Polyols and Organic Acids Adsorption Onto Activated Carbon, and Its Role in Aqueous-Phase Catalytic Hydrogenation Rates

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1. INTRODUCTION

Increasing global energy demands have driven research in both alternative renewable energy supplies and synthesis of commodity chemicals from bio-based feedstocks. Many prior studies have used noble metal supported on activated carbon as catalysts for hydrogenation reactions that are often required for such commodity chemical production and often take place in aqueous solution. To gain a deeper understanding of aqueous-phase catalysis involving activated carbon-supported catalysts, it is necessary to study interactions between species in solution and the activated carbon support. This is because the activated carbon micropores and functionalized carbon surfaces facilitate selective adsorption of organic species from water; at equilibrium this adsorption typically leads to local reactant and product concentrations in the catalyst vicinity (e.g. in activated carbon micropores) that are significantly different than those in the bulk solution phase outside the carbon support. If chemical reaction kinetics and mass transport were characterized in terms of thermodynamic activity, these differences in concentration would be inconsequential, because at equilibrium the thermodynamic activity of solution and adsorbed species are the same. However, because chemical kinetics and mass transport are commonly represented in terms of solution concentration or mole fraction, a correct description of reaction kinetics must account for the difference in concentration between solution and pore. Thus, to practically characterize reaction kinetics and product inhibition of GO hydrogenolysis and gain further insight into aqueous-phase catalytic reactions in general, we have undertaken this study to characterize the adsorption of glycerol, lactic acid, propanoic acid, and their hydrogenolysis products into activated carbon supports, with the goal of characterizing local concentrations in the catalyst pores and eventually incorporating local pore concentration into kinetic modeling and reactor design of hydrogenolysis.

2. EXPERIMENTAL

2.1. Materials

The solutions for this study were made using HPLC grade water (J.T. Baker, Phillipsburg, NJ). Glycerol, propylene glycol, lactic acid, propionic acid, and sulfuric acid for the HPLC mobile phase were supplied by Sigma-Aldrich (St. Louis, MO) and were used as received. Ruthenium sponge catalyst was also supplied by Sigma-Aldrich.

2.2. Carbon Characterization

The carbons used in this study were a 0.8 mm extrudate activated carbon (ROX 0.8, lot #520020, Norit Americas, Marshall, TX) and a powder activated carbon (designation 3310, lot #28850, Johnson Matthey, Sevierville, TN). Both of these carbons have served as support

materials for catalysts we have used in hydrogenation and hydrogenolysis studies. The total surface area of each carbon was characterized by BET nitrogen physisorption at 78 K over a relative pressure of P/P_0 from 0.0 to 0.2 in a Micrometrics ASAP 2010 (Micrometrics Instrument, Norcross, GA). Surface area was calculated from the BET equation; micropore volume was determined using the t-plot method and total pore volume was characterized as volume adsorbed at the maximum relative pressure of 0.99. A summary of the carbon characterization results is given in Table 1.

Table 1. Carbon Characterization by N_2 Adsorption at 78 K.

Carbon Type	**3310**	**ROX**
BET Surface Area (m^2/g)	715.6	833.6
Micropore Area (m^2/g)	374.8	585.8
Total Pore Volume (cm^3/g)	0.654	0.536
Micropore Volume (cm^3/g)	0.173	0.272

2.3. Adsorption Measurements

The quantity of material adsorbed onto activated carbon in this study was determined by the difference in initial and final species concentration in solution, which were measured prior to and following exposure to activated carbon catalyst supports, respectively.

$$C_{AS} = \frac{(C_{Ao} - C_A) \cdot V_{solution}}{m_{carbon}} \quad (1)$$

Isothermal adsorption experiments at 25°C were performed using 8.5mL glass vials with Teflon-lined plastic lids. The vials were initially washed in HPLC-grade water, air-dried, and weighed in preparation for experiments. Carbon was weighed and added to the vials based on the total concentration of the solute(s) to be studied (0.1g carbon ≤ 0.1 M < 0.5g carbon ≤ 0.750 M < 1.0g carbon ≤ 2.0 M) in order to maintain at least a 15% change in solution concentration before and after adsorption. A quantity of solution of known concentration was then added to the vials to give approximately 7mL total solution + carbon in the vial. The final vial weight was then recorded for analysis following reaction. The vials were capped and rotated end-over-end on a rotator overnight to ensure thorough mixing and equilibration. Upon removal from the rotator, the vials were either centrifuged or left standing for approximately 30 minutes to allow the suspended carbon in the sample to settle. One milliliter samples were then taken and analyzed via HPLC using the method described below.

