Review article

Production of organic acids from biomass resources

Weiping Deng [a, b], Ye Wang [b, **], Ning Yan [a, *]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, 117585, Singapore
[b] State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

ABSTRACT

Catalytic synthesis of valuable organic acids such as lactic acid, levulinic acid, formic acid, acetic acid, 2, 5-furandicarboxylic acid (FDCA), and sugar acids (e.g. gluconic acid and glucosaminic acid) from renewable carbon resources is of high interest for a sustainable chemical industry in the future. A number of efficient catalytic systems have been recently developed to convert biomass into organic acids. Herein we highlight new strategies and catalysts that are effective for the transformations. The mechanisms and catalyst functions involved in several typical reactions are analyzed for the rational design of more efficient catalytic systems.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The non-sustainable nature of fossil resources and increasing concerns on the environment have stimulated extensive research interest in producing chemicals and fuels from alternative starting materials [1–5]. Biomass, including cellulose, lignin and chitin, represents the most abundant renewable carbon resource on earth [2–4]. Transformation of biomass into platform molecules, which can be used directly or serve as building-blocks for synthesizing other useful materials, is a promising route for biomass utilization.

Catalytic biomass conversions into glucose [6], polyols [7–9], 5-hydroxylmethyl furfural (HMF) [10,11], alkyl glucosides [12,13] and aromatic compounds [14–16] have been extensively studied. Meanwhile, transformations of biomass into valuable organic acids including lactic acid, levulinic acid, formic acid, acetic acid, FDCA, and gluconic acid have also received considerable attention [17–20]. Compared to many other routes of biomass valorization, these reactions are conducted under anaerobic or aerobic conditions, and do not consume expensive reagents such as hydrogen. Furthermore, these acids, ranging from C_1 to C_6, play a vital role in the chemistry industry. For example, acetic acid, as one of the most

important organic acids with a global production of 12.9 million tons in 2014, can be used as a food additive, and a key industrial chemical for polyvinyl acetate and synthetic fibers production [21]. Lactic acid is employed for synthesizing polylactic acid, which has the potential to replace petroleum-based polystyrene and polyethylene terephthalate [22]. FDCA is also considered as an alternative to petroleum-derived terephthalate [23].

Significant advancement in transformation of biomass into organic acids has been witnessed since the last decade. Fig. 1 summarizes the typical catalytic reactions that will be discussed in this review. These reactions include both anaerobic and oxidative cleavage of C–C bonds in biomass molecules. We provide several selected examples that focus on newly developed strategies and efficient catalytic systems, while comprehensive understanding on the synthesis of these organic acids can be found elsewhere [20,22–25].

2. Lactic acid and levulinic acid

Conventional production of lactic acid is based on carbohydrates (e.g. glucose and fructose) fermentation. However, this process suffers from problems of high enzyme price and low productivity. Hence, numerous chemo-catalysis systems using trioses such as glycerol, dihydroxyacetone (DHA) and glyceraldehyde (GLY) as feedstocks have been studied [22]. Among the three trioses,

---

* Corresponding author.
** Corresponding author.
E-mail addresses: wangye@xmu.edu.cn (Y. Wang), ning.yan@nus.edu.sg (N. Yan).
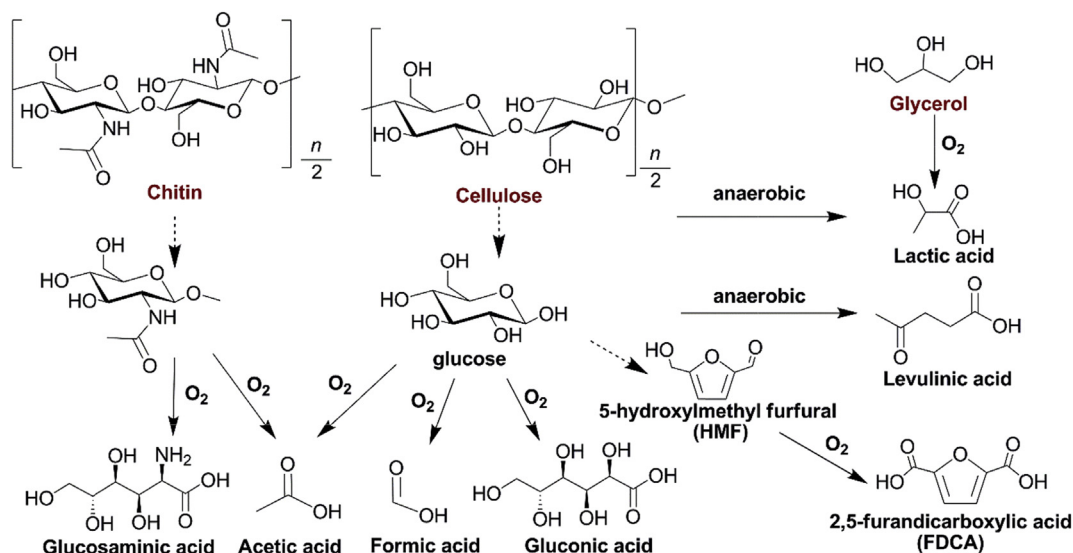
Fig. 1. Selected examples of conversion of renewable biomass to organic acids.

