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Catalytic Hydrogenation of Amino Acids using Polymer-Derived Microenvironments

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CATALYTIC HYDROGENATION OF AMINO ACIDS WITH POLYMER-DERIVED MICROENVIRONMENTS

by

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ABSTRACT

Amino acids are organic compounds that can be found all around us in the world in the building blocks of proteins and peptides. One class of compounds which can be synthesized from amino acids are amino alcohols, another critical compound in society. Amino alcohols are key components in agricultural products and pharmaceutical products. Therefore, developing an efficient and cost-effective method for performing this transformation is an important area of research. The currently used industrial process is to reduce petroleum-derived amino acids with $NaBH_4$. However, this process is time-consuming and costly because of the need for an intermediate stage esters and further processing afterwards to produce the amino alcohols.

A proposed alternative to $NaBH_4$ is hydrogenation using ruthenium supported on carbon catalyst in the presence of phosphoric acid. The advantage of this reaction over the currently used industrial process is that Ru-catalyzed hydrogenation has been shown to have high selectivity to amino alcohols and can maintain the optical purity, a critical component in the use of amino alcohols in pharmaceuticals. Unfortunately, this process is not currently cost-effective or reproducible on an industrial scale because of the expense of the catalyst and the fact that the acid co-catalyst cannot be recycled, adding to the cost. Our proposed solution was to impregnate the catalyst with a polymer that can created acidic active sites within the catalyst pores, eliminating the need for the acid. By impregnating 2.9 wt% polyacrylate onto a Ru supported by alumina catalyst, we were successful in converting 51.8% of our alanine to alaninol without the addition of any acid co-catalyst. The catalyst can then be filtered out and reused, adding a major economic and environmental advantage for hydrogenation versus the current industrial process.

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1. INTRODUCTION

Amino acids are organic compounds which have a wide variety of industrial uses. They account for about 40% of the human nutrition and health market as well as 55% of the animal-nutrition sector, where they provide important animal feed additives.[1] Amino acids are also key chemical components within products like catalysts, flavor enhancers and intermediates for medicines like antibiotics.[2] Amino acids also make up the building blocks of critical biological materials such as proteins and peptides. One of the most useful class of compounds derived from amino acid reactions are amino alcohols. These alcohols provide building blocks in agricultural products and in pharmaceutical and peptide chemistry[3] as well as intermediates for synthesis of insecticidal reagents and chiral auxiliaries.[2]

As a result, developing efficient and cost-effective methods for transforming amino acids into amino alcohols is an important area of research. However, it is not simply a matter of economics anymore. A pattern can be seen in the previous research on methods of producing amino acids. Newer methods of producing amino acid focus on being both economically beneficial and environmentally friendly. Today, amino acid starting blocks can be produced from sugars naturally occurring in biomass instead of through time-consuming and expensive chemical process that produce waste streams.

In keeping with this pattern, current research on the production of amino alcohols focuses on increasing both the efficiency and reducing the environmental impact of these processes. One method that offers both an economical and environmentally-friendly alternative to previous methods of production is direct aqueous-phase catalytic hydrogenation of amino acids with a ruthenium supported on carbon (Ru/C) catalyst in

the presence of an acidic reaction solution.[3] This process is atom-economical and can maintain the chirality of the amino acid starting block. This is a critical requirement because enantiomerically pure amino alcohols are economically beneficial.[1] Furthermore, this process has shown favorable selectivity and optical purity and is amenable to continuous processing without creating byproduct waste streams.[3]

Previous Methods of Amino Acid Production

Extraction of Amino Acids

Production of amino acids can be achieved via extractive processes, chemical processes, or biological processes.[1] The original method of producing amino acids is extraction. In the extraction process, protein-rich biological material is subjected to hydrolysis, after which the amino acid within the protein hydrolysate can be isolated.[1] Extraction allows for direct access to a series of different amino acids. However, for this process to be feasible, the amino acid must have properties that differ significantly from other amino acids in the protein hydrolysate An example of such a physical property difference would be if the desired amino acid lacks solubility and can be separated by removing the fraction of water soluble amino acids. One disadvantage of this method is the formation of salts as by-products, making this a less desirable method from an environmental standpoint.[1]

Chemical Synthesis of Amino Acids

Racemic mixtures of α-amino acids can be produced using four different methods: The Hell-Volhard-Zelinsky reaction, the Amidomalonate synthesis, reductive amination, or the Strecker synthesis. The Hell-Volhard-Zelinsky reaction (Figure 1) is the oldest

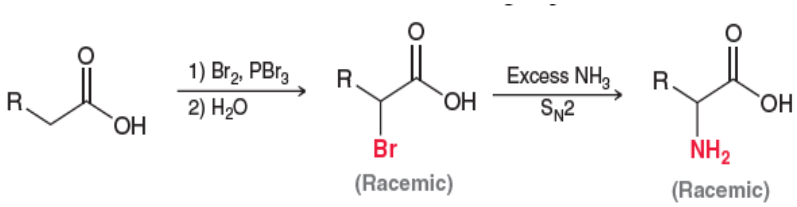

Figure 1. Hell-Volhard-Zelinsky Reaction[4]

method for preparing racemic mixtures of α-amino acids. This reaction has two steps. First the α position of a carboxylic acid is functionalized with a halide. Then the halogen is replaced with an amino group in an S_N2 reaction.[4] The Amidomalonate synthesis involves four steps[5]: (1) deprotonation, (2) S_N2 alkylation with a primary alkyl halide, and (3) hydrolysis of the amide group and esters, and (4) decarboxylation. During deprotonation, diethyl acetamidomalonate is converted into an enolate ion using a base. In the second step, the identity of the amino acid is determined by the choice of alkyl halide used.[4]

Reductive amination allows for the synthesis of α-amino acids converting the carbonyl group of an aldehyde or ketone into an amine via an intermediate imine. This method is considered the most important way to make amines. Most of the amines used in the pharmaceutical industry are made this way.[5] The final is the Strecker synthesis

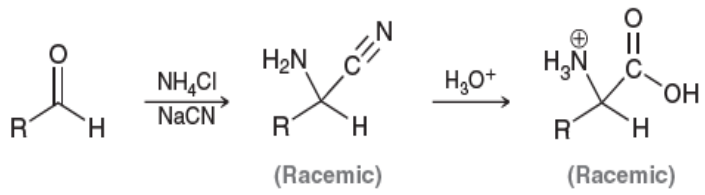

Figure 2. The Strecker Synthesis[4]

(Figure 2). This reaction produces α-amino acids from aldehydes by converting the aldehyde into an α-amino nitrile followed by hydrolysis of the cyano group to yield a carboxylic acid group.[4]

Chemical Synthesis of L-Alanine

There are two well-known methods for producing racemic mixtures of Alanine. The first is through the reductive amination reaction described previously. Through this method pyruvic acid is treated with ammonia in the presence of $NaBH_4$.[5] The second is through the Strecker synthesis (Figure 3). In both the Strecker synthesis and reductive amination, a racemic mixture of (L,D)-alanine is produced. The amino acid used

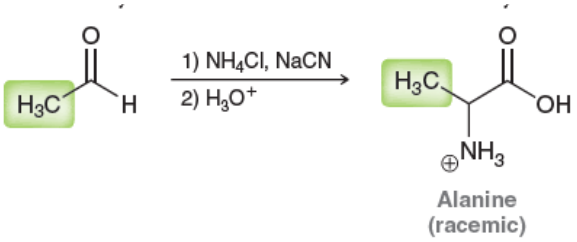

Figure 3. Strecker Synthesis of Alanine[4]

throughout this thesis is L-alanine. To obtain this optically active amino acid, the racemic mixture must undergo resolution with a chiral catalyst. A resolution is the separation of racemates into their component enantiomers.[6] This process proves difficult because enantiomers have identical physical properties. Therefore, racemates are reacted with an enantiomerically pure chiral reagent to give a mixture of diastereomers. Diastereomers have different physical properties and can be physically separated. Once separated, the diastereomer reaction is reversed to produce the two separated enantiomers.[6]

Environmental Evolution for Producing Amino Acids

Biocatalytic Synthesis

In biocatalysis, enzymes are employed as catalysts to perform chemical transformations on organic compounds. Before the discovery of enzymes, wild type microorganisms were used because they could accumulate amino acids given suitable media and conditions.[7] This process was not applicable industrially because there was a limited range of amino acids that could be produced with this process and those that could, had low concentrations. The discovery of mutants and microbial enzymes pushed genetic biochemistry further, allowing for biocatalyics on an industrial scale to be plausible.[7]

Today, the most common enzyme systems used industrially are hydrolases, lyases, and racemases.[9] There are numerous advantages of enzymes production. For instance, enzymes are capable of performing reactions with high chemical selectivity in terms of substrate selectivity, stereoselectivity, regioselectivity, and functional group selectivity.[8] Additionally, enzyme reactions can be carried out under moderate temperature and pressure, have minimal byproducts, and high catalytic efficiency.[1,8] Furthermore, enzymes are environmentally friendly because they are completely biodegradable, can results in processes with fewer waste disposal issues, and require lower energy input.[8] Despite these advantages, biocatalysis is not considered a commercially viable method by many synthetic chemists. It is commonly believed that enzymes are too expensive, lack stability and productivity, and cannot catalyze industrially interesting reactions.[8]

Biocatalytic Synthesis of L-Alanine

As previously stated, L-alanine can be produced via the synthesis of a racemic mixture and resolution process. One major disadvantage to this process is that it is less efficient and costlier because half of the starting material is wasted if only one enantiomer is desired.[4] An alternative to this process is biotransformation (Figure 4)[1]. With this method, an enzyme can be utilized in place of chiral catalysts to perform enantioselective catalysis. Only a small amount is required to prepare amino acids with very high enantioselectivity.[4] Through this reaction, fumarate is reacted with ammonia and the lyase enzyme to produce L-aspartic acid which is then decarboxylated. One disadvantage to this method is that the formation of CO_2 gas bubbles leads to inhomogeneity in the reactor bed. Therefore, this reaction is done in a special pressure reactor at a pressure of 10 bar.[1]