Adsorption measurements were performed at elevated temperatures (40°C – 160°C) using a Parr 5000 multireactor system (Parr Instrument Company, Moline, IL). This system has six 75mL stainless steel reactors with internal stirring, independent temperature control, and continuous pressure monitoring. For these experiments, the reactors were cleaned and air-dried, and then carbon was added to the reactors according to the solution concentration to be examined: one gram of carbon was used for 0.05 M and 0.2 M concentrations of GO or PG, and four grams were used for a 0.5 M concentration. A Teflon stir-bar and 60mL of solution were added to the reactor. All starting, intermediate, and final weights were recorded. The desired

temperature was set and the reactor contents were held for at least two hours at the desired temperature, after which a liquid-phase sample was taken. (The two-hour equilibration time was verified by room temperature experiments in vials for different time periods from 0.5 to 24 hr.) Sampling consisted of removing 1.5mL of waste to clean the sampling line, followed by removal of 1.0 mL as a sample. Typically, multiple temperatures between 40 and 160^{o}C were examined in each experiment. All waste aliquots and samples were collected and weighed at the conclusion of the experiment to check for mass loss via system leaks. Samples were analyzed using the HPLC method described below.

2.4. Analysis

All samples from adsorption experiments were analyzed using a high pressure liquid chromatography system consisting of a Waters 717Plus autosampler (Waters Corporation, Milford, MA), a Perkin Elmer pump (Perkin Elmer, Wellesley, MA), a Waters 410 differential refractometer, and a Perkin Elmer LC 90 UV spectrophotometric detector. The system used Bio-Rad HPX87H column (Bio-Rad Laboratories, Hercules, CA) with 5mM sulfuric acid solution as the mobile phase. The column was operated isocratically at 40^{o}C and a mobile phase flow rate of 0.6 ml/min.

A sample injection size of five microliters was used for samples above 0.1 M concentration; ten microliter injections were used for samples below or at 0.1 M. Samples with a concentration above 0.5 M were diluted by a factor of four to maintain an injected concentration between 0.1 M and 0.5 M. A three-point calibration curve was used to determine response factors for GO and PG – no internal standards were thus used in determining species concentrations.

3. RESULTS

3.1. Glycerol (GO) and Propylene Glycol (PG) Adsorption on ROX carbon

Adsorption experiments were conducted on ROX carbon for PG and GO solution concentrations ranging from 0.01 M to 2.0 M and at temperatures ranging from 25^{o}C to 160^{o}C. All data from single component adsorption experiments were modeled using both the Freundlich and Langmuir isotherms to obtain adsorption constants at each temperature.

$$\text{Freundlich:} \quad C_{AS} = K_F \, C_A^{\,n} \tag{2}$$

$$\text{Langmuir:} \quad C_{AS} = \frac{K_A \, C_A \, C_{TA}}{1 + K_A \, C_A} \tag{3}$$

For the Freundlich isotherm, the coefficients K_F and n were found by a least-squares linear regression of experimental data as $ln(C_{As})$ vs. $ln(C_A)$ to give slope n and intercept $ln(K_F)$. For the Langmuir isotherm, a plot of experimental data as (C_A/C_{As}) vs. C_A gives a slope $1/C_{TA}$ and an intercept $(1/K_AC_{TA})$. Once adsorption constants at each temperature were determined, a plot of $\ln(K_A)$ vs. 1/T was made to determine the heat of adsorption ΔH_a and preexponential factor K_o. A summary of the calculated parameters for each adsorption isotherm is given in Table 2. Figure 1 compares the experimental quantities adsorbed with those predicted by the Freundlich and Langmuir isotherm models for individual adsorption of GO and PG on XOR

activated carbon at room temperature. As can be seen, the Langmuir isotherm gives the best fit of GO adsorption over the entire concentration range studied. For PG, the Langmuir model gives the best fit below 0.75 M, but the Freundlich model better describes the data at concentrations above 0.75 M. The observed isotherm for PG suggests that the quantity adsorbed reaches a plateau at the Langmuir maximum of C_{TA} ~ 1.64 mol/kg at about 0.75 M in solution and then adsorbs by another mechanism at higher concentration. Glycerol shows no tendency to adsorb beyond its Langmuir maximum of C_{TA} = 1.77 mol/kg. While the reported value of the Langmuir C_{TA} for GO is ~8% larger than that for PG, we do not believe that the difference in the two values is significant. Because GO and PG have nearly identical molar volumes of 73.0 mL/mol, the volume of species adsorbed according to the Langmuir model is likewise similar. It is significant, however, that the molar quantity of PG adsorbed is greater than that of GO at any concentration below the Langmuir maximum; this is reflected by the fact that the calculated adsorption equilibrium constant for PG is approximately three times that for GO.

