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Effect of biogenic fermentation impurities on lactic acid hydrogenation to propylene glycol

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Abstract

The effect of residual impurities from glucose fermentation to lactic acid (LA) on subsequent ruthenium-catalyzed hydrogenation of LA to propylene glycol (PG) is examined. Whereas refined LA feed exhibits stable conversion to PG over carbon-supported ruthenium catalyst in a trickle bed reactor, partially refined LA from fermentation shows a steep decline in PG production over short (<40 h) reaction times followed by a further slow decay in performance. Addition of model impurities to refined LA has varying effects: organic acids, sugars, or inorganic salts have little effect on conversion; alanine, a model amino acid, results in a strong but reversible decline in conversion via competitive adsorption between alanine and LA on the Ru surface. The sulfur-containing amino acids cysteine and methionine irreversibly poison the catalyst for LA conversion. Addition of 0.1 wt% albumin as a model protein leads to slow decline in rate, consistent with pore plugging or combined pore plugging and poisoning of the Ru surface. This study points to the need for integrated design and operation of biological processes and chemical processes in the biorefinery in order to make efficient conversion schemes viable.

Keywords: Catalysis; Deactivation; Impurities; Hydrogenation; Lactic acid

1. Introduction

The production of propylene glycol (PG) from lactic acid (LA) represents a prototypical pathway for producing commodity chemicals from biorenewable resources, as it involves integration of fermentation with chemical catalysis to produce a value-added product. Lactic acid is the largest bio-based commodity chemical produced via fermentation, and PG is produced worldwide in volumes exceeding one billion kg with annual growth >7% because of its nontoxic properties and applications as a monomer, antifreeze component, industrial solvent, and additive in consumer health and hygiene products. Formation of PG has been known from LA esters since Adkin's work in the 1930s (Adkins and Pavlic, 1947; Adkins and Billica, 1948; Bowden and Adkins, 1934), and a number of studies have appeared that use free LA (Broadbent et al., 1959; Carnahan et al., 1955; Antons, 1998; Cortright et al., 2002; Mao et al., 2003; Werpy et al., 2006). In these studies, selectivity to PG exceeding 90% has been reported over Re black (Broadbent et al., 1959), copper on silica (Cortright et al., 2002), and supported Ru in several forms (Antons, 1998; Mao et al., 2003; Werpy et al., 2006). In our laboratory, we have also used Ru catalysts to convert free LA in aqueous solution to PG in yields as high as 92% of theoretical (Zhang et al., 2001, 2002). Reactions were conducted in stirred batch autoclaves at temperatures ranging from 90 to 150 °C and hydrogen pressures from 3.5 to 12.0 MPa. We have also determined reaction kinetics following careful evaluation of mass transport resistances in the three phase system (Zhang et al., 2002); the reaction is described by a

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Langmuir–Hinshelwood model with surface hydrogenation of LA as the rate-limiting step; the presence of product PG has little effect on reaction rate.

Prior studies have been conducted with reagent grade LA, which is an appropriate choice when developing active catalysts, measuring intrinsic reaction kinetics, and evaluating mechanistic pathways. However, for PG production from LA to compete with petroleum-based routes from propylene involving either the hydroperoxide intermediate or direct hydration of propylene oxide (Szmant, 1989), it is necessary to consider the use of less pure, lower cost LA as a feedstock. This is because conversion of propylene to PG requires only 0.6 kg propylene/kg PG, while conversion of LA to PG requires 1.25 kg lactic/kg PG. As with many routes to commodity chemicals, renewable feedstock costs must be much lower (on the order of one-half in this case) than the petroleum-based counterpart in order for the process to be competitive.

Currently, LA is produced primarily by fermentation of glucose using *Lactobacillus* microorganisms. The fermentation step is highly optimized, with LA yields approaching the theoretical limit of 1.0 kg LA/kg glucose consumed. The fermentation media consists of a complex mixture of nutrients and minerals, and base (typically $Ca(OH)_2$) is added during fermentation to neutralize the acid as it forms. Following fermentation, lactate in the product broth is acidulated with H_2SO_4 to form LA; the acid is then concentrated and purified in multiple steps to obtain the final product (typically 88 wt% acid in solution).

