Aqueous-Phase Catalytic Hydrogenation of Organic Acids and Their Mixtures

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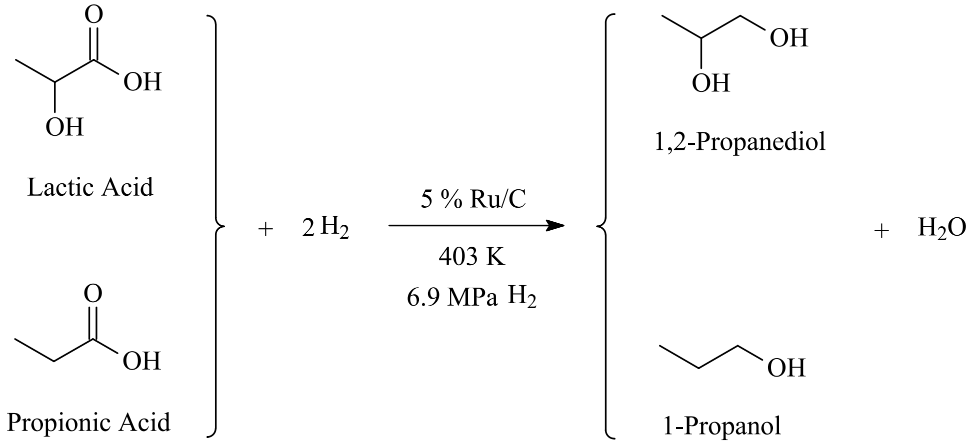
Abstract

The Ru/C-catalyzed hydrogenation reactions of lactic acid and propionic acid in aqueous solution were performed in a laboratory-scale stirred batch reactor. Kinetic data were collected over the ranges of temperature (343-423 K), hydrogen pressure (3.4-10.3 MPa) and acid feed concentration (0.05-5 M). The adsorption and reduction of individual acids, acid mixtures, and combinations of acids with their alcohol products on fully reduced catalyst were investigated. The acid conversion rates were not limited by mass-transport resistances over the reaction conditions studied. A Langmuir-Hinshelwood kinetic model was proposed to fit the acid conversion kinetics; rate constants and competitive adsorption coefficients for the reaction species were determined.

I. Introduction

Biomass-based organic acids are attractive feedstocks for chemicals production because they are available in quantity and can undergo a variety of reactions to form useful products. Hydrogenation of organic acids over metal catalysts in water produces alcohol products that are important building blocks for pharmaceuticals, foods, agriculture, and polymers. The development of low-cost, high-efficiency hydrogenation routes will open economically viable pathways from renewable resource-derived materials as alternatives to today's petroleum-based chemicals.[1,2]

To develop an improved mechanistic understanding of the conversion of organic acids to alcohols, we seek to investigate substrate-metal interactions in aqueous solution, and then to relate those adsorption properties to efficacy for hydrogenation. The aqueous-phase hydrogenation of lactic acid and propionic acid over 5 wt % Ru/carbon catalyst was performed in a three-phase stirred batch reactor (Scheme 1). Kinetic data were collected for reactions at 343-423 K, 3.4-10.3 MPa hydrogen pressure and 0.05-5 M acid feed concentration. The adsorption and reduction of individual acids, acid mixtures, and combinations of acids with their alcohol products on fully reduced catalyst were investigated to understand the relative binding strengths of the substrates on the metal surface, and how the presence of one species at the surface influences the reactivity of another. A Langmuir-Hinshelwood (L-H) kinetic model is presented in which lactic acid and propionic acid compete for one type of surface catalytic site and hydrogen dissociatively adsorbs on a second type of site. The research presented here provides insight into the catalytic reaction mechanism and forms the basis for further investigation of the organic acids hydrogenation.