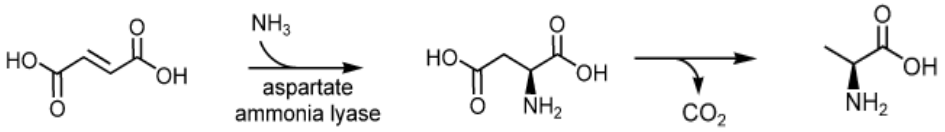

Figure 4. Biotransformation of L-Alanine in A Lyase Enzyme System[1]

Fermentation and Biomass

Fermentation is achieved by charging a fermentation tank under sterile conditions with a culture medium containing a carbon source and the required gaseous elements (such as nitrogen, sulfur, and phosphorus). Microorganisms in the tank produce the acid which is then obtained through crystallization.[9] In addition, there are numerous microorganisms available to perform a wide variety of fermentation reactions.[10] Today, the commonly used carbon source are petrochemicals. This is because petroleum is one

of the most abundant and cheapest source of organic carbon. Some of the major disadvantages to using crude oil products are the depleting fossil feedstocks, increasing oil prices, and the use of co-reagents such as chlorine and ammonia needed to introduce the desired functionality.[11]

A more environmentally friendly alternative carbon source are biomass-derived sugars. Biomass contains sugars such as sucrose and glucose naturally and often have the desired functionality without the need of harmful co-reagents.[11] Furthermore, biomass is a more energy-efficient raw material because the biomass materials have calorific values and chemical structures similar to the desired chemical products. To use crude oil products would require additional energy because the chemical products have significantly lower calorific values compared to the original fossil raw material. This concept is represented in Figure 5.[11]

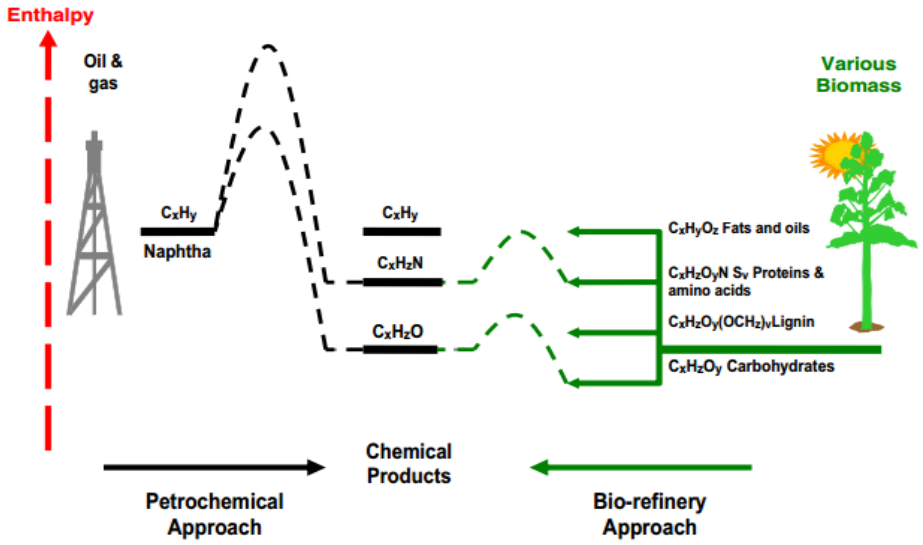

Figure 5. Comparison of Calorific Requirements for the Conversion of Petrochemicals vs Biomass Materials into Chemical Products[11]

Previous Methods of Production for Amino Alcohols

Racemization & Chemical Synthesis

A patent released by Antons *et al* provides an outline of previously developed methods for preparing optically active amino alcohols by way of reduction processes.[12] Originally, optically active amino alcohols were produced via Karrer's method by reducing optically active amino acid esters with sodium in ethanol, but this process produces significant racemization.[13,14] The issue of racemization was resolved when it

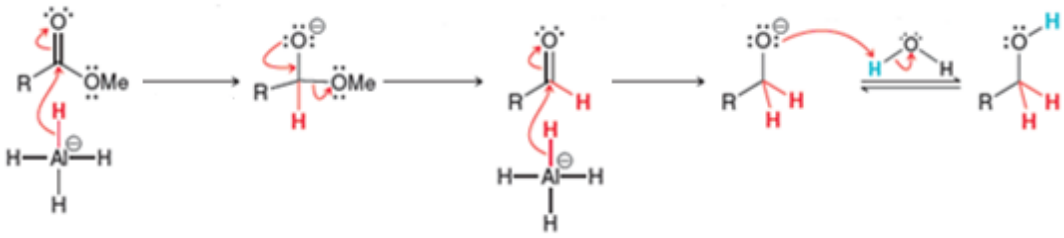

Figure 6. Mechanism for the Reduction of an Ester with LAH[4]

was discovered that the reduction reaction could be done with lithium aluminum hydride ($LiAlH_4$ or LAH) [15,14]. This process is done in a two steps with an ester intermediate which is reducted according to the mechanism in Figure 6.[4,16] The intermediate ester would contain an amino group where the R group is within the mechanism and the group attached to the oxygen on the opposite side does not need to be a methyl group. The major disadvantage to this procedure is that LAH is a hazardous chemical, uneconomical due to high costs, and results in widely varying yields.[14] Additionally, the two-step process is time consuming and expensive.[17]

The Current Industrial Standard

The currently-used industrial process utilizes $NaBH_4$ in a reduction reaction similar to the LAH reduction reaction described by Antons *et al*.[12] First an activator is combined with the amino acid and heated to form a reaction mixture with an ester intermediate.[16] The activator is usually sulfuric acid (H_2SO_4).[1] The reaction mixture is then converted into the amino alcohol with the addition of an alkaline earth borohydride (sodium borohydride in this case)[16]. This reaction is considered a simple "single vessel" process because there is no need to isolate the ester from the intermediate reaction mixture and the sodium borohydride does not need to be activated.[16] This method is an improvement over LAH from a safety and cost standpoint, and can produce optically pure materials because the configuration of the stereogenic center is retained. Additionally, the products are isolated in good yields and the reaction can be easily scaled up without risk of explosion.[1,21]

A New Method of Producing Amino Alcohols

Reduction of amino acids via hydrogenation in the presence of ruthenium catalysts was first introduced in a patent by *Antons et al* in 1996.[12] This patent showed that catalytic hydrogenation could produce optically active amino alcohols in a simple and cost effective manner, but lacked mechanistic details.

Mechanism of Amino Acid Hydrogenation

A follow-up study done in 2002 by *Jackson et al* proposed a mechanism (Figure 7) that explained the stereoretentive behavior of the hydrogenation process by studying the conversion of L-alanine to L-alaninol over a Ru/C catalyst.[12,14] First is the hydrogenation of the protonated amino acid (alanine) to form the gem-diol, followed by loss of water to form the aldehyde, and a second hydrogenation to the alcohol product.[2] The original C2 configurational information is maintained because a surface-bound intermediate is produced as a result of the catalyst directly removing H from the amine-bearing sp^3 carbon (α-carbon) site.

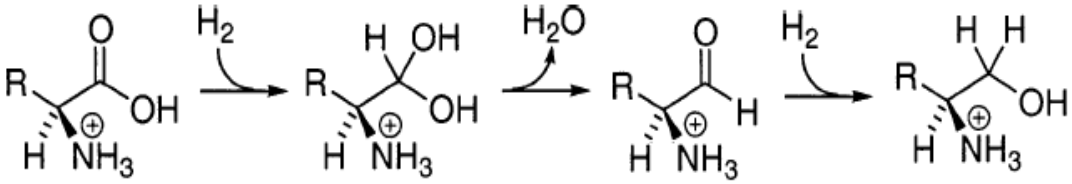

Figure 7. Reaction Mechanism for the Hydrogenation of L-alanine to L-alaninol[3]

Another discovery made in the 2002 study was that the presence of excess acid causes the reaction to proceed faster and with greater selectivity. This is because, for the hydrogenation to be thermodynamically feasible, the carboxylic acid functionality must be undissociated. Therefore, forms **2** and **3** in Figure 8 are not thermodynamically suitable starting materials for the hydrogenation reaction. During the study, only partial conversion occurred when the amino acid existed within a solution that had a pH between 5 and 9. Conversion halted when the pH rose due to basic product formation (i.e. the alcohol). However, when sufficient acid was used, L-alaninol was formed with selectivity exceeding 95% and optical purity over 99%.[14] These results demonstrated that for the hydrogenation reaction to proceed to completion with high selectivity and optical purity, the protonated form of the amino acid (**1** in Figure 8) must be maintained

throughout the duration of the reaction. If insufficient acid is present, formation of the amino alcohol raises the solution pH, leading to amino acid deprotonation, carboxylic acid dissociation and cessation of the reaction.[2]

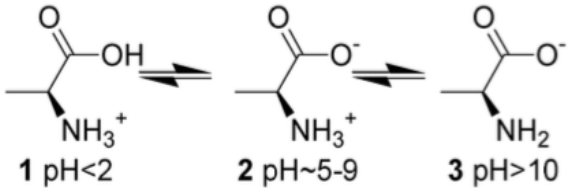

Figure 8. Forms of Amino Acids Based on pH.[3]

Kinetics of the Hydrogenation of L-Alanine

A succeeding publication by *Miller et al* in 2004 provided a rigorous kinetic model[14] which numerically describes the mechanistic details outlined in their 2002 previous study.[2] The study proposed that the alanine hydrogenation is modeled by a two-site Langmuir-Hinshelwood (L-H)-type reaction. The L-H mechanism can be described using the following series of reaction steps:

$$A + S_1 \Leftrightarrow AS_1 \quad (1a)$$

$$B + S_2 \Leftrightarrow BS_2 \quad (1b)$$

$$AS_1 + BS_2 \Leftrightarrow Product \quad (1c)$$

In general, the mechanism states that when two molecules (A and B) adsorb on neighboring sites (S_1 and S_2) they undergo a bimolecular reaction.[15] However, hydrogenation of L-alanine in not a simple bimolecular reaction. Instead, the protonated amino acid (in this case alanine) and undissociated phosphoric acid (H_3PO_4) compete for one surface catalytic site (S_1) while the hydrogen dissociatively adsorbs on another neighboring site (S_2). Specifically, it is proposed that hydrogen adsorbs on the Ru metal

surface in between the interstices while the acid sits above the surface. *Miller et al* expands upon the L-H reaction mechanism with the following series of elementary reaction steps[2] (Equations 2a-2f). While not all steps are kinetically significant, they provide mechanistic details as to the site adsorbing and/or blocking behavior of the species involved in this reaction.

