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Aqueous-phase hydrogenation of lactic acid to propylene glycol

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Abstract

The metal-catalyzed hydrogenation of lactic acid to propylene glycol (PG) in aqueous solution is investigated in a laboratory-scale stirred batch reactor. Ruthenium on activated carbon is identified as an active catalyst for the reaction, with nearly complete conversion achieved at reaction temperatures of 100–170°C and hydrogen pressures of 7–14 MPa. Selectivity to PG in excess of 90% at 95% lactic acid conversion has been obtained at optimal reaction conditions. Potassium and calcium lactate salts cannot be directly converted to PG, but simple addition of sulfuric acid suffices to convert the salt to free acid, which is then hydrogenated. The ready availability of low-cost lactic acid, produced via fermentation of corn-derived carbohydrates, makes this biomass-based route an attractive alternative to the traditional petroleum-based pathways to PG. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Biomass-based organic acids are attractive feedstocks for chemicals production because they can have multiple reactive functionalities and are becoming increasingly available in commercial quantities at low cost. Lactic acid is one such material; the synthesis of biodegradable poly-lactic acid polymer from lactic acid has sparked extensive research by several major corporations to produce and recover pure lactic acid via fermentation of corn-derived glucose. Worldwide production of lactic acid (2-hydroxy-propionic acid) has increased steadily since the early 1990s, and will rise still further as commercial ventures come on-line [1].

Propylene glycol (PG) is a valuable commodity chemical (450,000 t per year in 1998 [1], US $ 0.48/lb)

that finds many uses in foods, consumer products, and chemical applications. Currently, all commercial production of PG comes from the hydration of propylene oxide, made in a multistep reaction sequence using either hydroperoxidation chemistry or the antiquated chlorohydrin process [2].

The earliest report of PG formation from lactate was from Adkins and coworkers in the 1930s and 1940s [3–5], who converted neat ethyl lactate to PG over Raney Ni in yields exceeding 80% at very high pressures (>25 MPa). By using high catalyst loading, they could hydrogenate esters of alpha-substituted acids to their corresponding alcohols at temperatures as low as 50°C. At these temperatures, the optical activity of acid was transferred to the alcohol. Broadbent et al. [6] conducted the first catalytic hydrogenation of free lactic acid using unsupported rhenium black as catalyst. With 1 g rhenium per mole lactic acid, they achieved 84% PG after 8 h at 150°C and 27 MPa. In similar studies, Ford [7] and Carnahan et al. [8] used

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ruthenium-based catalysts to directly hydrogenate carboxylic acids at low temperature, but they had to use pressure in excess of 50.7 MPa for best results.

Over the course of the work described in this paper, several patents have been awarded to Antons and coworker [9,10] for the preparation of optically active alcohols by reducing optically active carboxylic acids with hydrogen in the presence of ruthenium catalysts. In these patents, carboxylic acids with an alpha or beta substituent are reduced with hydrogen at temperatures <160°C and pressures <20 MPa.

The focus of this study is to identify improved catalysts to achieve higher reactions rates and better selectivities to PG at milder conditions than have been previously reported in the literature.

2. Experimental

2.1. Reactor system

All reactions were conducted using a 300 ml capacity laboratory-scale stirred batch autoclave reactor (Parr Instruments, Model 4561). The reactor is made of T316 stainless steel and has a quartz liner to protect the vessel from corrosion in acidic media at elevated temperature. The reactor is equipped with a gas inlet valve for continuously charging gas into the reactor and a gas release valve for releasing pressure and gas sampling. A dip tube containing a particulate filter is connected to a liquid sampling valve and is used to withdraw liquid samples without interrupting the reaction. A thermocouple measures fluid temperature and is used as the control thermocouple during reaction. A stirring shaft with gas-entraining impeller is used to vigorously mix the fluid phase in order to suspend the catalyst and entrain gas into the liquid phase. The reactor is controlled by a Parr Model 4852 controller that provides adjustable stirring speeds and automatic temperature control via the heating mantle and the air-cooling loop inside the reactor.