Scheme 1. Hydrogenation of Lactic Acid and Propionic Acid

II. Experimental Section

Materials. Reagent-grade D,L-lactic acid (85 % solution in water) and 1-propanol (99 %) were purchased from Aldrich Chemical Co. Propionic acid with purity of > 99 % was obtained from J.T. Baker. 1,2-Propanediol (99.5 %) was ordered from Jade Scientific. The water used was of HPLC-grade purity (J.T. Baker). Ultrahigh-purity hydrogen gas (99.999 %, AGA) was used for all runs. The catalyst used was 5 wt % ruthenium on activated carbon powder obtained from PMC, Inc. The catalyst had a mean particle diameter of 150 μm, a N_2 BET surface area of 715.6 m^2/g, a porosity of 0.6, and a dry particle density of 800 kg/m^3. The ruthenium metal dispersion of the as-received catalyst, measured by volumetric hydrogen chemisorption in a Micromeritics ASAP 2700 instrument, was 8.8 %. The catalyst came as a 50.89 wt % slurry in water. Catalyst loadings and reaction rates are reported in the paper on a dry catalyst basis.

Reactor System. Reactions were carried out in a Parr series 5000 multiple reactor system equipped with a magnetically coupled stirring unit. The system contains six 75 ml reactors constructed of 316 stainless steel and rated to a maximum pressure of 20 MPa at 573 K. Each reactor is equipped with its individual heating mantle and ports for gas and liquid sampling.

Procedure. Reactions were typically conducted by adding 0.5 g of Ru/C catalyst (dry basis) to the dry reactor. The catalyst was pre-reduced in situ: The reactor was purged with nitrogen and heated to 423 K, and then charged with hydrogen to 3.4 MPa, and held at these conditions for 12 h. After the reactor was cooled to room temperature and the hydrogen was vented, 50 ml acid feed solution (0.05-5 M) was forced into the reactor from a sample cylinder under hydrogen pressure. The stirring speed was set to 1000 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 (343-423 K), the reactor was pressurized with hydrogen gas (3.4-10.3 MPa) to initiate the reaction. Liquid samples (1–2 ml) were typically taken at 1 h intervals throughout the reaction. Reaction time ranged from 5 to 30 h. At the end of the reaction, the reactor was cooled and the pressure was reduced.

Analytical. Liquid-phase samples were analyzed on a Spectra Tech P1000 HPLC (Thermo Separation Products, Inc.) with RI detection and UV detection at 250 nm. The separation was carried out on a Biorad Aminex HPX-87H column at 323 K. The mobile phase was 0.005 M H_2SO_4 in HPLC grade water with a flow rate of 0.45 ml/min. An internal reference (2-propanol) was used for quantitative analysis. Gas-phase samples were analyzed on a Varian 3300 GC instrument. Data from the HPLC and GC were used to calculate acid conversion, product yield, product selectivity, and overall closure of the material balance for the experiment.

III. Results and Discussion

Reaction Rate Data. Hydrogenation of lactic acid, propionic acid, acid mixtures, and combinations of acids with their alcohol products were performed at selected conditions within the following range: acid feed concentrations from 0.05 to 5 M, temperatures from 343 to 423 K, and hydrogen pressures from 3.4 to 10.3 MPa. The catalyst loading was 0.5 g (dry basis)/50 ml aqueous solution for all experiments. The selectivity to 1,2-propanediol for lactic acid hydrogenation ranged from 75 to 99 %, while the hydrogenation of propionic acid gave 1-propanol with < 50 % selectivity in most experiments. Methane, ethane, and propane were detected as the primary side products for both reactions. The results of these experiments are represented in part by the data points in Figures 1-4 (LA = lactic acid; PA = propionic acid; PG = 1,2-propanediol; 1-PrOH = 1-propanol).

The reaction rates were calculated via differential analysis: The acid conversion vs. time data were fit to an *nth*-order polynomial, which was then differentiated and evaluated at various times over the course of reaction. By incorporation of the acid concentration and the quantity and properties of the catalyst, reaction rate on a catalyst basis (kmol of acid/kg of catalyst/s) or on a fluid basis (kmol of acid/m^3 of solution/s) was determined.