$$A^+ + S_1 = A^+S_1 \quad (2a)$$

$$P^+ + S_1 = P^+S_1 \quad (2b)$$

$$H_2 + 2S_2 = 2HS_2 \quad (2c)$$

$$2HS_2 + A^+S_1 \rightarrow A^+{}_1S_1 + 2S_2 \quad (2d)$$

$$2HS_2 + A^+{}_1S_1 = Alol^+S_1 + 2S_2 \quad (2e)$$

$$Alol^+S_1 = Alol^+ + S_1 \quad (2f)$$

Where A^+ is the protonated amino acid, P is the phosphoric acid, $A_1{}^+S_1$ is the combined diol and aldehyde species in the mechanism shown in Figure 7, $Alol^+$ is the amino alcohol, and H is hydrogen. Equations 2a-2c depict the competition and adsorption of the amino acid and phosphoric acid onto catalytic site S_1 and the hydrogen adsorbing onto catalytic site S_2. Equations 2d-2f are the bimolecular reaction steps depicted in Figure 7. *Miller et al* propose that the rate limiting step is reaction 2d. Using Reaction 2d as the RLS, the rate expressions for the rate of alanine consumption (Equation 3) can be derived and the kinetic parameters determined from experimental data (Table 1).[3]

Table 1. Rate of Alanine Consumption Constants[3]

rate or equilibrium constant	value at 373 K	preexponential factor (K_0)	activation energy or heat of adsorption (kJ/mol)
k_1 (kmol/kg_{cat}-s)	3.46×10^{-6}	9.07×10^{5}	81.5
K_{A^+} (m^3/kmol)	191	8.41×10^{-10}	−80.9
K_P (m^3/kmol)	40.3	1.24×10^{-14}	−111
K_{H_2} (m^3/kmol)	102	2.38×10^{-8}	−68.8

$$-r_A = k_1 \left[\frac{K_A + C_{A+}}{(1 + K_{A+}C_{A+} + K_P C_P)} \frac{K_{H_2} C_{H_2}}{\left(1 + \sqrt{K_{H_2} C_{H_2}}\right)^2} \right] \quad (3)$$

Hydrogenation versus the Industrial Standard

Hydrogenation with a ruthenium supported on carbon (Ru/C) catalyst is an improvement upon the industrial standard both economically and environmentally. Hydrogenation uses less hazardous and less expensive chemicals than the current industrial method. It also produces no inorganic byproducts, eliminates the need for intermediate processing steps, and allows for the use of water as a reaction medium.[18] Despite these benefits, reduction of amino acids with $NaBH_4$ is the preferred method of producing amino alcohols because of the lack of affordability of the Ru/C catalyst and the acid solvent. The current market price for Ruthenium according to the Hong Kong trading desk is $40 per troy ounce or $1236 per kilogram.[22] In addition to the cost of catalyst, the reaction solution requires the use of an acid. Miller suggests using phosphoric acid, which is priced between $150 to $160 per Liter according to the ICIS Indicative Chemical Prices.[23] These costs make producing amino alcohols via catalytic hydrogenation on an industrial scale difficult. Since the acid co-catalyst cannot be recycled, all of the phosphoric acid required for the reaction is wasted and a fresh feed must be used every run. This also causes the catalyst to be non-reusable because the adsorbed acid cannot desorb from the catalyst without the removal of phosphoric acid.

Improving the Hydrogenation Reaction

This thesis proposes a process to combat these issues by utilizing a polymer that can create acidic active sites within the Ru/C catalyst, eliminating the need to use an acidic solvent altogether. This process matches the selectivity and optical purity of Miller's proposed hydrogenation reaction[3] while improving on reaction rates and creating a reusable catalyst. By doing so, we will keep with the pattern of developing both an economically and environmentally advantageous method of producing amino alcohols.

Impregnated Polymer Characteristics

Before choosing the polymer that creates the acidic microenvironments within the catalyst pores, an investigation of the protonation step must be done. Two experiments were done using two different acidic solutions allowed us to determine if the conjugate base influences the protonation of the amino acid. Currently, Millar suggests the use of phosphoric acid which contains a phosphate group.[3] An identical experiment was done using trichloroacetic acid, a chemical which contains a carboxylic acid in the reaction solution. The role of the acid in the catalytic hydrogenation reaction is to dissociate in the aqueous solution, providing the H^+ that allows for the protonation of alanine. The stronger the acid is, the more completely it will dissociate and the lower the pKa value. Phosphoric acid has a pKa of 2.12. Trichloroacetic acid has a pKa of 0.66.[24] This experiment allows us to determine whether there is a difference in the effectiveness of protonation between phosphate and carboxylic groups.

Should the kinetics of these two experiments match, the reaction can be described as "Specific Acid Catalysis" and the polymer only requires a general proton donating

group. This is because the reaction rate (Equation 4) is dependent on the equilibrium for protonation and is independent of the concentration and specific structure of the various proton donors. In the reaction rate (Equation 4) [X] and [Y] are concentration of the reactants.[25]

$$rate = k[H^+][X][Y] \quad (4)$$

If they do not match, the reaction can be described as "General Acid Catalysis" and the polymer requires a phosphate group as the proton donating group. For this type of catalysis, the nature and concentration of proton donors impacts the reaction rate (Equation 5). In this equation [X][Y] are the concentration of the reactants and HA^1 and HA^2 are kinetically significant proton donors.[25] In this case there is only one proton donor, meaning the HA^2 term disappears.

$$rate = k_1[H^+][X][Y] + k_2[HA^1][X][Y] + k_3[HA^2][X][Y] \quad (5)$$

The category of polymer we propose for specific acid catalysis is an anionic polymer. Anionic polymers contain negatively charged ion groups that attract positively charged particles, like the H from the amine-bearing sp^3 carbon (α-carbon) site required for amino acid protonation. A common method to create anions is to use salts because they completely dissociate in water, leaving behind a negatively charged group. The anionic polymer we used was sodium polyacrylate. The polymer was treated with phosphoric acid during the catalyst synthesis procedure in order to exchange it to its proton form. The catalyst synthesis procedure is described later in the Methods and Materials section. The same strategy could be used for general acid catalysis. Possible polymers include poly(sodium phosphate) or sodium triphosphate

Catalyst Impregnation

The type of impregnation being performed is incipient wetness impregnation (IWI). The method depends on retaining the polymer within the pores during drying and does not require a chemical bond. When adding the impregnation solution, the objective is to add a volume equal to the volume of the pores.[26] Figure 9 depicts the pores during impregnation (a) and after subsequent drying (b). As the figure demonstrates, we are filling only the pores and not the space between the various catalyst particles. To maintain the polymer within the pores, a cross-linking agent will be added to the impregnation solution which will link polymer chains together, creating large molecules which cannot escape the pores. The cross-linking agent we are using is benzoyl peroxide due to its photo-reactivity. The cross-linker will not react with the polymer until it is exposed to light. This allows us to add the maximum amount of polymer because the polymer chains will remain small during impregnation but can grow longer during cross-linking.

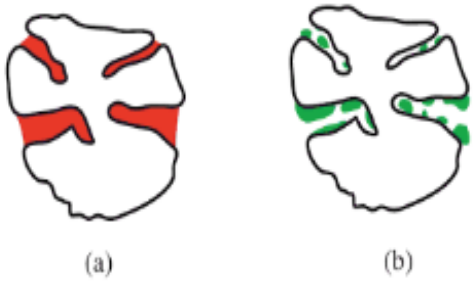

Figure 9. Impregnated Catalyst Before and After Drying[26]

2. METHODS AND MATERIALS

Materials

The following is a list of all chemicals and equipment used throughout this thesis:

1. L-Alanine (99%): CAS 56-41-7
2. L-Alaninol (98%): CAS 2749-11-3
3. Phosphoric Acid (85%): CAS 7664-38-2
4. Trichloroacetic Acid: CAS 76-03-9
5. Ru/Alumina (5 wt% Ru): No CAS # - Sigma Aldrich
6. Benzoyl Peroxide (>98%): CAS 94-36-0
7. Poly(Acrylic Acid, sodium salt) (35 wt% in water): CAS 9003-04-7
8. Batch Reactor: Parr Instruments Non-Stirred Vessels

   S/N 4790-1607-50661 - 50 mL - 3000 psi at 350 °C
9. Temperature Controller: Automation Direct Solo 4848
10. IR Spectrometer: ABB FTLA200 Series Laboratory FT-IR Spectrometer

    Equipped with a Pike ATR cell and Zinc-Selenide Crystal
11. Thermogravimetric Analyzer: TA Instruments - TGA Q500 V20.10 Build 36

Impregnated Catalyst Synthesis

To make this process more applicable to an industrial-scale process, ruthenium on **γ-**alumina (Al_2O_3) was used as the catalyst because it is difficult to prepare pelletized carbon materials with high mechanical stability.[27] An oxide support like alumina is available in a variety of sizes and shapes, making it suitable for large-scale industrial

applications. Another important component of this synthesis is that it was done entirely in the dark until the vacuum drying was complete. This is because, if exposed to light too early, the benzoyl peroxide would have activated and began cross-linking with the polymer too soon. We did not want cross-linking to occur until after the drying process was complete to allow for maximum linking within the pores.