glycerol is the most desirable starting material as it is easily available from the biodiesel refinery process, although DHA and GLY are chemically less challenging to be converted. Au and Pd-based catalysts can promote glycerol conversion in alkaline (e.g. NaOH) or Lewis acid (e.g. $AlCl_3$) solution [26–29]. Metals catalyze the dehydrogenation of glycerol into DHA and GLY, which are subsequently transformed to lactic acid through isomerization and intermolecular Cannizaro reactions with base or Lewis acid catalyst. Side-reactions such as oxidation of GLY to glyceric acid may also occur, decreasing the lactic acid selectivity. A recent report identified an iridium complex that prevented the over-oxidation of GLY [29]. Other side-reactions including the C–C bond cleavage and hydrogenation of intermediates were minimized as well. In the direct conversion of crude glycerol, this iridium complex provided 97% conversion and 96% lactic acid selectivity at 403 K. Since crude glycerol from biodiesel process contains various impurities, such direct transformation without pre-purification is beneficial to cost reduction and makes the process more environmental friendly [29].

The conversion of lignocellulosic biomass, in particular cellulose, to lactic acid is more attractive and more challenging. This reaction requires not only the cleavage of glycosidic bonds that link the glucose units, but also that of particular C–C bond in glucose units. Efficient catalytic systems for direct conversion of cellulose to lactic acid are limited [30,31], though several successful cases have been achieved on Sn-based catalysts for mono- or disaccharides (e.g. glucose and sucrose) transformation [32–35]. Encouragingly, a recent study using a series of metal salts as catalysts showed that dilute metal cations (e.g. Pd^{II}, Al^{III}, and VO_2^{II}) in hot water could efficiently convert cellulose and even raw biomass to lactic acid under inert atmosphere [36,37]. Kinetic studies and DFT calculations indicated that the formation of lactic acid involved three key successive reactions: the isomerization of glucose to fructose, retro-aldol condensation of fructose to trioses (e.g. DHA, GLY), and dehydration-isomerization of trioses to lactic acid (Fig. 2). The retro-aldol reaction has the highest energy barrier ($\Delta G = 32.8$ kcal mol^{-1}), and thus is the rate-determining step. However, metal cations (e.g. Pb^{II}) markedly reduced this energy barrier ($\Delta G = 22.4$ kcal mol^{-1}), working multi-functionally and affording lactic acid with high yield [37].

Levulinic acid, obtained from cellulose or cellulose-derived carbohydrates, is generally formed via a series of tandem reactions: isomerization of glucose to fructose, dehydration of fructose to HMF, subsequent rehydration and rearrangement of HMF to levulinic acid and formic acid. Brønsted acids including mineral acids (e.g. H_2SO_4 and HCl) and solid acids (e.g. zeolites, sulfonated metal oxides, and resin materials containing SO_3H) have been widely studied for the reaction [38–40]. Among them, the materials with SO_3H groups exhibit unique and efficient performances. The strong acidic groups (SO_3H) act as active sites, while their neighboring functional groups work as co-factors to affect the reaction. In a chloromethyl polystyrene resin, which contains both sulfonic and chlorine groups, the chlorine sites may facilitate the adsorption of cellulose through hydrogen bonding between chlorine atoms and hydroxyl groups of cellulose [41]. Because of the easy access to catalytic sites (-SO_3H), the reaction rate was enhanced. Additionally, neighboring functional groups (e.g. NH group in oxindoles) may interact with acidic sites through formation of intramolecular hydrogen bonds [42]. This interaction retarded the isomerization of glucose to fructose, and accelerated HMF transformation, making the entire reaction proceed under low concentrations of these reactive intermediates, and thus decreasing the possibility for humins generation.

3. Formic acid and acetic acid

The oxidative conversions of cellulose-derived carbohydrates have been reported for formic acid formation; however, high alkaline concentration and expensive H_2O_2 are generally employed [20]. Alternatively, vanadium-based catalysts (e.g. $H_5PV_2Mo_{10}O_{40}$) combined with O_2 have been recently developed for the reaction [43–45]. Formic acid was the major liquid product, but the maximum yield was only 50% with CO_2 as the main by-product. Nevertheless, CO_2 was not originated from decomposition of formic acid, which was stable under the vanadium sulfate catalyzed reaction conditions [37]. To gain insights into the formation pathway of formic acid and CO_2, catalytic transformation of model compounds was carried out over $VOSO_4$ catalyst at 413 K in water [37]. The C–C bond that connected an aldehyde group (i.e. terminal carbon) and a hydroxyl/aldehyde group was readily cleaved. The terminal carbon was transformed to formic acid or a carboxylic group, whereas the hydroxyl/aldehyde moiety was oxidized to a corresponding aldehyde or carboxylic group. Once acid intermediates were formed, particularly those with an α-carbon linking with another oxygen-containing group, they underwent