. Renewable and sustainable sources are the only alternative to this rising global problem. Biomass [1], one of the largest renewable resources, is composed of cellulose, hemicellulose and lignin. Cellulose is composed in turn of carbohydrates. Carbohydrate research receives special attention from leaders in the field, as it forms the largest natural source of carbon [2]. An alternative way to use carbohydrates as feedstocks is their dehydration into furans and levulinic acid. Levulinic acid (LA) and 5-hydroxymethylfurfural (HMF) are among the most desirable biomass-derived platform chemicals, polymer precursors and feedstocks that can be efficiently converted into fuel additives and other valuable chemicals [1]. Levulinic acid is categorized by the US Department of Energy as one of the top

12 building block chemicals among the 300 potential biorefinery products identified [3–5].

The presence of reactive carbonyl functional groups make LA a very attractive precursor for a variety of value-added chemical products. Ethyl/methyl-levulinate can be used as diesel additives, methyl-tetrahydrofuran (MTHF) and γ -valerolactone (GVL), obtained from the hydrogenation of levulinic acid, can be directly used as solvents and gasoline blenders [6–11]. LA is generally obtained from the hexose sugars of cellulose through a consecutive dehydration and rehydration process in the presence of acid catalysts according to the mechanism proposed by Horvat et al. [12–19]. The bottleneck in the reaction mechanism is the formation and stability of the intermediate HMF under the specified reaction conditions in an aqueous medium [16,20–22]. Conventionally, LA has been produced with homogeneous catalysts such as mineral acids (HCl, H₂SO₄, H₃PO₄ etc.) due to their ready availability, easy applicability, short reaction times and high catalytic activity [23–28]. However, the catalyst recovery process is energy intensive and waste disposal is costly due to the environmental impact exerted by these mineral acids.

Alternatively, development of efficient heterogeneous catalysts is an active field of research to minimize the problems posed by homogeneous catalysts. Easy separation from products and reusability are among the most important advantages of heterogeneous catalysts. The search for a solid acid catalyst possessing

* Corresponding author.

E-mail address: jgiorgi@uottawa.ca (J.B. Giorgi).

high stability and accessible strong acid sites which is economically amenable for LA production from carbohydrates is an ongoing process among researchers in the field [29,30]. Jow and coworkers have used LZV zeolite for the dehydration of fructose to LA at high temperature (383–433 K) over 8–15 h to yield 40% selectivity [31]. Similar results were observed with Y-Zeolite from glucose dehydration to LA under similar reaction conditions [32,33]. Increasing the reaction temperature to 453 K in an autoclave with ZRP zeolite containing different SiO₂/Al₂O₃ ratio did not improve the LA yield (36%) from glucose [34]. Recently, Dumesic and co-workers presented promising results of LA production (>70%) in monophasic THF-H₂O solvent with furfural alcohol using H-ZSM-5 as catalyst [35]. Following this research Requies and co-workers published the improved LA yield (77%) from furfural alcohol using ZSM-5 under an optimized reaction conditions [36]. Lourvanij and Rorrer studied a pillared clay as a solid acid catalyst for the dehydration of glucose with typical LA yields of 20% [37]. Wang and co-workers used sulfated TiO₂ for cellulose dehydration to LA, produced 32% yield (38% of theoretical) under their optimum conditions [38]. Recently, Chen and co-workers reported use of a solid superacid (S₂O₈²⁻/ZrO₂-SiO₂-Sm₂O₃), at high temperature (473 K) which yielded 23% of LA from rice straw [39].

Commercially available ion exchange resins have been used in various industrially important chemical transformations such as alkylation, *trans*-alkylation, isomerization, oligomerization, acylation, esterification and nitration [40]. However, only limited studies have explored the potential of ion exchange resins as catalysts for HMF and LA formation [21,41–44]. Acidic ion-exchange resins (Dowex MSC, Amberlysts), studied by Schraufnagel and Rase for the formation of HMF and LA, afforded moderate yields (24 mol%) after 24 h reaction time at 100 °C [45]. Improved yields were reported by Sanborn and co-workers with a solid acid cation exchange resin, Amberlyst 35, which produced 41% and 62% of LA from fructose and high-fructose corn syrup at 423 K in an autoclave over 4.5 and 18 h, respectively [29]. Smith, and co-workers made use of Dowex 50 × 8–100 for the production of HMF from fructose in acetone-water by a microwave heating technique [41]. At 2 wt% fructose concentration the HMF yield was 73.4%, which was reduced to 54.3% when the fructose concentration was increased to 20 wt%, likely due to the formation of soluble and insoluble polymers (humins) at higher initial fructose concentrations [41]. Ebitani and co-workers reported the synthesis of LA from fructose using Amberlyst 15 at 393 K obtaining 52% yield in water [6,7–11]. Amberlyst 70 was used as a solid acid catalyst for hydrothermal decomposition of cellulose to LA by the group of Huber, however, the LA selectivity was low (28% of theoretical) [46]. An encouraging discovery was reported by the group of Dumesic for conversion of cellulose to LA with Amberlyst 70 in a mixture of 90% GVL and 10% water which produced 69% LA [47]. In recent studies they have reported the use of Amberlyst-70 for the formation of HMF from fructose and glucose in GVL and in THF which produced 80% and 25–32% HMF selectivity at 90% conversion [48,49]. Recent studies have been published by the group of Horvath to use GVL as a green solvent to convert Fructose, Glucose and HMF into LA in presence of H₂SO₄ catalyst [50]. Other solvent systems have been reported previously for LA formation such as fluorinated solvents [51,52], acetone, water, supercritical carbon dioxide [53–55] and ionic liquids [56–59]. A recent publication by the group of Li and co-workers have also highlighted the importance of solvent polarity on the LA yield as well as polymer formation [59].