The first step was to take a 50-50 mixture of water and THF, polymer, and cross-linker and add it drop wise to a gram of catalyst, mixing it periodically to ensure equal dispersion. This mixture was made up of a gram of water, a gram of THF, 0.7 grams of sodium polyacrylate, and 0.25 grams of benzoyl peroxide. The incipient wetness point was reached after 0.792 grams of mixture was added. At this point the pores of the catalyst were full, but not the space between the catalyst particles[12]. The catalyst was then covered in aluminum foil and transported to a vacuum oven for two hours to remove the water and THF. After vacuum drying was complete, the catalyst powder was uncovered and sat overnight in a well-lit room. During this time, the cross-linking process occurred.

Upon completion, the powder underwent a Soxhlet extraction to remove any un-linked polymer and benzoyl peroxide. What was left behind was the finished product Ru/Al_2O_3 with long polymer chains containing polyacrylate groups and sodium cations within its pores. The final step was to treat the catalyst with acid and exchange the sodium cations from the catalyst pores. This was done by adding the catalyst to a beaker of 200 mL of 1 M phosphoric acid (23.059 grams) and stirring for twelve hours. The solution had to be stirred well enough that the catalyst was suspended in the aqueous

solution. Afterwards, the solution was filtered using a Büchner funnel and a 500-mL water wash followed by a two-hour drying time in the vacuum oven.

Analytical Analysis of Alanine and Alaninol

Inrared spectroscopy was used to determine whether the reaction was successful in converting L-Alanine to L-Alaninol. As can be seen in the mechanism of Figure 7, the hydrogenation reaction reduces a carbonyl group into an alcohol group. Each of these functional groups contains a distinct IR absorbance. Standards of L-Alanine and L-Alaninol in Milli-Q water (18 MΩ) were created and analyzed in the IR. Figure 10 compares the absorbance of the two solutions side by side for a wavelength range of 1560 to 1360 cm^{-1}.

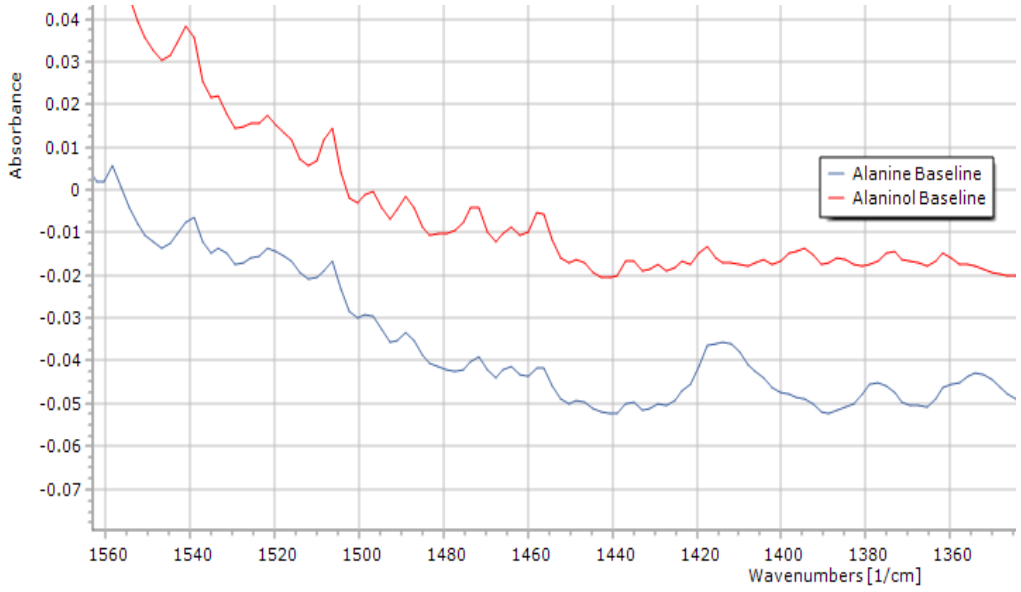

Figure 10. IR Spectra for the Absorbance of Alanine and Alaninol Standards from 1560 cm^{-1} to 1360 cm^{-1}

The curves appear to be similar except for an absorbance in the alanine curve around 1416 cm^{-1}. We attributed this peak to the carbonyl group present in the alanine but not

the alaninol. Figure 11 demonstrates the same comparison as Figure 10, but for a wavelength range of 1250 to 950 cm^{-1}. The identifying absorbance in this wavelength range is the alaninol peak around 1050 cm^{-1}, which corresponds with the C-O stretching of an alcohol functional group. This absorbance will signify the presence of alaninol.

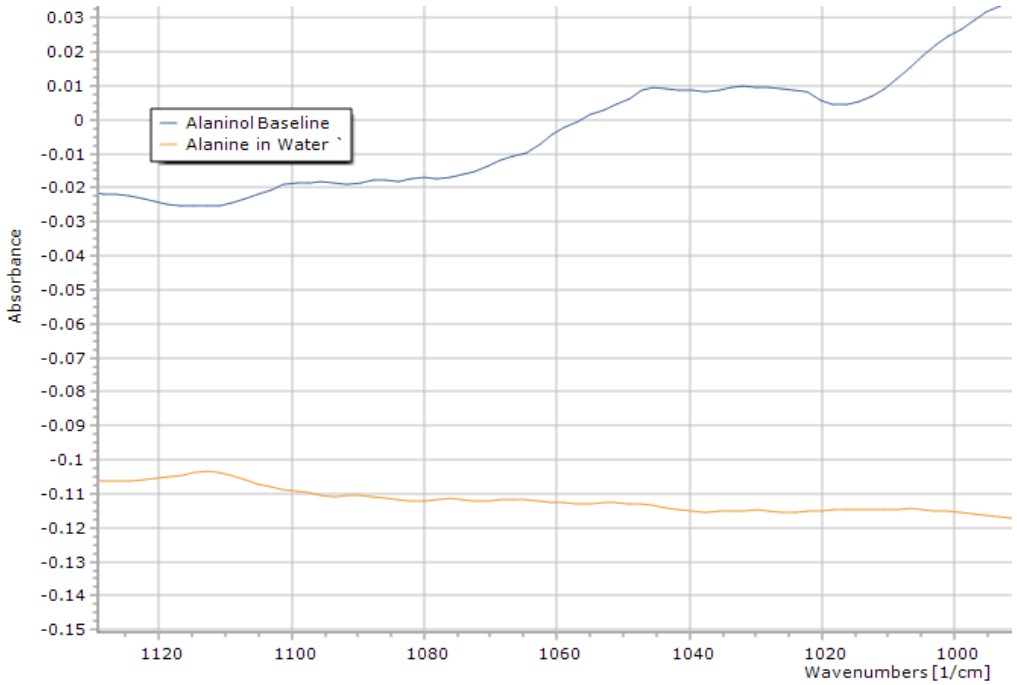

Figure 11. IR Spectra for the Absorbance of Alanine and Alaninol Standards from 1250 cm^{-1} to 950 cm^{-1}

Calibration of Infrared Spectroscopy

With distinct IR peaks identified, a group of standards were made for both alaninol and alanine to produce a calibration curve that relates concentration to absorbance area. This type of plot is commonly referred to as a Beer's Law plot. The concentrations used were 17 grams per liter (gm/L), 15 gm/L, 3 gm/L, and 1 gm/L. Table 2 shows the absorbance area at each concentration for both alanine and alaninol. These data points create two linear plots (R^2 values of 0.972 and 0.998) that will allow us to

Table 2. Absorbance Areas at Various Concentrations of Alanine and Alaninol

Concentration (gram/Liter)	Alanine Peak Area	Alaninol Peak Area
17	0.2674	0.4007
15	0.2105	0.3569
7	0.1208	0.1661
3	0.06794	0.07822
1	0.02217	0.03477

determine the concentration of both species in a product solution by analyzing the peak areas. For alanine, this curve can be described by equation 6. Alaninol can be described using equation 7.

$$C_{gL} = {Peak\ Area}/{0.0151} \quad (6)$$

$$C_{gL} = {Peak\ Area}/{0.0237} \quad (7)$$

Procedure for the Hydrogenation Reaction

The procedures used in all our experiments are the same as in a study done by *Miller et al* in 2004.[3] Because the batch reactor in their study was 300 mL and we had a 50-mL batch reactor, our process was a one-fifth-scale of the original. To begin, 0.2 gm of Ru/Alumina catalyst was combined with 10 gm of Milli-Q water in the reactor vessel and sealed tightly. The vessel was then purged with helium to flush out the oxygen and pressurized to 1.7 MPa of hydrogen. Then the unit was heated to 423 K using a ramp function which raised the temperature 5 K every minute for 25 minutes. This temperature and pressure was held for an hour to reduce the catalyst. Once the vessel cooled to room temperature, it was charged with a 10 gram solution comprised of 0.22 M alanine and 0.29 M phosphoric acid. This equated to 0.194 grams of alanine, 0.254 grams of phosphoric acid, and the rest, Milli-Q water. Once added and the vessel

resealed, it was purged with hydrogen to flush out the oxygen and pressurized to 3.4 MPa of hydrogen. The unit is heated to 373 K using a ramp function which raised the temperature 5 K per minute for 20 minutes. This temperature and pressure was held for an hour to achieve low conversion of alanine.

Upon completion, the vessel was cooled to room temperature and the final mass recorded. Since the acidity of the product solution would damage the zinc selenide crystal on the IR, the catalyst was filtered out using 0.45 μm nylon syringe filter and then neutralized using sodium bicarbonate ($NaHCO_3$). The mass of $NaHCO_3$ was not an important variable. Figure 12 in Appendix I shows the IR Spectra for the transmittance of $NaHCO_3$. An absorbance peak would correspond to a downward peak on a transmittance graph. As the spectra shows, there are no absorbance peaks at 1416 cm^{-1} or 1050 cm^{-1} (the absorbances for alanine and alaninol, respectively). Therefore, the addition of sodium bicarbonate did not impact the spectra readings for either alanine or alaninol.

Variations in the Hydrogenation Reaction

1. Because the original study done by *Miller et al* used a Ru/C catalyst, one experiment was performed using 0.2 grams of Ru/C instead of Ru/Alumina to verify that Ru/Alumina behaved similarly to Ru/C and was a valid catalyst.
2. The tank being used in our lab could only pressurize the vessel to 2.9 MPa of Hydrogen. Therefore, all reactions were done at 2.9 instead of 3.4 MPa.