A typical experiment was conducted by first placing the catalyst in the reactor, sealing and purging the reactor with nitrogen, and then adding hydrogen to 3.4 MPa and heating to 150°C to reduce the catalyst. After reduction for 2–12 h, the liquid feed, held in a Whitey sample cylinder under hydrogen pressure, was forced into the reactor. The stirring rate was then set to 1000–1200 rpm, a value determined to be high enough to avoid external mass transport limitations in the reactor. When the reaction temperature stabilized at the desired value, hydrogen pressure was increased to the prescribed value, and the reaction commenced. Liquid samples (1–2 ml) were typically taken at 30 min intervals; gas samples were withdrawn continuously from the reactor. These samples were analyzed as described below.

2.2. Product analyses

An Ametek Dycor M100M Quadrupole Mass spectrometer with a detection limit of 100 ppm (v/v) was used to continuously analyze effluent gas. A small quantity of gas was bled from the reactor and directed past a 1 mm o.d. × 1 m length glass capillary tube which opened directly into the vacuum chamber containing the mass spectrometer. Calibration of the mass spectrometer was performed by injecting a certified standard multicomponent gas mixture (AGA Gas, Inc.) containing 2 vol.% of light alkanes in hydrogen just upstream of the capillary. Peak intensities were used to calculate species concentrations ($m/e = 15$ for CH_4; $m/e = 30$ for ethane; $m/e = 43$ for propane) using response factors from the calibration mixture.

Liquid phase products were analyzed using a Spectra Tech P1000 High Pressure Liquid Chromatography system (Thermo Separation Products, Inc.) with an HPX-87H Aminex ion exchange column (Biorad, Inc.). The column temperature was maintained at 50°C using a heating tape for optimal resolution and low pressure drop. The mobile phase was 5 mmole H_2SO_4 in HPLC grade water. An internal reference (sucrose or ethanol) was used for quantitative analysis.

Raw data from the HPLC and mass spectrometer were transferred into a spreadsheet to calculate lactic acid conversion, yield, selectivity, and overall closure of the material balance for the experiment. Yield of PG is defined as moles of PG formed per mole lactic acid or lactate present initially; selectivity is defined as moles PG formed per mole lactic acid converted. The material balance closure is determined as a percent of lactic acid/lactate carbon initially present in the reactor.

Table 1
Catalyst properties

Catalyst/support	Source (designation)	Support surface area (N_2 BET, m^2/g)	Metal loading (wt.%)	Metal dispersion (%)
Pd/carbon	Englehard Corp. (type M/UR)	–	5	–
Ni/Al$_2$O$_3$	Pressure Chemicals, Inc. (5222)	–	60	–
CuCrO$_x$	United Catalyst (CuCrG-99B-13)	–	–	–
Raney nickel	Pressure Chemicals, Inc. (A7063)	–	100	
Ru/TiO$_2$	Degussa (H7701 X/D)	49	3	40
Ru/Al$_2$O$_3$	Degussa (H214 XR/W)	–	5	–
Ru/carbon	PMC, Inc. (1940C)	850	5	34
Ru/carbon	In-house (Cameron-Yakima CG6M carbon)	730	5	13

2.3. Materials

Racemic lactic acid (85%, J.T. Baker), diluted in HPLC-grade water, was used as the feedstock. Ultra high purity hydrogen (AGA, 99.999%) was used without further purification. Catalysts were obtained from commercial sources, and in the case of ruthenium on carbon, prepared in the laboratory for comparative purposes. This was done by impregnating a carbon support (Cameron-Yakima CG6M) with RuCl$_3 \cdot$H$_2$O using the incipient wetness method, followed by slow drying at 80–90°C and reduction in helium/hydrogen mixtures for several hours at a temperature of 400°C.

Properties of the catalysts used in this study are given in Table 1. Ruthenium dispersion was measured by hydrogen chemisorption: samples were first outgassed at 750 K, then exposed to hydrogen and cooled to 273 K. Hydrogen was replaced with argon and the sample was heated at 10 K/min. The chemisorbed hydrogen was taken as the peak desorbed at 400–500 K. Dispersion was not determined for some catalysts, particularly those that were not active.

3. Results

3.1. Catalyst screening and product characterization

3.1.1. Catalyst screening

Control experiments showed no PG formation in the absence of either catalyst or hydrogen. Several catalysts previously reported to be active for hydrogenation of carboxylic acids and esters were examined as candidates for lactic acid conversion to PG. Results of these screening studies are given in Fig. 1. It is clear that ruthenium on activated carbon support is the most active of the catalysts examined: nearly complete conversion within 5 h reaction time was achieved at the specified conditions. The ruthenium on alumina support was also moderately active, but carbon is superior and is expected to be more resilient in aqueous acidic solution. The Ru/C catalyst prepared in-house has somewhat higher activity than the commercial Ru/C catalyst, but to avoid lengthy and expensive catalyst preparation the additional experiments in this study were conducted with the commercial 5 wt.% ruthenium catalyst on activated carbon (PMC, Inc.).