Table 2. Langmuir and Freundlich isotherm coefficients for GO and PG on ROX carbon.

	GO	**PG**
Langmuir		
C_{TA} (mol/kg)	1.77	1.64
$K_{A,298K}$ (M^{-1})	4.75E-03	1.63E-02
ΔH (kJ/mol)	-15.91	-14.68
K_0 (M^{-1})	7.73E-06	4.36E-05
R^2 Fit	0.983	0.997
Freudlich		
K_F	0.105	0.202
n	0.379	0.323
R^2 Fit	0.946	0.916

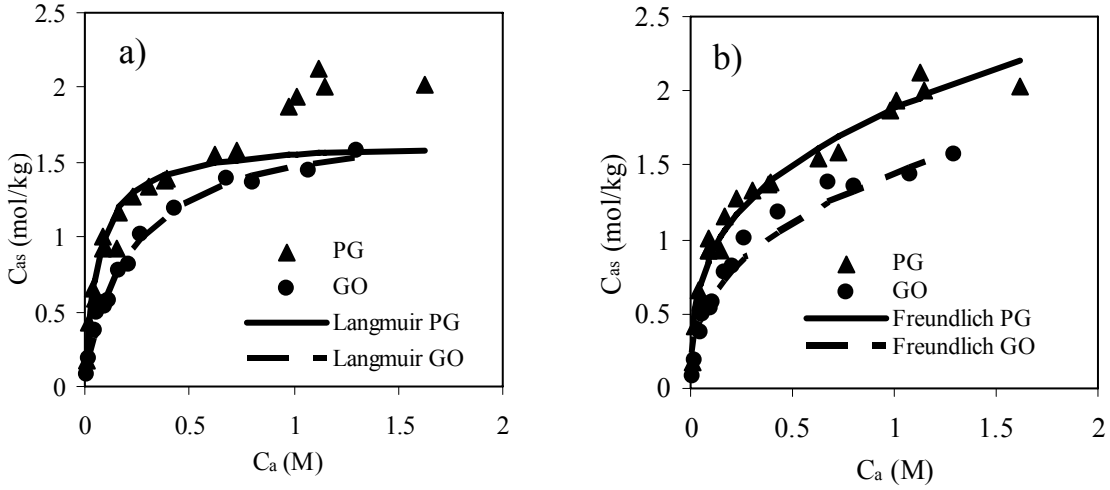

Figure 1. Experimental and predicted a) Langmuir and b) Freundlich adsorption isotherms for PG and GO at 25°C on ROX carbon.

Adsorption from aqueous solutions of PG and GO at total species concentrations ranging from 0.05 to 0.5 M and species fractions of PG and GO ranging from 0 to 1.0 were conducted at room temperature and at elevated temperatures. The extended Langmuir model (Eq. (4) and (5)) has been applied as the model of choice for mixed solute adsorption; the denominator of the extended Langmuir model accounts for competitive adsorption of the two species (A=GO; B=PG) into the activated carbon micropores.

$$C_{AS} = \frac{K_A C_A C_{TA}}{1 + K_A C_A + K_B C_B} \tag{4}$$

$$C_{BS} = \frac{K_B C_B C_{TB}}{1 + K_A C_A + K_B C_B} \tag{5}$$

All coefficients (C_{TA}, C_{TB}, ΔH_A, ΔH_B, K_{Ao}, K_{Bo}) required in the extended Langmuir model were taken from the single component results reported in Table 2.

Figure 2 shows the predicted two component adsorption isotherms on ROX carbon at 25°C and total initial concentrations of 0.05 M, 0.3 M, and 0.5 M. The abscissa in Figure 2 is the fraction of glycerol in the total solute present (GO/(GO+PG)) – not mole fraction in solution. The data are reported in this fashion to show comparison of model with experiment and accentuate the different adsorption behavior of GO and PG. It is seen that the extended Langmuir model accurately predicts the adsorption of propylene glycol and glycerol over the studied concentration range. The preference for PG adsorption is clear; in fact, at equimolar concentrations the quantity of PG adsorbed is approximately three times that of GO, in accordance with the ratio of equilibrium constants determined in single component experiments.