LA has historically found use as a food acidulent and tanning agent, but these uses have now been eclipsed by production of polylactic acid (PLA) polymers. In PLA production, LA purity requirements are stringent, and purification costs are estimated to account for as much as half of the overall production cost of the acid. With PLA selling prices approaching $2.20/kg, it is clear that polymer grade LA is too expensive to be a suitable feed for PG production. Lowering LA cost is therefore imperative to make manufacture of PG feasible. Unfortunately, barring some breakthrough in fermentation that would simplify nutrient requirements or alleviate the need for pH adjustment, the only reasonable strategy is to use less highly refined LA. To do this, the effects of key biogenic impurities present from fermentation on catalyst performance for PG formation must be characterized, and then the purification scheme for LA can be accordingly altered to focus on those impurities deleterious to PG formation. This paper examines the first part of this strategy, that of identifying the key biogenic impurities in LA fermentation and ascertaining their effect on catalyst performance for PG production.

2. Methods

2.1. Materials

Purified LA, referred herein as "refined", was obtained from Purac, Inc. (FCC Grade, 88 wt%). Several additional samples of LA, both refined and partially-refined, were taken from different points along the purification train of a continuous demonstration-scale LA production facility shown in Fig. 1. These samples are referred to as Samples 1–3 in this paper. Sample 1 is fully refined lactic acid and is similar in purity to FCC grade material. Sample 2 has been withdrawn following the extraction/back extraction step and is semi-transparent with a light brown color. Sample 3 has had little refining beyond acidulation and filtration and was opaque with a dark brown color.

The identity and quantity of impurities present in Samples 1–3 were not fully disclosed, but a partial characterization of the sample compositions is given in Table 1. Organic acids include glyceric, succinic, formic and acetic acids; predominant amino acids include alanine, serine, glutamine, and glycine. Elemental analyses were performed using Ion Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Unidentified impurities likely include protein (cell mass) fragments, color bodies, residual nutrients from fermentation, and fermentation byproducts. All samples were diluted to desired concentrations for hydrogenation with HPLC grade water.

Hydrogen gas of UHP Grade 5.0 (AGA, 99.999%) was used in hydrogenation experiments without further purification. Model impurities were all reagent grade materials obtained from Aldrich Chemical Company.

The catalyst used in this study was ruthenium (5 wt%) supported on a granular (15–30 mesh) activated carbon (CGM-6 Yakima Carbon, Inc.). The catalyst was prepared by impregnation of an aqueous solution of $RuCl_3$ (Aldrich) to incipient wetness, followed by slow drying in a tube furnace under He at 80 °C, reduction at 150 °C in 20 vol% H_2 in He for 4 h, and further reduction at 250 °C in 100% H_2 for 4 h. The catalyst was finally passivated in 2.0 mol% O_2 in N_2 to facilitate transfer to the flow reactor. Catalyst metal dispersion was measured by hydrogen chemisorption at 80 °C in a Micromeritics ASAP 2010 adsorption apparatus and found to be $12 \pm 2\%$ for all samples examined. This corresponds to a surface site concentration of 6×10^{-5} mol Ru/g catalyst. Total activated carbon support surface area

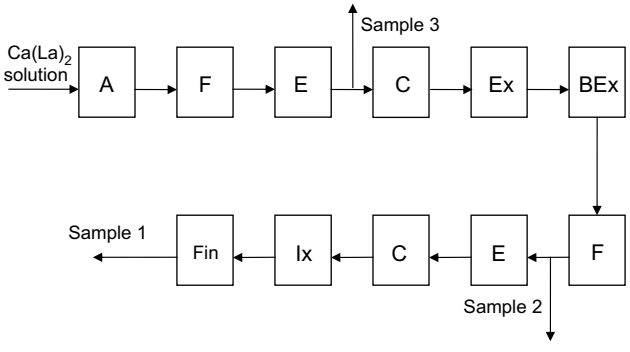

Fig. 1. Process for purification of calcium lactate solution from fermentation. A – acidulation; F – filtration; E – evaporation; C – carbon treatment; Ex – solvent extraction of LA; BEx – back extraction of LA into aqueous solution; Ix – Ion exchange; Fin – finishing step.