Initial rates at time zero were calculated by applying the same differential method described above. These data were used to estimate the initial activation energy, and the dependence of rates on feed concentration and hydrogen pressure. This initial rate evaluation avoids possible complications from side reactions and catalyst deactivation. The values of initial activation energy for lactic acid and propionic acid hydrogenation are 56.61 kJ/mol and 67.13 kJ/mol, respectively. These values are consistent with a chemically controlled rate process.

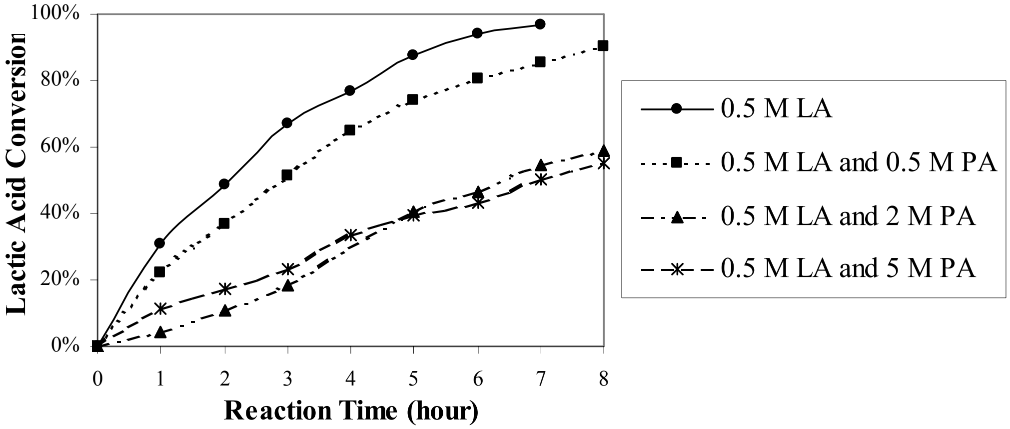


Figure 1. Effect of propionic acid on lactic acid hydrogenation rate.
Conditions: T = 403 K, P_{H2} = 6.9 MPa, 0.5 g catalyst/50 ml solution, 1000 rpm.

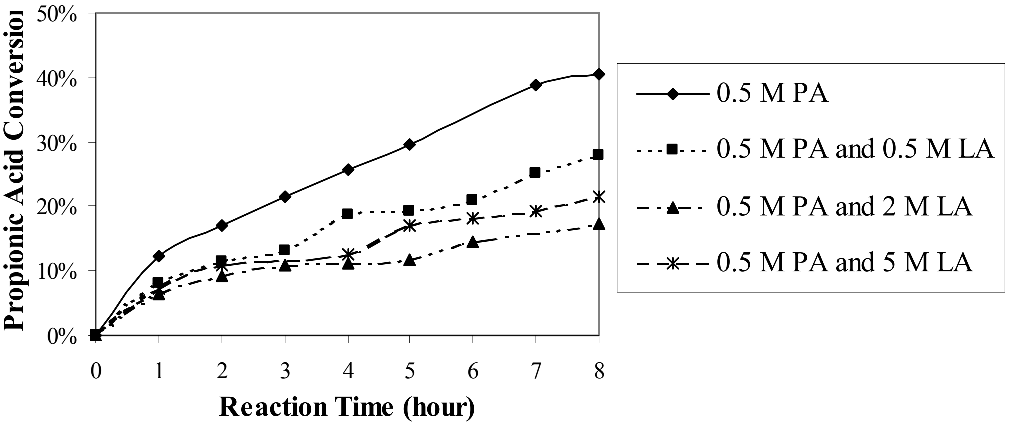


Figure 2. Effect of lactic acid on propionic acid hydrogenation rate. Conditions: T = 403 K, P_{H2} = 6.9 MPa, 0.5 g catalyst/50 ml solution, 1000 rpm.