3. To determine whether hydrogenation involved "specific acid catalysis" or "general acid catalysis" 0.423 grams of trichloroacetic acid were substituted for the 0.254 grams of phosphoric acid.
4. The reaction time for the Acid Catalysis Test was six hours instead of the traditional one hour to achieve high conversion of alanine. The results for this experiment were compared to a six-hour Ru/Alumina reaction under the conditions outlined above.
5. All experiments done with the impregnated catalyst were run identically to the above reaction except that no phosphoric acid was be added along with the alanine feed. The feed was only alanine and water.

Calculations

The initial concentration of the 0.22 M alanine solution was 19.60 grams per Liter. This value was converted into mmol with equation 8

$$C_i = \frac{19.60 * (M_i/1000)}{MW_{nine}} * 10^6 \quad (8)$$

Here M_i was the initial mass of the entire solution in the reactor (catalyst and feed solutions). MW_{nine} was the molar mass of alanine. The numerical value of 1000 is the density of water in grams per Liter and 10^6 was a conversion factor from mol to mmol. Equation 9 was used to get the final concentration of alanine (C_f). The concentration in grams per Liter (C_{gL}) was based on the peak areas (Equation 6) and the final mass of the entire solution in the reactor (M_f).

$$C_f = \frac{C_{gL} * (M_f/1000)}{MW_{nine}} * 10^6 \quad (9)$$

To obtain the final concentration of alaninol (C_{nol}) we used equation 9, but with the grams per Liter concentration based on peak area for alaninol from equation 7 and the molar mass of alaninol. An example of these calculations are shown in Figures 13 and 14 of Appendix II for the Duplication of Baseline Reaction experiment. From the concentrations we calculated two properties that helped verify our claims that our process was comparable to the current hydrogenation reaction proposed by *Miller et al*.[2] The conversion of alanine was found using equation 10.

$$Conv = \frac{19.60 - C_f}{C_i} \tag{10}$$

We calculated the selectivity of alaninol in the product solution using equation 11.

$$S = \frac{C_{nol}}{C_i - C_f} \tag{11}$$

3. RESULTS AND DISCUSSION

Prior to running a reaction with an impregnated catalyst, a series of reactions were done to validate our reactor set-up and learn key details pertaining to the hydrogenation reaction. For instance, the outcome of the general versus specific acid effect experiment contributed to the selection of polymer for the impregnation testing. These results provided the foundation I needed to claim a proof of concept at the end of my thesis experience.

IR Spectra Analysis of Feed Samples

After viewing a few spectra, it became apparent we were unable to detect the alaninol peak because the addition of the acid created a peak that overshadowed it. Figure 15 shows a three different feed samples: alanine in phosphoric acid, and alanine in trichloroacetic acid, and alanine in water. There exists a peak around 1000 cm^{-1} on the

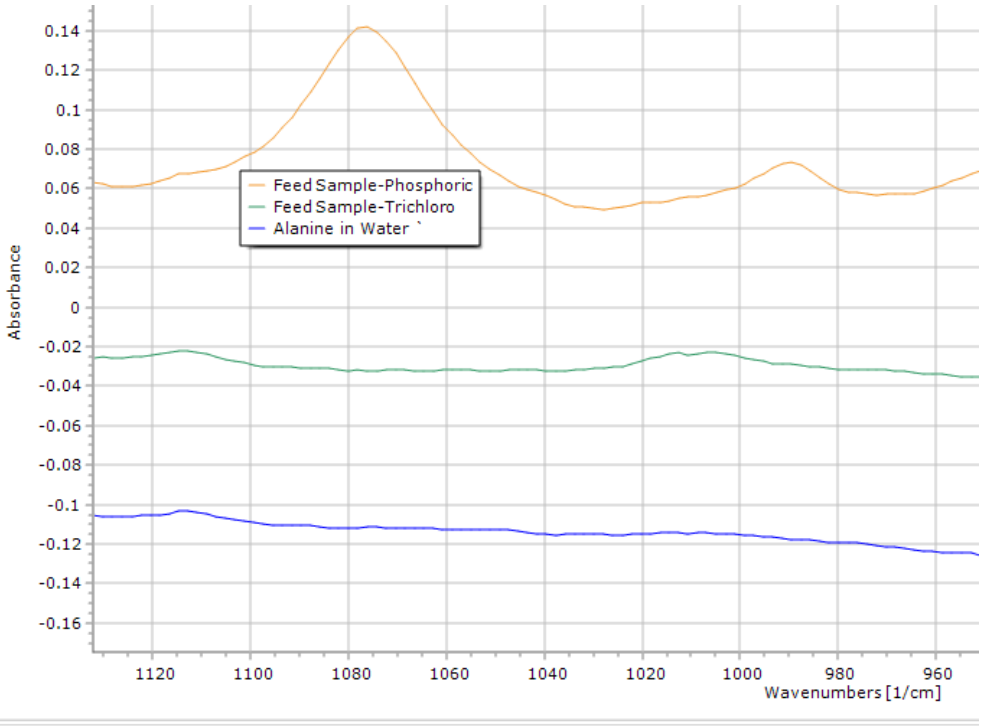

Figure 15. Feed Samples in Phosphoric Acid, Trichloroacetic Acid, and Water

spectra for the acid samples but not the baseline alanine spectra. This wavenumber matches the range we found the alaninol peak at in Figure 11 of the Methods & Materials section. As a result, we could not determine the peak area for alaninol with complete certainty, but because this is a hydrogenation reaction, it was reasonable to assume only alaninol is being produced from the converted alaninol, based on available literature.[2]

Duplication of Baseline Reaction

No additional claims could be made without testing the validity of our setup and experiments against the study published by *Miller et al*.[2] The hydrogenation reaction outlined previously was performed using the Ru/C catalyst. At 373 K and 6.9 MPa, the conversion of alanine from the Miller study[2] was around 30%. Since we were running at a lower pressure (2.9 MPa), we hypothesized that our conversion to be lower than the value achieved at 373 K and 6.9 MPa because a lower hydrogen concentration should decrease the rate. Figure 16 shows the IR spectra for this experiment. With a starting concentration of 19.60 gm/L (0.22M) and a final concentration of 14.79 gm/L, our

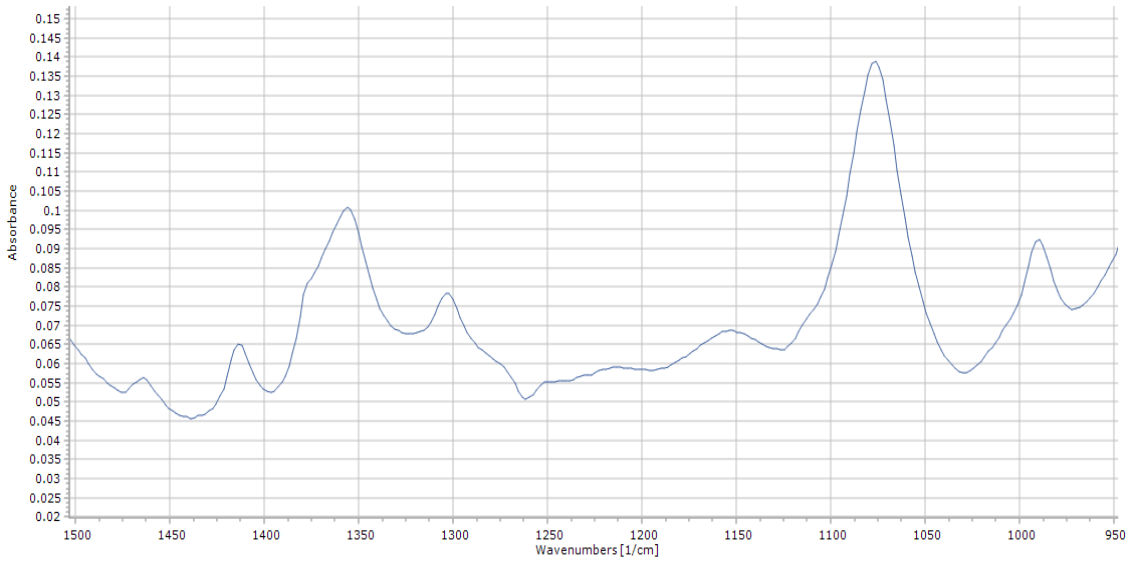

Figure 16. Complete IR Spectra for the Duplication of Baseline Reaction Experiment

conversion of alanine was 43.8%. There are a few reasons why our conversion was higher than that of the study, despite our decreased hydrogen pressure.

The first possibility was that there was a difference in the dispersion of our Ru/C catalyst versus the one used in the original study. Disperson is the ratio of of the number of surface metal atoms to the total number of metal atoms. This property is dependent on how the catalyst was prepared. Some metal reactions are dependent on metal dispersion since the metal dispersion determines the number of active sites available.[29] The increased activity of our Ru/C catalyst could be due to better dispersion of Ru atoms. Without information on how our Ru/C catalyst or the Ru/C catalyst from the study was prepared or what the dispersion values are, a definitive statement cannot be made as to how significant of an impact this had on the conversion.

The second possibility is that there existed a difference in space time between our reactor and the original study. The rate of our reactor could be calculate using the same rate equation as the one presented in the original study. Doing this would allow us to analyze the amount of conversion we should get if our reactor operated at the same rate as the original study. The concentration of both the protonated alanine and protons would need to be found to complete this calculation. This is a non-trivial calculation due to the nonlinear nature of the charge balance.[3] Therefore, we assumed our rate was the same as the original study, that there had to exist a difference in space time since conversion is related to both space time and rate.[28] Overall, it is reasonable to state our reactor performs comparably to the baseline experiments.