3.2 Adsorption and Hydrogenation of Lactic Acid and Propionic Acid

Adsorption experiments with lactic acid (LA) and propionic acid (PA) were performed on 3310 activated carbon. Representative results of these adsorption studies are shown in Figures 3, as the quantity of each acid adsorbed as a function of temperature at 0.25 M solution concentration. The results indicate that propionic acid is more strongly adsorbed into the carbon pore structure than is lactic acid. Based on a micrcopore volume of 0.173 cm^3/g (Table 1) for 3310 carbon, the local concentration of propionic acid at 100-150^oC, which is the typical reaction temperature for hydrogenation, is 7-8 times that of the bulk concentration of 0.25 M. In contrast, lactic acid pore concentration is only 2.5 – 3 times the bulk concentration at those temperatures.

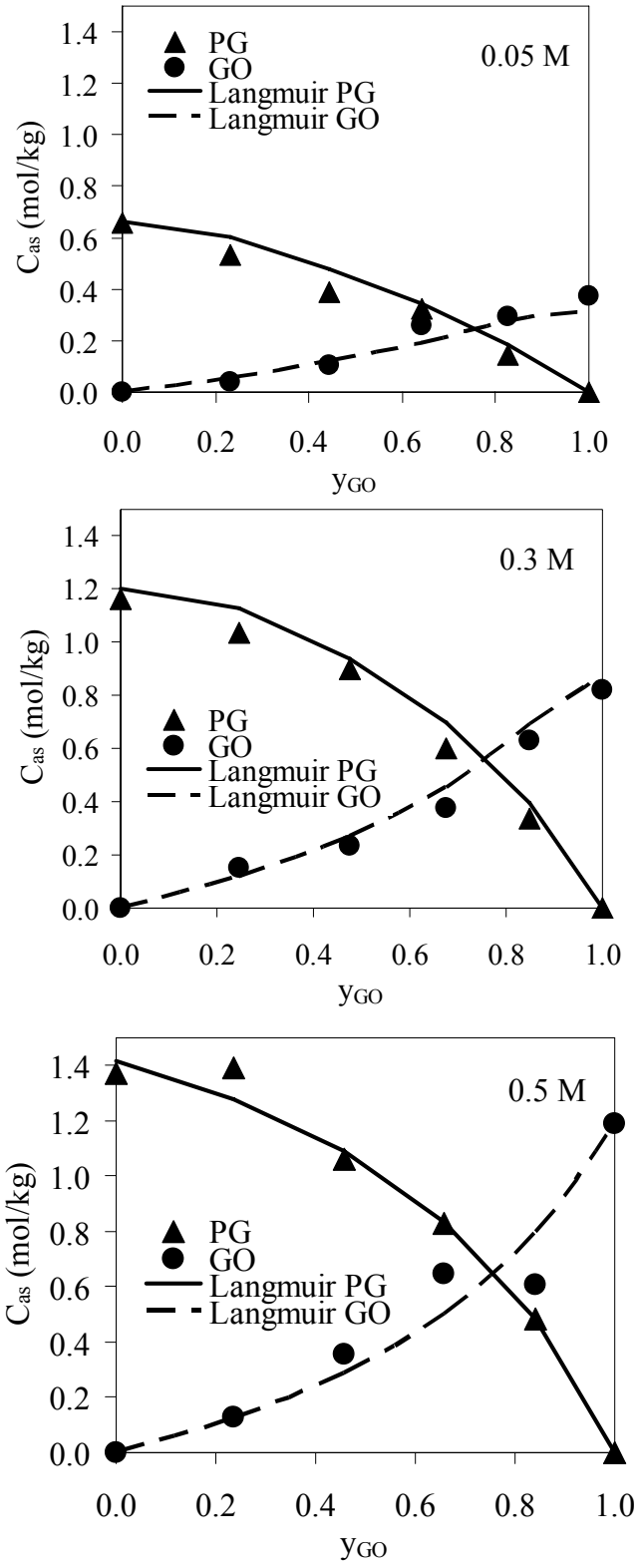

Figure 2. Experimental and predicted Langmuir isotherms for mixtures of GO and PG on ROX carbon at 25°C and 0.05 M, 0.3 M and 0.5 M total species concentration. Abscissa is fraction of GO in the total species (GO + PG) present.