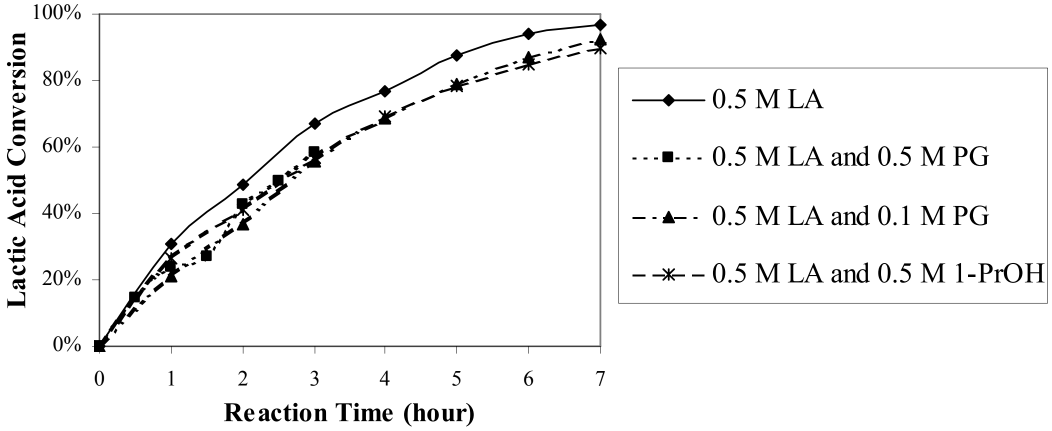


Figure 3. Effect of 1,2-propanediol and 1-propanol on lactic acid hydrogenation rate. Conditions: T = 403 K, P_{H2} = 6.9 MPa, 0.5 g catalyst/50 ml solution, 1000 rpm.

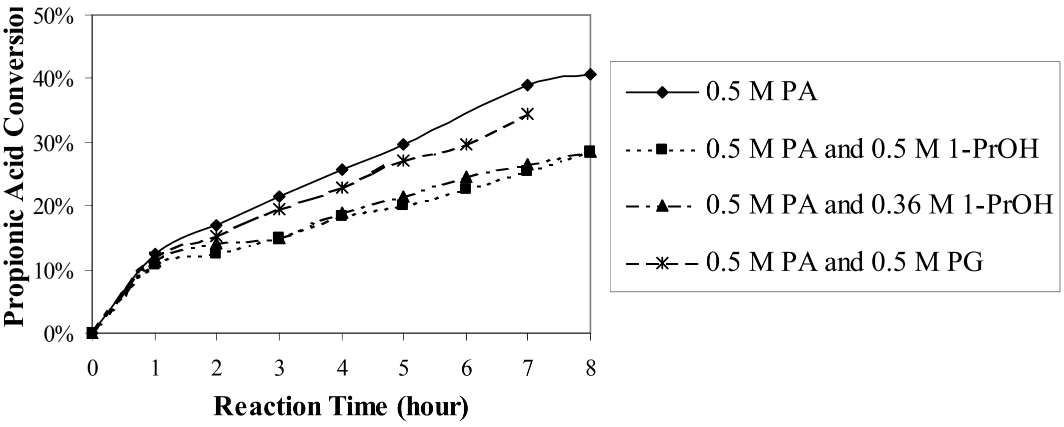


Figure 4. Effect of 1,2-propanediol and 1-propanol on propionic acid hydrogenation rate. Conditions: T = 403 K, P_{H2} = 6.9 MPa, 0.5 g catalyst/50 ml solution, 1000 rpm.

Kinetic Model. The catalytic hydrogenation of an organic acid to the corresponding alcohol product is a three-phase reaction involving hydrogen gas, aqueous solution of the organic acid and its alcohol product, and the solid catalyst. A thorough mass-transfer analysis showed that the reactor contents were well mixed and the acids conversion rates were not limited by mass-transport resistances over the ranges of temperature and acids feed concentration investigated, therefore the experimental rate profiles represent intrinsic reaction kinetics and are suitable for kinetic model development.