Comparison of Ru/C and Ru/Alumina

As was discussed previously, the catalyst was switched from Ru/C to Ru/Alumina due to the industrial availability of oxide supports in pelletized form.[27] We compared the performance of Ru/C and Ru/Alumina by doing duplicate experiments with both catalysts. Figure 17 shows a comparison of the two catalysts around the 1416 cm^{-1} absorbance identified earlier as an alanine peak. A full IR Spectra of the Ru/Alumina experiment can be seen in Figure 18 of Appendix I. The Ru/C peak is smaller than the

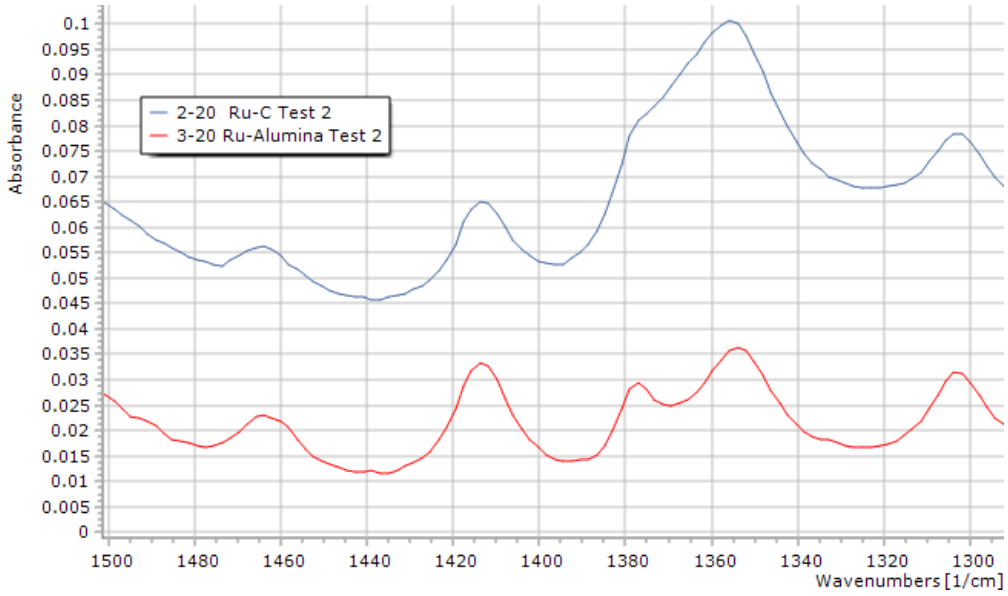

Figure 17. Alanine Conversion with Ru/C versus Ru/Alumina around 1416 cm^{-1}

Ru/Alumina with peak areas of 0.2233 and 0.3256, respectively. This corresponded to a 24.4% conversion for the Ru/Alumina catalyst versus 43.8% for the Ru/C catalyst. The Ru/Alumina experiment was repeated again with a reaction time of two hours instead of the original one hour. For a reaction time of two hours the conversion of alanine was 37.7%. Given these results, we concluded that the Ru/Alumina catalyst was not as efficient at performing the hydrogenation reaction.

The different conversion rates between the two catalysts was attributed to the dispersion principle described previously. A study done by *Betancourt et al* proved experimentally that the Ru content impacts the hydrogenation rate with a Ru/Alumina catalyst.[30] As we discussed before, Ru/C demonstrates a similar behavior. This means that how well the metal particles were dispersed on their supports impacted the catalyst activities for both catalysts.[29] A study done by *Betancourt et al* also indicated that Ru/Alumina works better as a hydrogenation catalyst at low ruthenium content.[30] Despite these results, the Ru/Alumina catalyst contained properties that are critical in later experiments and was used from here on out.

Acid Catalysis Test

To test of the importance of the functional group of the acid on the conversion rate, phosphoric acid (a phosphate group) was compared to trichloroacetic acid (a carboxylic acid group). These experiments were done with matching molar concentration (0.29 M). Figure 19 shows a comparison for a six-hour reaction time around the 1416 cm^{-1} alanine absorbance. As shown in the spectra, the alanine absorbance for the trichloroacetic curve is larger than the phosphoric curve. With peak areas of 0.1310 and 0.2757, respectively, phosphoric acid has a conversion of 71.6% while trichloroacetic acid is 41.0%. The full spectra for this test can be found in Figure 20 of Appendix I. The acid test was done twice to verify our findings and the second experiments produced nearly identical results (Figure 21 in Appendix I). These results told us that phosphoric acid was more effective as an acidic environment when using equal molarity. One possibility was that the difference in pH of the two acids, and as a result proton

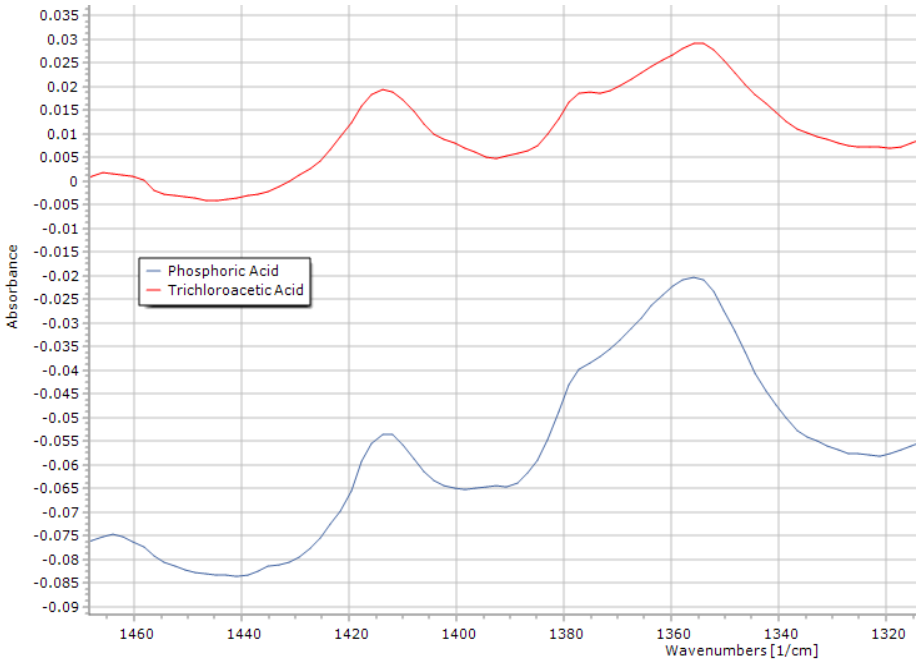

Figure 19. Alanine Conversion for Phosphoric Acid versus Trichloroacetic Acid around 1416 cm^{-1}

concentration, was the source of the discrepancy. 0.1 M Trichloroacetic acid has a pH around 1.2 which equates to a proton concentration [H^+] of 0.0631 mol/L. Phosphoric acid of the same molarity has a pH around 1.5 and a [H^+] value of 0.0316 mol/L.[31] Despite having half the proton concentration, phosphoric acid achieved much higher conversion meaning this was most likely not the source of the discrepancy.

The other possibility is that the chlorine in the trichloroacetic acid inhibited the Ru catalyst. It is common for chlorine to act as a "poison" for reduced metal catalysts. When chlorine is present in the reaction solution, it deposits on the catalyst surface, occupying an active site.[32] This means an H_2 must remove the Cl and produce HCl so that the hydrogen atom can adsorb to the surface. As a result, the amount of H_2 present on the surface or in the gas phase is critical to combatting the catalyst deactivation causes by chlorine.[32] There existed a "self-poisoning" caused by the interactions between the metallic phase and HCl produced. To verify if this was the cause of the decreased

conversion, a separate test would need to be run to determine if there exists any HCl in the product solution.

Impregnated Catalyst Test

The Blank Experiment

Prior to running an experiment with the impregnated polymer, a "blank" experiment was run. This experiment included the Ru/Alumina catalyst being reduced in water like in previous experiments, but the feed solution was only water and alanine. Since no phosphoric acid was added to the feed solution, any change in alanine conversion between the blank and the impregnated experiment would be the impregnated catalyst. After a six-hour reaction, 10.8% of the alanine was converted. This coincides with the results from a previous study done by Jere *et al* where the experiment was done with a 0.22 M alanine solution at 373 K and 6.9 MPa for six hours and obtained 13% conversion.[19]

The Impregnated Experiment

The reaction was duplicated with the polymer impregnated Ru/Alumina catalyst instead of the regular Ru/Alumina catalyst and run for six hours. Just like in the blank experiment, no phosphoric acid was added to the feed solution. Figure 22 shows a comparison of the impregnated catalyst test versus the blank test around the absorbance for alanine. The peak area for the synthesized catalyst is smaller than the blank

experiment at 0.2390 and 0.3359, respectively. With that peak area, the synthesized catalyst achieved an alanine conversion of 51.7%.

Thermogravimetric Analysis of a 15 mg of same of impregnated catalyst was analyzed used to determine the weight percent of polymer within the pores. This type of analysis works by monitoring the mass of a sample as a function of (in this case)

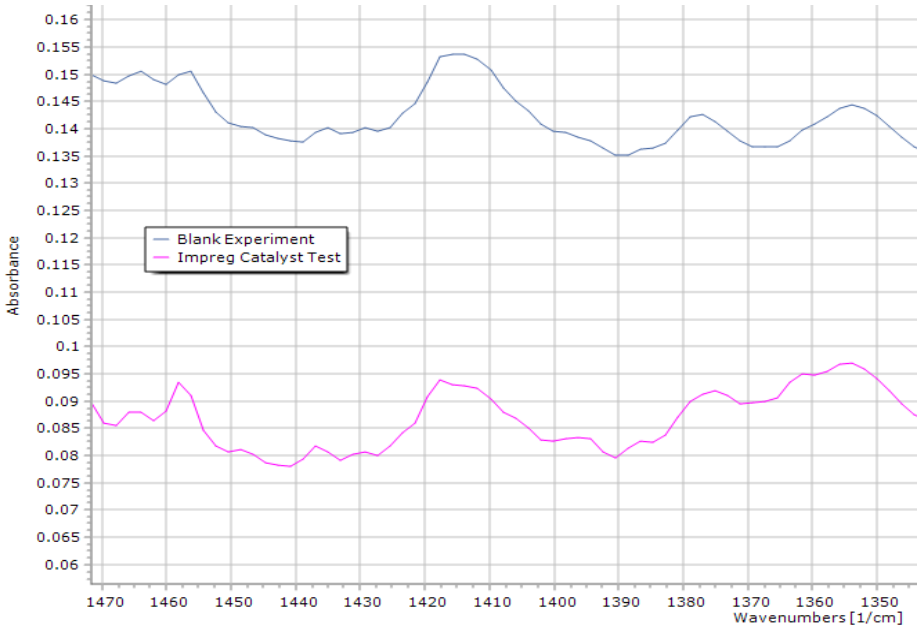

Figure 22. IR Spectra for the Impregnated Catalyst versus the Blank Experiment around 1416 cm^{-1}

temperature as the sample is subjected to a controlled temperature program.[34] As the material is heated in air, the weight percentage decreases. The first region on the graph around 100°C is due to water being vaporized off. The second region (marked by the arrows) in Figure 23 of Appendix I represents the part of the curve where the polymer was burnt off. According to the analysis there was about 2.9 wt% polymer within the catalyst pores.