3.1.2. Product characterization

At reaction temperatures <170°C and with catalyst loadings at or <1 g/100 g reacting solution, the only liquid product detected was PG. When reaction temperature or catalyst loading was increased above 170°C or 1 g/100 g solution, 1-propanol, ethanol, and trace amounts of 2-propanol were formed. A sample chromatogram of the liquid product phase from a reaction over Ru/C catalyst at 170°C is given in Fig. 2. The total yield of all byproducts was not >5% of the lactic acid fed, on a molar basis, in any experiment.

At temperatures <170°C, the major byproducts of the reaction were light hydrocarbons methane, ethane, and propane. Continuous monitoring of the batch reactor during reaction, shown in Fig. 3 for a reaction at 170°C over Ru/C, indicates that most gas products were formed in the first 2 h of hydrogenation. The molar concentrations of the three hydrocarbons as shown in Fig. 3 were very similar; however, byproduct gas composition and yield varied as a function of
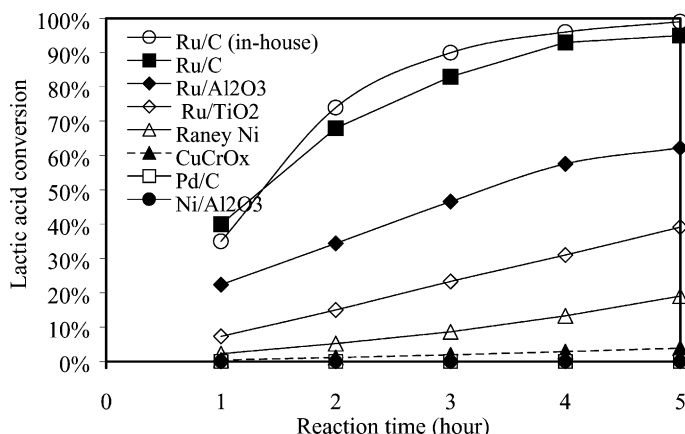
Fig. 1. Results of catalyst screening for conversion of lactic acid to propylene glycol. Feed: 100 ml of 0.55 M (5 wt.%) lactic acid in water. Conditions: $T = 150°C$, $P = 14.5$ MPa H_2, catalyst loading, 1.0 g.

reaction conditions and support material. For instance, for ruthenium on alumina at the same conditions as in Fig. 3, the dominant gas byproduct was methane. The total quantity of lactic acid converted to byproduct gas never exceeded 10% of the lactic acid fed, and was as low as 1–2% at low temperature and high pressure.

The reaction is, therefore, a relatively clean conversion of lactic acid to PG. With both liquid and gas products analyzed, the carbon balance closure was in the range of 95–103% for all experiments.

3.2. Parametric studies

3.2.1. Temperature and pressure

The effect of hydrogenation temperature and pressure on yield of PG is given in Fig. 4. At low temperature, the rate of lactic acid conversion and, hence, PG yield are both low. Yield increases until cracking and secondary reactions become important at high temperature and lead to extensive byproduct formation. Thus, there exists an optimal temperature that maximizes PG yield from lactic acid in the batch reactor.
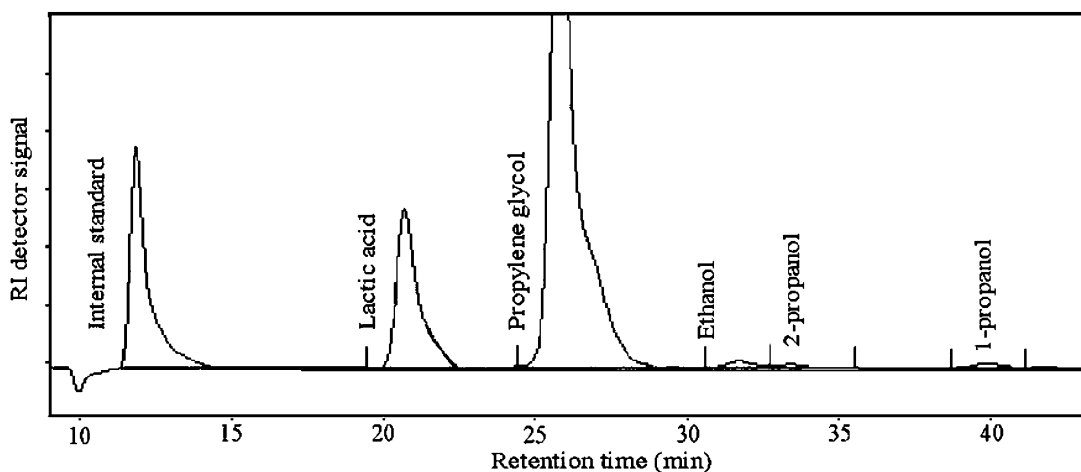