To describe the hydrogenation reactions for lactic acid, propionic acid and their mixture, a Langmuir-Hinshelwood-type kinetic model was postulated in which the acid adsorbs on one type of surface catalytic site (S_1) and hydrogen dissociatively adsorbs on a second type of site (S_2).[3] The following model structure was used for both individual acids:

$$\text{Acid} + S_1 = \text{Acid}\cdot S_1 \quad \text{(fast)} \quad \text{(1a)}$$

$$H_2 + 2S_2 = 2H\cdot S_2 \quad \text{(fast)} \quad \text{(1b)}$$

$$2H\cdot S_2 + \text{Acid}\cdot S_1 \longrightarrow \text{Intermediate}\cdot S_1 + 2S_2 \quad \text{(slow)} \quad \text{(1c)}$$

$$\text{Intermediate}\cdot S_1 + 2H\cdot S_2 = \text{Alcohol}\cdot S_1 + 2S_2 \quad \text{(fast)} \quad \text{(1d)}$$

$$\text{Alcohol}\cdot S_1 = \text{Alcohol} + S_1 \quad \text{(fast)} \quad \text{(1e)}$$

The rate-limiting step is the surface reaction that is considered irreversible, and the adsorption of water is neglected. Combining the rate expressions for the above elementary reaction steps and invoking the steady-state assumption for adsorbed intermediates yields the following expressions for the rate of individual acid consumption.

$$-r_{Acid}(kmol/kg\ of\ cat./\text{sec.}) = \frac{kC_{Acid}P_{H_2}}{(1+K_{Acid}C_{Acid})\left(1+\sqrt{K_{H_2}P_{H_2}}\right)^2} \qquad \text{(2a)}$$

$$k = k_s K_{Acid} K_{H_2} C_{t1}(C_{t2})^2 \qquad \text{(2b)}$$

where k_s is the surface reaction rate constant; K_{Acid} and K_{H2} are the adsorption constants for the acid and hydrogen, respectively; C_{t1} and C_{t2} are the total catalyst site concentrations for acid and hydrogen adsorption, respectively; both of them are considered constants. Figure 3 showed that LA has a much higher affinity for adsorption sites than its alcohol product PG.[4] Therefore the PG term in the denominator of the L-H rate equation for LA hydrogenation was eliminated. The same simplification was also used for 1-PrOH term in PA hydrogenation, although 1-PrOH showed a larger effect than PG on the acid reaction rates (Figures 3 and 4).

For the hydrogenation of acids mixtures, competitive adsorption occurs between lactic acid and propionic acid which affects their relative reaction rates. Figures 1 and 2 showed that adding a second acid significantly decrease the conversion rate of the first acid. This competition was addressed in the denominator of the two acid rate equations shown below. The denominator terms in the L-H rate expression represent the relative concentrations of vacant, hydrogen-occupied, lactic acid-occupied, and propionic acid-occupied surface sites.

$$-r_{LA}(kmol/kg\ of\ cat./\mathrm{sec.}) = \frac{k_1 C_{LA} P_{H_2}}{(1+K_{LA}C_{LA}+K_{PA}C_{PA})\left(1+\sqrt{K_{H_2}P_{H_2}}\right)^2} \qquad (3a)$$

$$k_1 = k_{s1} K_{LA} K_{H_2} C_{t1} (C_{t2})^2 \qquad (3b)$$

$$-r_{PA}(kmol/kg\ of\ cat./\mathrm{sec.}) = \frac{k_2 C_{PA} C_{H_2}}{(1+K_{LA}C_{LA}+K_{PA}C_{PA})\left(1+\sqrt{K_{H_2}P_{H_2}}\right)^2} \qquad (4a)$$