4. CONCLUSION

An important area of research today is finding greener and more cost-effective way to transform amino acids into amino alcohols. Currently, amino alcohols are produced by reducing amino acids derived from petrochemicals with the use of $NaBH_4$ as a reducting agent.[16] Although this method provides high yields and can produce amino alcohols with little to no racemization, it is time-consuming and expensive due to the need for an intermediate ester stage along with further processing of the product streams. Previous studies[3,12] have proposed synthesizing the alcohols via hydrogenation in an acidic solution with a ruthenium supported on carbon catalyst. This type of synthesis has shown favorable selective and optical purity, and provides a method which is atom-economical and avoids byproduct waste streams.[3] To improve upon this synthesis method, we proposed impregnating a Ru/C catalyst with a soluble polymer which could be cross-linked within the catalyst pores to create the acidic actives sites needed to perform the hydrogenation. This synthesized catalyst would match the reaction rates proven in previous studies[3], while eliminating the need for the acid solution. Furthermore, by eliminating the acid solution, the synthesized catalyst would be recyclable, decreasing costs and making the process more environmentally friendly.

Preliminary tests were run prior to testing the synthesized catalyst to develop a better understanding of the hydrogenation process. First, a duplicate experiment to the one performed in the baseline study by Miller *et al* was run to verify our reaction behaved comparably. The original study achieved around 30% alanine conversion after a reaction time of one hour. Under the same conditions, we achieved 43.8%. It was determined

that the difference in conversion was most likely due to a combination of two things: space time and dispersion.

It was then decided that instead of using Ru/C, we would use ruthenium support on alumina because of the industrial accessibility of alumina versus carbon pellets. The next preliminary experiment was to determine if Ru/Alumina performed comparably to Ru/C. A duplicate reaction was run with Ru/Alumina for an hour and the conversion of alanine was 24.4%. The difference in conversion between Ru/C and Ru/Alumina was associated to better metal dispersion on the Ru/C catalyst. The activity of both catalysts are depended on how well the metal Ru particles were dispersed and how that dispersion may have caused a variation in the number of active sites.

Then next test was to determine if there existed a general or specific acid catalysis effect in this reaction. The reasoning behind this test was determine whether the impregnated polymer needed to contain the same functional group as the acid solution (phosphate) or if it could be a general proton donor. The results of duplicate six-hour reactions provided 71.6% conversion with phosphoric acids and 41% conversion for trichloroacetic acid. Despite the results, we proceeded to use a general proton donor in sodium poly(acrylate). This is because we believe the difference in conversion is due to the well-known deactivation of reduced metal catalysts by the chlorine in trichloroacetic acid.

With the preliminary experiments complete, a solution containing water, THF, polymer, and benzoyl peroxide was impregnated into Ru/Alumina via incipient wetness impregnation. The incipient point was reached after adding 0.792 gm of solution. After completing the necessary filtration and drying steps, a six-hour reaction was run with the

impregnated catalyst and no phosphoric acid. A duplicate experiment was done with regular Ru/Alumina and no phosphoric acid to use as a baseline comparison. The baseline experiment achieved 10.8% conversion of alanine while the synthesized catalyst experiment achieved 51.7% conversion of alanine. The sample was analyzed using TGA and the results verified that there was 2.9 wt% polymer within the catalyst pores. Therefore, we were successful in synthesizing a catalyst that had cross-linked polymer chains impregnated in the pores that could act as acidic sites for the hydrogenation reaction to occur on. By doing so we discovered a more environmentally friendly and cost-effective manner to transform amino acids into amino alcohols with comparable efficiency.

Future Work

Despite the initial experiment with the impregnated catalyst proving to be a success, there is still plenty of future research to be done. The first step would be to synthesize another batch of catalyst and reproduce the results presented in this thesis. Once it is shown that these results are reproducible, experiments should be done to test the recyclability of the catalyst. A major factor in why the impregnated catalyst is important is that it would significantly reduce costs if the catalyst was reusable. If the catalyst proved to be reusable, this method of synthesis would take a large step towards being capable of commercialization. An entirely different branch of research could be done on characterizing, developing mechanistic details, outlining kinetic equations and parameters, and optimizing the catalyst.

Another way to improve the hydrogenation reaction would be to replace the ruthenium with cobalt. Cobalt is a much more affordable option that behaves in similar ways to Ru. In combination with the impregnated catalyst, hydrogenation would become far more cost-effective while still being able to produce amino alcohols with high selectivity and optical purity. Any of these future avenues of research would provide a breakthrough in amino chemistry.

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APPENDIX I. INFRARED SPECTROSCOPY RESULTS

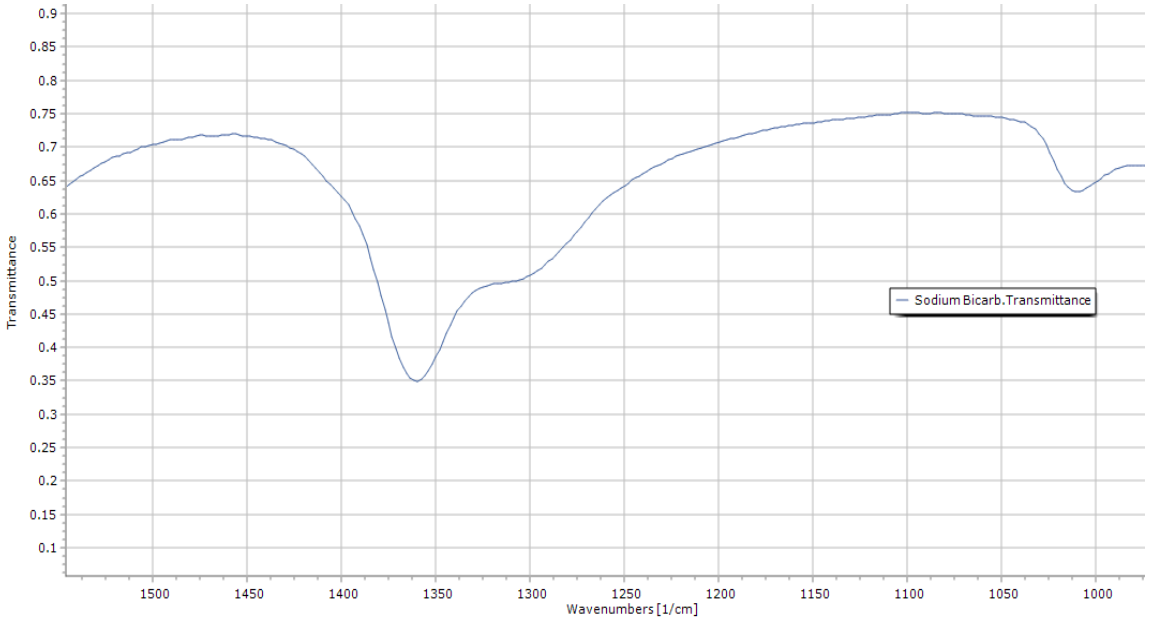

Figure 12. IR Spectra for the Transmittance of Sodium Bicarbonate (1500-1000 cm^{-1})