Fig. 2. Chromatogram of liquid products. Reaction conditions: $T = 170°C$, $P = 14.5$ MPa H_2, 0.5 g Ru/C in 100 ml 0.55 M lactic acid in water.
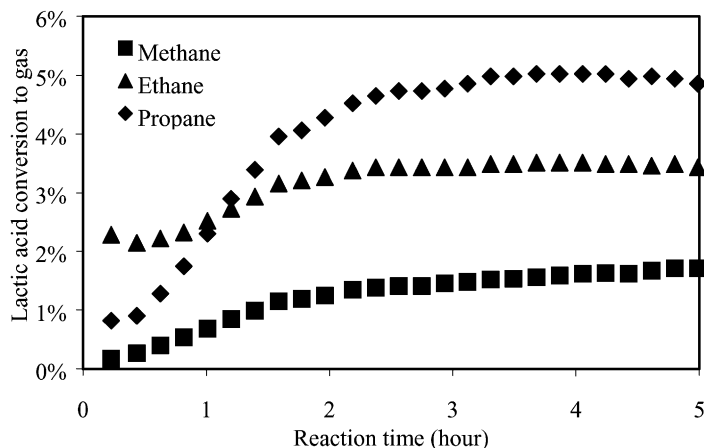
Fig. 3. Gas phase product formation. Conditions: $T = 170°C$, $P = 14.5\,MPa$ H_2, 0.5 g Ru/C catalyst in 100 ml 0.55 M lactic acid in water.
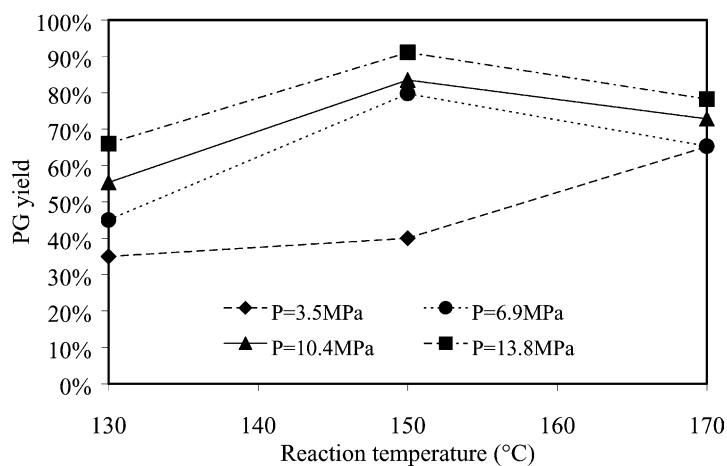

Fig. 4. Propylene glycol yield after 4 h reaction as a function of temperature and pressure. Conditions: 0.5 g Ru/C catalyst in 100 ml of 0.55 M lactic acid solution in water.

Because the solubility of hydrogen in aqueous solution is very low, elevated pressure must be used to increase the hydrogen concentration in liquid phase and thus achieve reasonable conversion rates. For the range of pressure used here, rate of formation and yield of PG continuously increase with increasing pressure. Thus, the optimal pressure for a lactic acid-to-PG process will have to ultimately be based on the economic tradeoff between reactor performance and equipment cost.