$$k_2 = k_{s2} K_{PA} K_{H_2} C_{t1} (C_{t2})^2 \qquad (4b)$$

The experimental data used to determine the rate constants in the kinetic model were taken from 27 experiments at 403 K. The regression results for L-H rate equations (3) and (4) are reported in Table 1. The parity plots illustrating the agreement between experimental and predicted rates at 403 K are shown in Figures 5-8. The fit of the model was quite good for hydrogenation of both individual acids (Figures 5 and 6) over a wide range of concentrations (0.1-5 M). For the hydrogenation of acid mixtures, the fit of lactic acid data was good (Figure 7). However, the experimental data for propionic acid at high total acids feed concentrations (4-5.5 M) fell outside the y = x line in the parity plot (Figure 8). The scatter of data may due to the formation of esters at high acid concentrations.

Table 1. Kinetic Constants in L-H Rate Expression (Equations 3 and 4)[a]

Constants	403 K
k_1 (m^3/kg of cat./MPa/s)	1.19E-05
k_2 (m^3/kg of cat./MPa/s)	1.66E-06
K_{LA} (m^3/kmol)	2.111918
K_{PA} (m^3/kmol)	1.349141
K_{H2} (MPa^{-1})	0.258207

[a]Conditions: 403 K; 7 MPa H_2; 0.5 g catalyst (dry basis)/50 ml of solution; 1000 rpm.

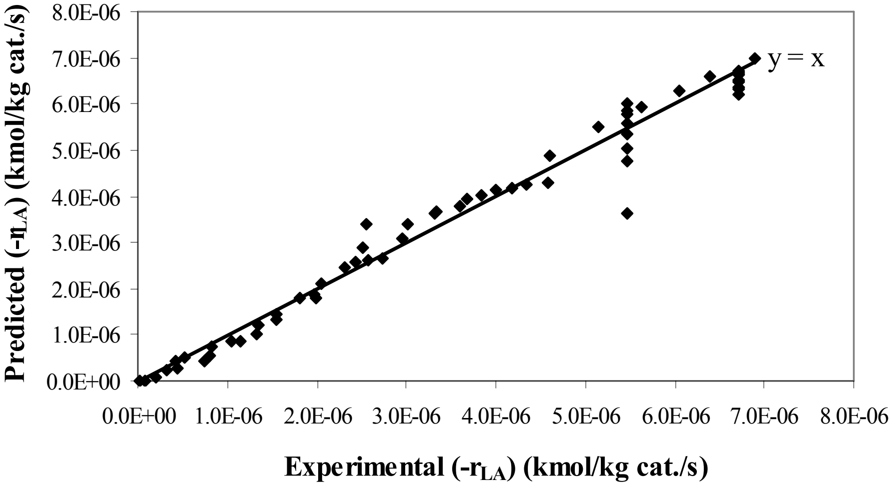


Figure 5. Comparison of experimental and predicted rates for individual lactic acid hydrogenation at 403 K.

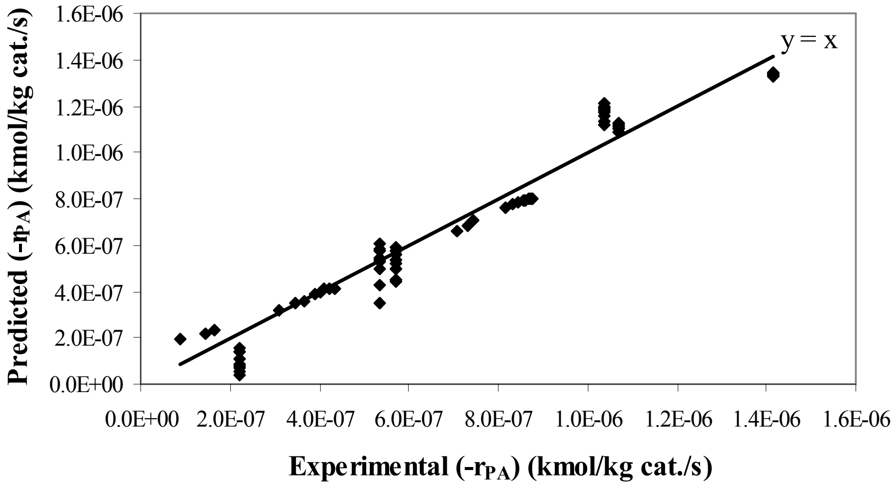


Figure 6. Comparison of experimental and predicted rates for individual propionic acid hydrogenation at 403 K.