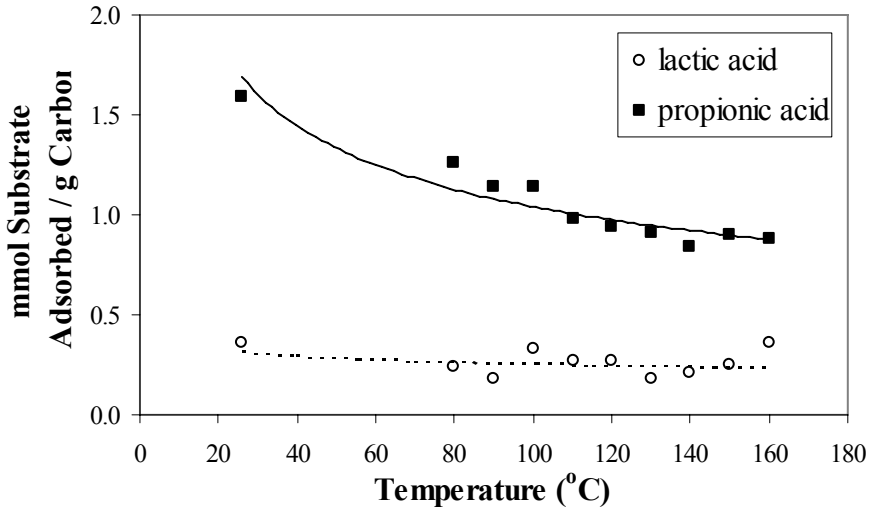

Figure 3. Temperature dependent adsorption of lactic acid and propionic acid on activated carbon 3310.

The aqueous-phase hydrogenation of lactic acid (LA), propionic acid (PA) and their mixtures was performed in a Parr 4560 batch reactor at 403 K and 7 MPa hydrogen pressure. Both 5 wt % ruthenium supported on 3310 activated carbon and nonporous Ru bulk sponge were used as catalysts to determine the effect of microporosity on reactivity. The metallic surface area of each catalyst, measured by volumetric hydrogen chemisorption in a Micromeritics ASAP 2010 instrument, is 1.6 m^2/g for the Ru/C and 0.2 ~ 0.4 m^2/g for the Ru sponge. For direct comparison of results between the two catalysts, both ruthenium catalysts were pre-reduced at the same conditions (473 K and 3.4 MPa hydrogen pressure for 12 hours). The acid conversion rates were calculated on a metallic surface area basis (mol acid / m^2 metallic surface area / s).

The initial hydrogenation rates of lactic acid, propionic acid, and their mixtures are summarized in Table 3. Both acids react faster on the carbon-supported ruthenium catalyst than on the ruthenium sponge. The lactic acid initial rate on Ru/C is 1.4 times the initial rate on Ru sponge, and the propionic acid initial rate on Ru/C is three times that on Ru sponge. This increase in hydrogenation rates observed on carbon-supported ruthenium catalyst results from higher local acid concentrations inside the carbon micropore.

Hydrogenation of an equimolar lactic acid / propionic acid mixture gives an initial rate of lactic acid 16 times that of propionic acid over the un-supported ruthenium sponge catalyst, while on the carbon-supported ruthenium catalyst the initial rate of lactic acid is only five times that of propionic acid. The ratio of initial rates in the carbon-supported ruthenium is much lower because of the local enhancement of propionic acid concentration in the carbon micropore, resulting in its enhanced reaction rate. No such enhancement is observed over the nonporous Ru sponge – we thus conclude that the actual ratio of reactivity of lactic acid to propionic acid is sixteen, but that value is disguised over Ru/C catalyst because of pore concentration enhancement.

Table 3. Comparison of the acid hydrogenation rates over carbon-supported and un-supported ruthenium catalysts

Catalyst	Starting Materials	Initial Rate × 10^7 (mol / m^2 metallic surface area / s)		Initial Rate Ratio (LA / PA)
		LA	PA	
2.7 g Ru Sponge	0.1 M LA	6.07		
	0.1 M PA		0.76	
	(0.1 M LA) & (0.1 M PA) mixture	6.27	0.39	16
0.5 g (5 wt % Ru/C)	0.1 M LA	8.27		
	0.1 M PA		2.08	
	(0.1 M LA) & (0.1 M PA) mixture	7.15	1.43	5

Conditions: T = 403 K, P_{H2} = 7 MPa, 50 ml aqueous solution, 1000 rpm.

4. CONCLUSIONS

The use of activated carbon-supported catalysts for aqueous phase catalytic conversion of biorenewable, water-soluble substrates leads to local enhancement in pore concentration of reactant and product species. Organic species with only modestly different structures show surprisingly different affinities for adsorption in activated carbon; this difference in affinity has a strong effect on the observed rate of reactivity of the species over carbon-supported catalysts. In order to properly characterize kinetics of biorenewable feedstock conversion, particularly when mixtures of materials are present, it is necessary to consider this adsorption behavior in kinetic modeling and reactor design.