3.2.2. Feed concentration

Lactic acid conversion rates at three different feed concentrations (0.55, 1.15 and 3.6 M) but otherwise identical reaction conditions are reported in Fig. 5. At the same reaction conditions, high lactic acid concentration results in lower conversion, although the absolute reaction rate (moles lactic acid/h/g catalyst) increases at higher lactic acid concentrations. This indicates that the reaction is not simply first-order in lactic acid, and suggests that a Langmuir–
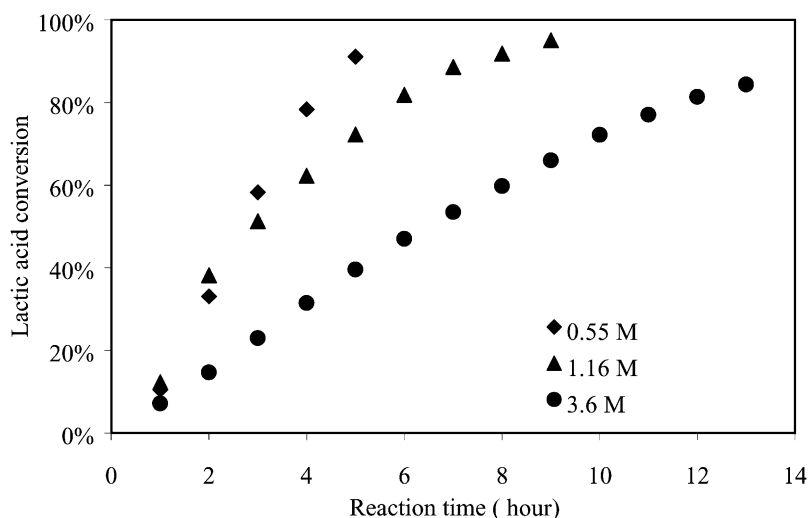
Fig. 5. Conversion of lactic acid at several feed concentrations. Conditions: $T = 150°C$, $P = 14.5$ MPa H_2, 0.5 g Ru/C in 100 ml feed.

Hinshelwood type of rate expression would better describe the reaction kinetics. A kinetic model will be presented in a forthcoming paper.

In this work, the primary concern with highly concentrated lactic acid, a known corrosion agent, was leaching or destruction of the ruthenium catalyst. For 3.6 M lactic acid feed, 85% conversion was achieved after 13.5 h of reaction and catalyst activity appeared to be undiminished. The major problem with high concentration lactic acid was corrosion to the stainless steel reactor components that were in contact with the liquid phase, but the catalyst metal was not affected.

3.2.3. Influence of catalyst loading

The conversion and selectivity to PG for three catalyst loadings are given in Fig. 6a and b, respectively. Conversion rate increases with catalyst loading as expected; a simple analysis based on the slope of the conversion versus time curve at similar lactic acid concentrations shows that the rate is reasonably proportional to catalyst loading. The same experiments were performed at 130°C, and rate per gram catalyst at the lower temperature was also the same at the same lactic acid concentration. Selectivity to PG declines slightly as catalyst loading is increased, because of the increased exposure of product PG to the catalyst.

3.3. Hydrogenation of lactate salts

As lactic acid is formed in fermentation, it must be neutralized with base to maintain pH in the range that the microorganism will function. The raw product of fermentation is, therefore, an aqueous solution consisting of sodium, ammonium, or calcium lactate. To recover free lactic acid, the lactate salt has to be acidulated. This is typically done by addition of H_2SO_4, particularly when calcium hydroxide is used as the neutralizing agent in fermentation, so that the $CaSO_4$ formed immediately precipitates from solution.

Direct hydrogenation of carboxylic acid salts is difficult in aqueous-phase because the intermediates formed are not thermodynamically favorable. Adams et al. [11] did directly hydrogenate cadmium–nickel propionate to propanol at 24 MPa and 240°C under anhydrous conditions. Moderate yields were obtained. This is the only prior work attempting and reporting any success at direct hydrogenation of carboxylic acid salts, and it was done with cations of metals known to be hydrogenation catalysts and at conditions far removed from those in this study.