In this work, we take advantage of high throughput facilities to explore a selection of sulfonated polystyrene catalysts under multiple conditions of pressure, temperature, solvent and reactant concentration. Among these polymeric acid catalysts, Dowex 50 × 8–100, cation exchange resin with strongly acidic sulfonic groups has shown the most relevant activity for the synthesis of

LA from fructose in pure water and in selected co-solvents. We have also demonstrated that very high activity and selectivity for LA could be achieved using Dowex 50 × 8–100 resin under optimized reaction conditions. We have explored GVL as a solvent which was reported as the solvent of choice for solubilising char or humins formed during cellulose decomposition and consequently improved biomass conversion [47,60–62]. In addition to being derived from biomass, GVL is also an excellent solvent for the one-pot downstream process to upgrade LA to GVL as demonstrated by Dumesic [47]. Mechanistic insight, derived from identification of side-products formed during the dehydration of fructose to levulinic acid, is discussed and reusability of the catalysts is explored.

2. Experimental

Catalysts and reactants were purchased from Sigma-Aldrich, Dow, or Rohm and Haas as listed and used as supplied: Amberlyst[®] 15 cation exchange resin (Alfa Aesar), Amberlyst[™] 35 wet resin (Rohm and Haas), Amberlyst[®] BD20 (Rohm and Haas), Amberlyst[™] 70 (Rohm and Haas), Dowex[®] 50 × 8 (hydrogen form, strongly acidic, 50–100 mesh, Sigma-Aldrich), Dowex[®] 50 × 8 (Hydrogen form, 50–100 mesh, Sigma-Aldrich), Dowex[®] 50 × 8 (hydrogen form, strongly acidic, 20–50 mesh, Sigma-Aldrich), Dowex[®] Marathon[™] MSC (hydrogen form, Sigma-Aldrich), gamma-valerolactone (GVL, Sigma-Aldrich; 99%), water (LC-MS grade, Fisher Scientific, Oakville, ON), D-fructose (Sigma-Aldrich; >99%), tetrahydrofuran, acetonitrile, methanol (LC-MS grade, Fisher Scientific, Oakville, ON, Canada), trifluoroacetic acid (EMD Chemicals Inc.), sulphuric acid (Sigma-Aldrich; 99.9%), 5-(hydroxymethyl) furfural (5-HMF, Sigma-Aldrich; >99%), levulinic acid (Sigma-Aldrich; 99%), formic acid (Sigma-Aldrich; >95%) and used directly without further purification.

Fructose conversion was monitored by disappearance of the reactant and appearance of LA, formic acid (FA) and HMF products for a range of catalysts and reaction conditions as described below. In all cases, we can define the conversion for the reaction based on the disappearance of fructose (Eq. (1)) and the yield of each product based on its own quantification (Eq. (2)). When necessary, selectivity can be determined by the ratio of yield for a particular product to the conversion of fructose.

$$\text{Conversion (mol\%)} = \frac{[\text{fructose}]_i - [\text{fructose}]_f}{[\text{fructose}]_i} \times 100 \quad (1)$$

$$\text{yield product (mol\%)} = \frac{[\text{product}]_s}{[\text{fructose}]_i} \times 100 \quad (2)$$

Where, [fructose]_i = molar concentration of initial fructose (reactant), [fructose]_f = molar concentration of fructose in the product; [product]_s = molar concentration of species in the reaction product.

2.1. Conversion of fructose to LA, FA and HMF using sulfonic acid-based heterogeneous catalysts

2.1.1. Method A

Reactions were carried out using a Symyx High Throughput Module (Symyx Discovery Tools). In a typical experiment, fructose (0.28 mmol, 0.05 g, 9 wt%) was added to a mixture of GVL: H₂O (50:50; 0.5 mL) in 1 mL glass vials equipped with magnetic stir bars and loaded on the Core Module. To the resulting solution was added sulfonic acid-based solid acid catalysts (0.05 g) in each of the corresponding vials placed in a 96-well plate. Reaction mixtures were heated at temperatures ranging from 50 to 150 °C in different plates containing each of these reaction mixtures with continuous stirring (estimated as 500 rpm) for 24 h. After the reaction, 100 μL of the supernatant from each of the reaction vials were diluted with 900 μL of LC-MS grade water followed by filtration through

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