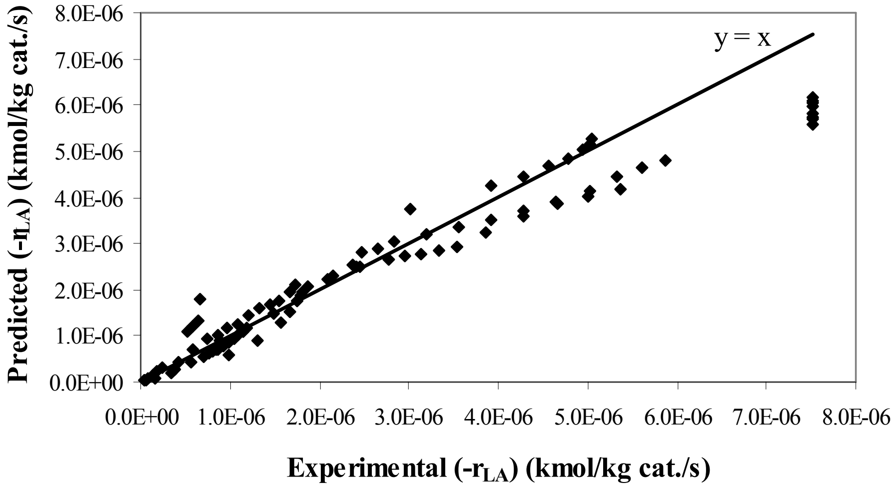


Figure 7. Comparison of experimental and predicted lactic acid rates for hydrogenation of acids mixture at 403 K.

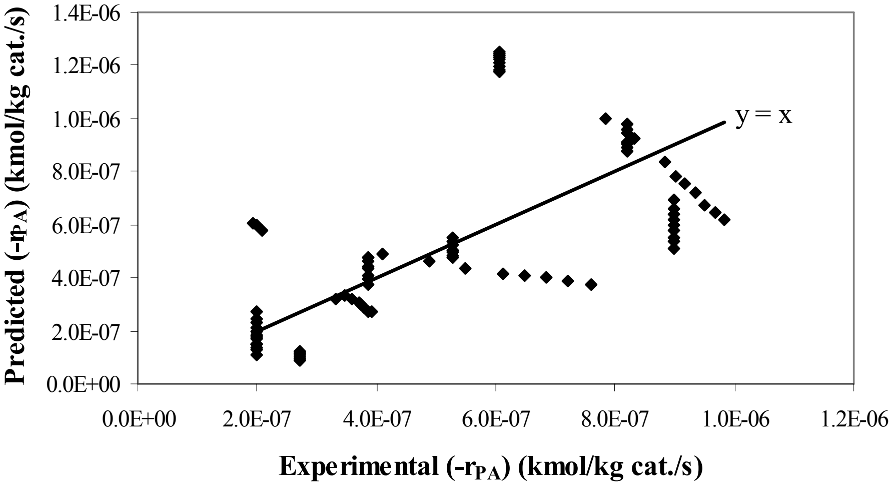


Figure 8. Comparison of experimental and predicted propionic acid rates for hydrogenation of acids mixture at 403 K.

IV. Conclusions

A Langmuir-Hinshelwood kinetic model was proposed from the experimental data to describe the hydrogenation of lactic acid, propionic acid and their mixture. Competitive adsorption between the two acids was incorporated in this model. Adsorption study of multiple organic acids and combinations of acids with other species on the Ru/C catalyst surface is ongoing in our laboratory, which will be helpful in developing an improved mechanistic understanding of the conversion of organic acids to alcohols.

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