We conducted hydrogenation of calcium lactate and potassium lactate at 150–170°C and 14 MPa and did not produce detectable quantities of PG. With ammonium lactate at the same conditions, we observed a small HPLC peak for PG, likely a result of cracking
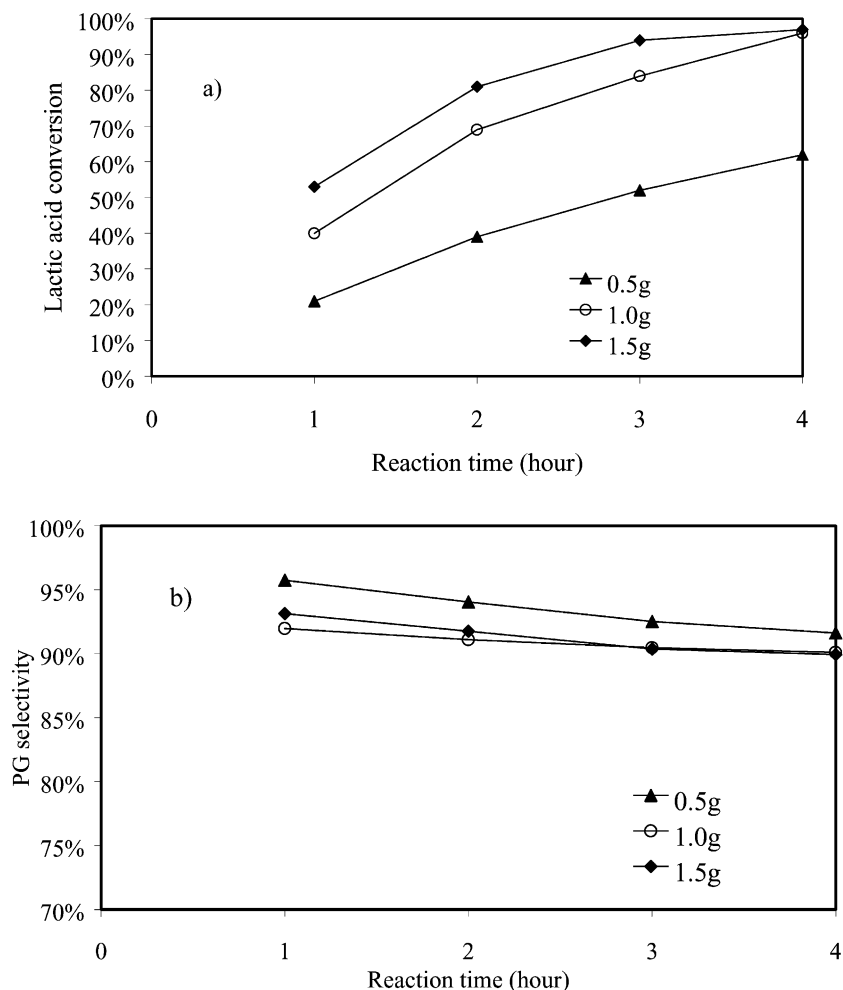
Fig. 6. Effect of Ru/C catalyst loading on (a) lactic acid conversion; (b) selectivity to PG. Conditions: $T = 150°C$; $P = 14.5$ MPa H_2, 100 ml 0.55 M lactic acid in water.

of ammonium lactate to ammonia and lactic acid, which is then hydrogenated. Thus, we conclude that lactate salts produced in fermentation cannot be directly hydrogenated, and must be acidulated to the free acid prior to hydrogenation. Further experiments described below illustrate the influence of salts and of partial acidulation of lactate salt on hydrogenation behavior.

3.3.1. Addition of potassium salts

To characterize incomplete acidulation of lactic acid, low concentrations of potassium hydroxide were added to 0.55 M lactic acid solution and the resulting

mixture was subjected to hydrogenation. Fig. 7 shows that conversion rate declines as KOH is added, but only in proportion to the quantity of base addition. Potassium hydroxide does not poison the catalyst, but leads to a decline in rate as a result of reducing the concentration of free lactic acid available for hydrogenation. It is noteworthy that potassium hydroxide is reported as a promoter in aqueous-phase hydrogenations of other organic compounds, but that is not the case for lactic acid.