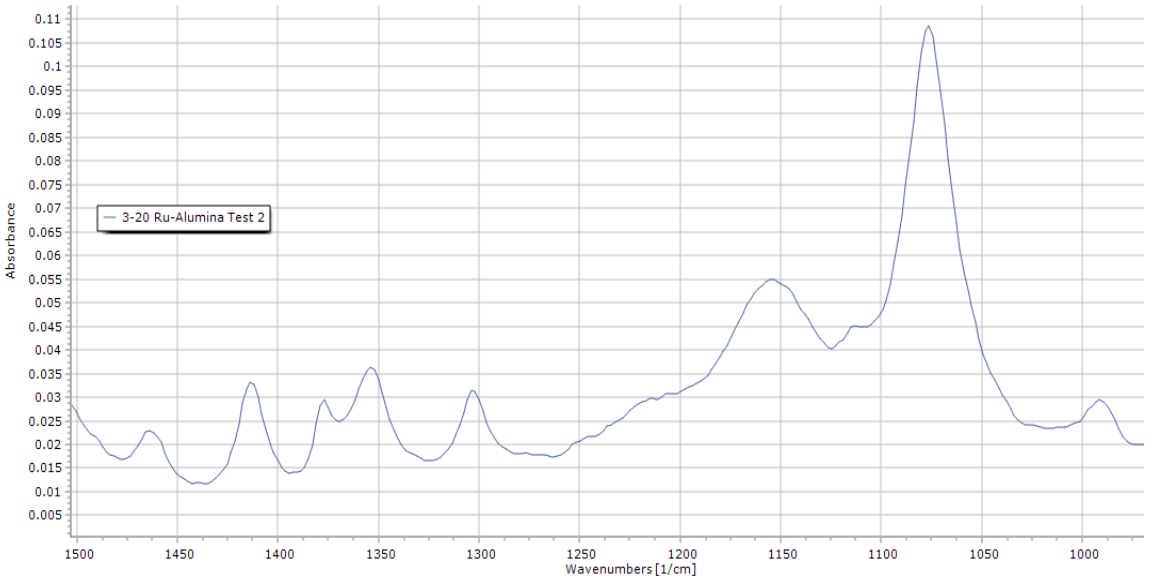

Figure 18. Complete IR Spectra for the Ru/C versus Ru/Alumina Experiment

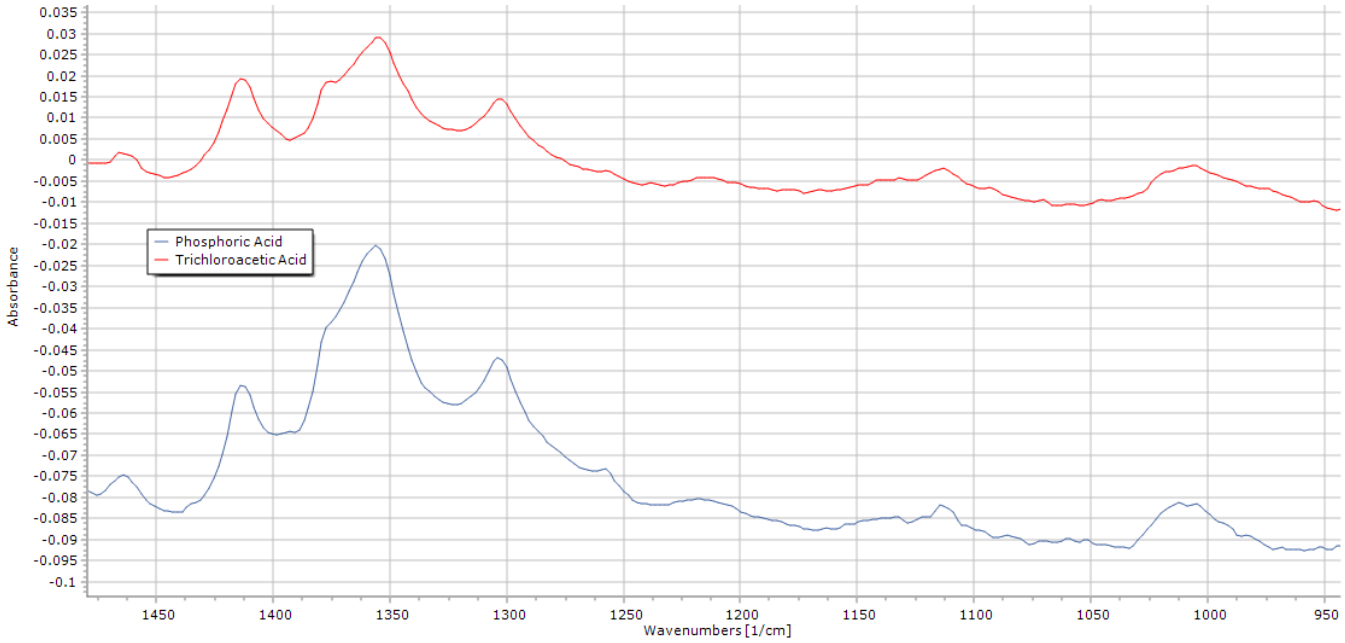

Figure 20. Complete IR Spectra for the Acid Catalysis Test

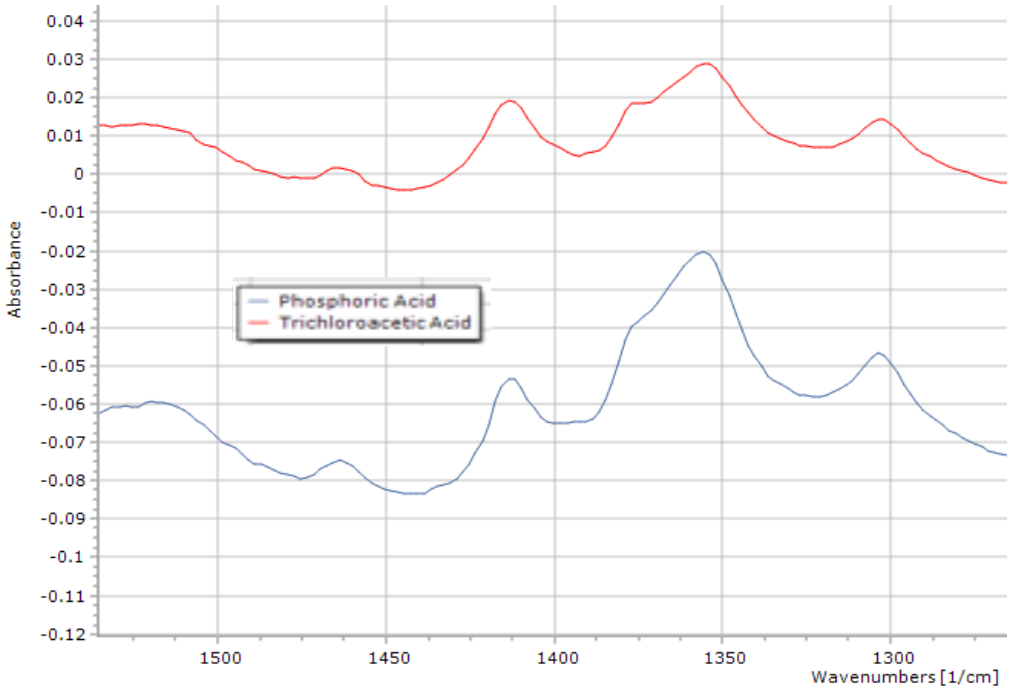

Figure 21. IR Spectra to Demonstrate Reproducibility of the Acid Catalysis Test

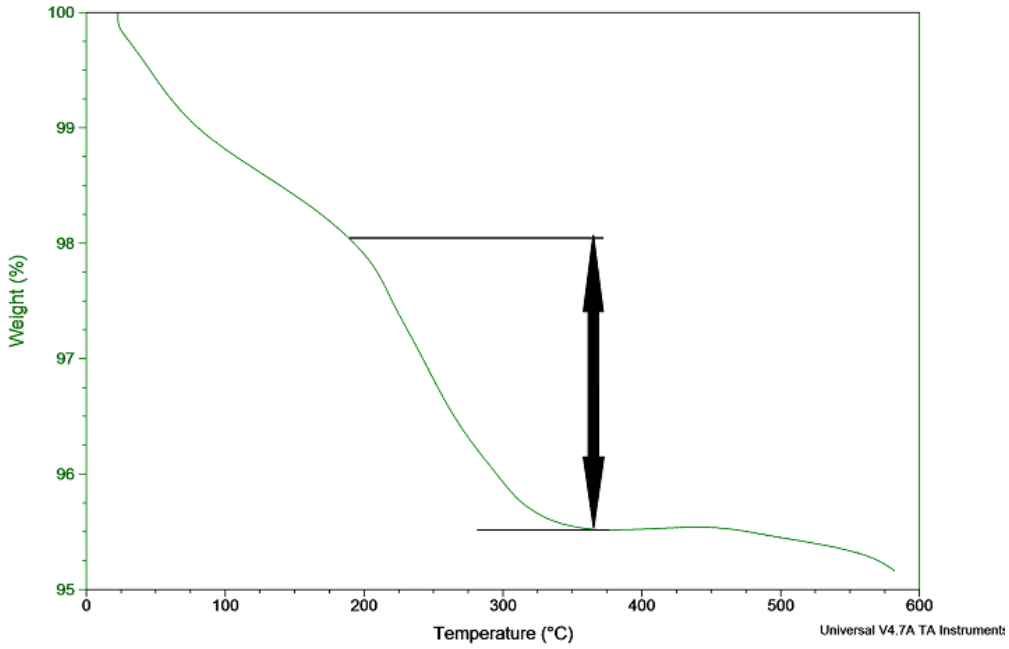

Figure 23. TGA Results for the Synthesized Catalyst

APPENDIX II: SAMPLE CALCULATIONS

$$M_i := 20.8946\ gm \qquad MW_{nine} := 89.09\ \frac{gm}{mol} \qquad mmol := 10^{-6}\ mol$$

$$C_i := \frac{\left(19.60\ \frac{gm}{L}\right) \cdot \left(\frac{M_i}{1000\ \frac{gm}{L}}\right)}{MW_{nine}} = 4596.86\ mmol$$

Figure 13. Initial Concentration of Alanine for the Duplication of Baseline Experiment

$$peak := 0.2233 \qquad slope_{nine} := 0.0151 \qquad C_{gL} := \left(\frac{peak}{slope_{nine}}\right) \frac{gm}{L}$$

$$M_f := 15.5757\ gm \qquad MW_{nine} := 89.09\ \frac{gm}{mol}$$

$$C_f := \frac{\left\langle C_{gL} \right\rangle \cdot \left(\frac{M_f}{1000\ \frac{gm}{L}}\right)}{MW_{nine}} = 2585.42\ mmol$$

Figure 14. Final Concentration of Alanine for the Duplication of Baseline Experiment

AUTHOR'S BIOGRAPHY

Rachel Karno was born in Los Angeles, California but grew up in Columbus, Ohio. She spent most of her childhood in Ohio until moving to Farmington, Maine. As a result, she is a diehard Ohio State fan. One of her favorite things to do is sit around the house watching college football. Her parents and I came to Maine because her mother accepted a position at University of Maine in Farmington teaching early childhood education. Moving here allowed her to reignite her true passion in life of playing soccer. Soccer has been in her life since she was four years old and she has enjoyed continuing to play it here at UMaine via the intramural program. She has also helped to run the intramural program alongside Thad Dwyer for four years now and will greatly miss being a part of the Campus Rec team.

After graduation, Rachel will begin a position at the Portsmouth Navy Shipyard as a Site Test Engineer in the nuclear engineering department. She is extremely excited about this opportunity as she has a deep passion for renewable and alternative energy and will have an amazing opportunity to learn about nuclear power. Her dream job would be to work as a researcher, helping to improve renewable technologies in the world and find a way to make them viable as a primary energy source. She is a literal proponent of the saying "be the change you want to see" or in her case "engineering the change I want to see".