CHEMSUSCHEM

DOI: 10.1002/cssc.201000457

Catalytic Conversion of Dihydroxyacetone to Lactic Acid Using Metal Salts in Water

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We herein present a study on the application of homogeneous catalysts in the form of metal salts on the conversion of trioses, such as dihydroxyacetone (DHA), and glyceraldehyde (GLY) to lactic acid (LA) in water. A wide range of metal salts (26 in total) were examined. Al^{III} salts were identified as the most promising and essentially quantitative LA yields (>90 mol%) were obtained at 140 °C and a reaction time of 90 min. A reaction pathway is proposed and a kinetic model using the power law approach was developed for the conversion of DHA to LA with pyruvaldehyde (PRV) as the intermediate. Good agreement between experimental data and the model was obtained. Model predictions, supported by experiments, indicate that a high yield of LA is favoured in dilute solutions of DHA (0.1 M) at elevated temperatures (180 °C) and reaction times less than 10 min.

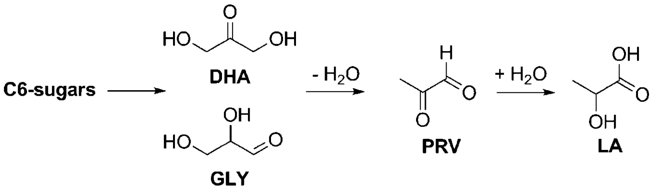
Introduction

High oil prices and environmental concerns have stimulated research on biofuels and biobased chemicals from lignocellulosic biomass. Attractive catalytic conversions to platform chemicals have been identified[1] and activities are ongoing to convert these findings to economically feasible processes on a large scale.[2] Examples of interesting platform chemicals are organic acids, such as levulinic acid, propionic acid, acrylic acid and, in particular, lactic acid (LA).

LA is a commodity chemical with an estimated demand of 300 000 tonnes per year (2010).[3] Traditionally, LA is used in food and food-related applications, such as bakery and meat products and confectionery.[3] In these applications, LA serves as a pH regulator, as a preservative or as an emulsifying agent. LA is also used for non-food applications and examples are found in cosmetic and pharmaceutical formulations.[3] In the last decade, the commercialisation of polylactic acid (PLA), which is a biopolymer with interesting applications, has boosted the production of LA considerably. Market projections indicate that the PLA market may reach up to 3 million tonnes in 2020.[4] Furthermore, LA also has potential as a platform chemical for the production of bulk chemicals, such as propylene glycol and acrylic acid.[5]

LA is currently produced by fermentation processes using carbohydrate sources. However, volumetric production rates are relatively low and product workup leads to the formation of large amounts of salts.[3,6] Therefore, novel methods to produce LA from lignocellulosic biomass through non-fermentative catalytic chemical transformations have attracted great interest in both academia and industry.

A number of studies have been reported in the literature and involve the use of C6 sugars (D-glucose and D-fructose),[7] C6 sugar precursors, such as cellulose,[7c] and trioses,[7a,g,8] such as dihydroxyacetone (DHA) and glyceraldehyde (GLY), as the feedstock. The reactions with C6 sugars or C6 sugar precursors are typically performed in subcritical water ($T > 250$ °C) in the presence of homogenous catalysts, such as bases (NaOH and $Ca(OH)_2$)[7b,e] or metal salts.[7a,c,g,8a] However, the reported yields of LA are relatively low (<45 mol%). Interestingly, these studies imply that trioses, such as DHA, GLY, as well as pyruvaldehyde (PRV), are intermediates when converting C6 sugars into LA (Scheme 1).



Scheme 1. Conversion of C6 sugars to LA.

These findings stimulated research activities on the conversion of trioses, such as DHA and GLY, into LA. Homo- and heterogeneous catalysts have been explored, mainly in protic solvents, such as water and alcohols (methanol and ethanol), and an overview is given in Table 1. When using dilute sulfuric acid as the catalyst in subcritical water (250 °C, 24.5 MPa), Antal et al. observed the formation of LA in low yields (15 mol%; Table 1, entry 1).[8a] Bicker et al. reported catalytic effects of var-

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