To determine the effect of salts in higher concentration, potassium sulfate was added to a 0.55 M (5 wt.%) lactic acid solution. As seen in Fig. 8,
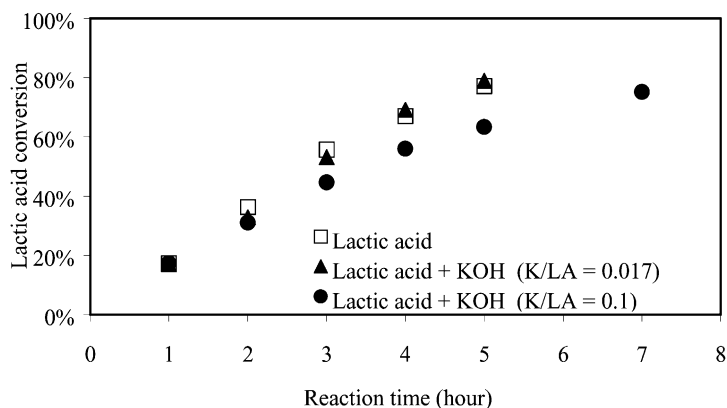
Fig. 7. Effect of potassium hydroxide addition on lactic acid conversion. Conditions: $T = 150°C$; $P = 14.5\,MPa$, 0.5 g Ru/C in 100 ml of 0.55 M lactic acid in water with KOH added as stated.

addition of 0.16 M K_2SO_4 reduces the reaction rate noticeably, and even more so at the higher concentration of 0.33 M. The catalyst is not poisoned, however, as conversion continues, albeit at a reduced rate. Simple calculation of ion concentrations based on pK_a (1.9 for HSO_4^- and 2.9 for lactic acid) indicates that free (protonated) lactic acid concentration declines by about 10% at the highest concentration of K_2SO_4 used. Thus, some of the decline in conversion rate can be attributed to a decline in free lactic acid concentration, but other effects must be present as well. Hydrogen solubility is known to decrease with increasing salt concentration [12]; this is primarily

responsible for the observed decrease in rate relative to lactic acid alone in solution. For instance, the solubility of hydrogen in 0.3 M Na_2SO_4 is 20% lower than in pure water; this difference accounts for the lower reaction rate in the batch reactor, as hydrogen is generally accepted to be the limiting reactant in aqueous-phase hydrogenations.

It is not likely that sulfate poisons the catalyst via irreversible adsorption, as the large quantities of sulfate present in solution are sufficient to completely deactivate the catalyst if poisoning were important. It is possible that either potassium or sulfate interact reversibly with the catalyst surface to inhibit
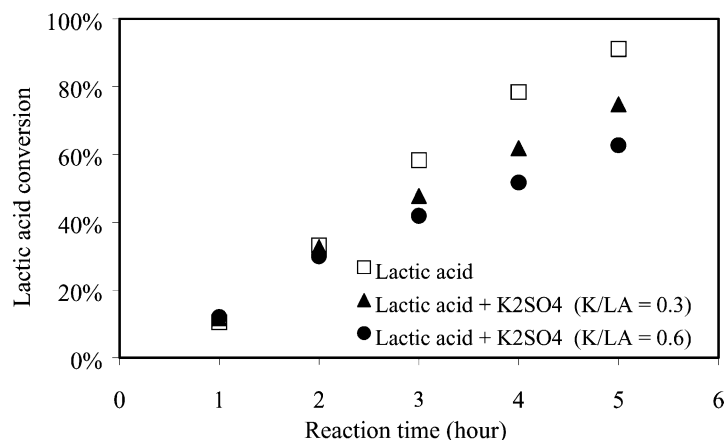

Fig. 8. Effect of potassium sulfate addition on lactic acid conversion. Conditions: $T = 150°C$; $P = 14.5\,MPa\ H_2$, 0.5 g Ru/C in 100 ml of 0.55 M lactic acid in water with K_2SO_4 added as stated.

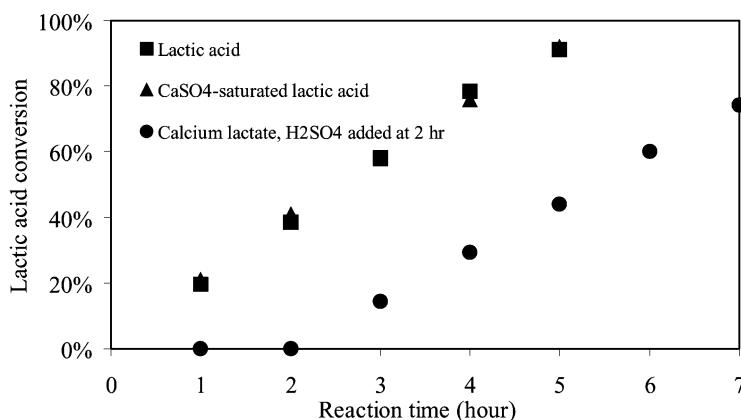Fig. 9. Influence of calcium salts on hydrogenation of lactic acid. Conditions: $T = 150°C$; $P = 14.5\,\text{MPa}\,H_2$, $0.5\,g\,Ru/C$ in $100\,ml$ of $0.55\,M$ lactic acid in water with calcium lactate added as stated.

activation of hydrogen or lactate, but further evaluation is beyond the scope of this study.

3.3.2. Calcium salts

Two experiments were conducted with calcium salts. First, a $0.55\,M$ (5 wt.%) lactic acid solution was saturated with $CaSO_4$ and then subjected to hydrogenation. As seen in Fig. 9, conversion of lactic acid and yield of PG were unaffected by the presence of calcium sulfate in solution. This is not unexpected, because the solubility of calcium sulfate in water is very low ($0.2\,g/100\,g$ water) and hydrogen solubility is unaffected.

A second experiment began with a solution of $0.55\,M$ calcium lactate. After being subjected to hydrogenation conditions for 2 h, during which no PG formation was detected, a molar quantity of H_2SO_4 equal to that of calcium lactate was added through the liquid sampling line of the reactor. Conversion of lactic acid and formation of PG were observed immediately. The reaction was continued for an additional 5 h, during which a substantial fraction of the lactic acid was converted. As seen in Fig. 9, the conversion rate was slightly lower than that of pure lactic acid. The $CaSO_4$ precipitates out of solution as it is formed; it is very likely that the precipitate also formed in the pores of the catalyst material and partially blocked the pores or catalyst surface, thus, reducing reaction rate. The reaction mixture was a gray slurry when removed from the reactor at the end of the experiment.

4. Discussion and conclusions

This study represents the first detailed study of hydrogenation of free lactic acid to PG in aqueous solution. The reaction takes place at mild temperatures (150°C optimally) and at moderate hydrogen pressures (10–14 MPa), especially when compared to prior work reported on lactate esters that used 20–30 MPa H_2. High pressure favors reaction rate and PG selectivity, but high temperature (>170°C) intensifies deep hydrogenation and secondary reactions to gaseous and liquid by-products. The high activity of ruthenium as a catalyst for hydrogenation of carboxylic acids has been noted previously [13], although few prior studies have been conducted in aqueous solution. Carbon is the favored support for the reaction because of its inertness in aqueous solution; a commercial catalyst and a prepared catalyst with 13% Ru dispersion performed in a similar fashion.

The finding that calcium lactate, the usual product of fermentation, can be readily converted to PG by adding a stoichiometric quantity of sulfuric acid and then hydrogenating has important implications for integration of this technology into a biomass-based manufacturing facility. Of course, the effect of other biogenic residues and impurities on the hydrogenation of actual lactate fermentation broths must still be examined, and will be the subject of continued study.

In summary, the present work illustrates the feasibility of converting lactic acid to PG in high yield and selectivity. Forthcoming results will examine additional aspects of the reaction, including operation in a continuous three-phase reactor.

Acknowledgements

References

[1] A. Thayer, Chem. Eng. News 75 (49) (1997) 14.
[2] H.H. Szmant, Organic Building Blocks of the Chemical Industry, Academic Press, New York, 1989.
[3] E. Brown, H. Adkins, J. Am. Chem. Soc. 56 (1934) 3689.
[4] H. Adkins, A. Pavlic, J. Am. Chem. Soc. 69 (1947) 3039.
[5] H. Adkins, H. Billica, J. Am. Chem. Soc. 70 (1948) 3121.
[6] H. Broadbent, G. Campbell, W. Bartley, J. Johnson, J. Org. Chem. 24 (1959) 1847.
[7] T. Ford, US Patent 2,607,807 (1952), to DuPont.
[8] J. Carnahan, T. Ford, W. Gresham, W. Grisby, G. Hager, J. Am. Chem. Soc. 77 (1955) 3766.
[9] S. Antons, B. Beitzke, US Patent 5,536,879 (1996), to Bayer.
[10] S. Antons, US Patent 5,731,479 (1998), to Bayer.
[11] P. Adams, R. Selff, B. Tolbert, J. Am. Chem. Soc. 74 (1952) 2416.
[12] W. Linke, Solubilities, 4th Edition, Van Norstrand, Toronto, 1958, pp. 1075–1083.
[13] R. Augustine, Catal. Today 37 (1997) 419.