ESTERIFICATION OF OLEIC ACID WITH ETHANOL CATALSED BY 12-TUNGSTOPHOSPHORIC ACID SUPPORTED ON ALUMINA

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We certify that the project entitled “Esterification of Oleic Acid with Ethanol catalysed by 12-Tungstophosphoric Acid supported Alumina” is written by Che Norrizuan Bin Che Abdul Rahim. We have examined the final copy of this project and in our opinion; it is fully adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering. We herewith recommend that it be accepted in fulfilment of the requirements for the degree of Bachelor of Engineering specializing in Chemical.

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ESTERIFICATION OF OLEIC ACID WITH ETHANOL CATALYSED BY 12-TUNGSTOPHOSPHORIC ACID SUPPORTED ON ALUMINA

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JUDUL : **ESTERIFICATION OF OLEIC ACID WITH ETHANOL CATALYSED BY 12-TUNGSTOPHOSPHORIC ACID SUPPORTED ON ALUMINA**

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Saya **CHE NORRIZUAN BIN CHE ABDUL RAHIM**

(HURUF BESAR)

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SUPERVISOR’S DECLARATION

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT’S DECLARATION

I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature:

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Date: 19 January 2012

For my beloved parents, sisters and brothers….

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ABSTRACT

Ester of organic acids and alcohols form an industrially important class of substances. They are mainly produced as components of esterification reactions. Esterification as well as transesterification reactions has been largely applied to the production of biodiesel, which may be defined as alkyl esters of long chain fatty acids derived from renewable resources such as biomass. This work presents an impregnation route to support 12-Tungstophosporic Acid (H_3PW) on Alumina (Al_2O_3) in acidic aqueous solution (HCl 0.1 mol/L) at different ratios (5, 10, 15, 25, 40 and 60 wt%). The catalyst were further applied in the esterification of oleic acid with ethanol. The samples calcined at 200°C for 4 h were characterized by Fourier Transform Infrared Spectrosocy (FTIR), X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA). The effect of the most relevant variables of the process such as ratio of catalyst (H_3PW/Al_2O_3) and reaction temperature was investigated in the present study. An optimum reaction performance , 80% of oleic acid conversion was achieved at 25 wt% catalyst loading, 60°C, 4 h reaction and 1:6 (oleic acid:ethanol) molar ratio. Studies show that the catalyst is feasible to be used for biodiesel production.

ABSTRAK

Ester asid organik dan alkohol membentuk kelas bahan-bahan perindustrian yang penting. Ia biasanya dihasilkan sebagai komponen tindak balas pengesteran. Pengesteran serta tindak balas "transesterification" sebahagian besarnya telah digunakan untuk pengeluaran biodiesel, yang boleh ditakrifkan sebagai alkil ester asid lemak yang berantai panjang yang diperolehi daripada sumber-sumber yang boleh diperbaharui seperti biojisim. Kerja ini membentangkan laluan penghamilan untuk menyokong 12-Tungstophosphoric Asid (H_3PW) ke atas Alumina (Al_2O_3) dalam larutan akueus berasid (HCl 0.1 mol/L) pada nisbah yang berlainan (5, 10, 15, 25, 40 dan 60% berat). Pemangkin terus digunakan dalam pengesteran asid oleik dengan etanol. Sampel yang "calcined" pada 200 °C selama 4 jam dicirikan oleh "*Fourier Transform Infrared Spectrosocy* (FTIR)", "*X-ray Diffraction* (XRD)" dan "*Thermogravimetric Analysis* (TGA)". Kesan pemboleh ubah yang paling relevan dalam proses seperti nisbah pemangkin (H_3PW/Al_2O_3) dan suhu tindak balas telah dikaji dalam kajian ini. Prestasi tindak balas yang optimum, 80% daripada penukaran asid oleik telah dicapai pada 25% berat pemangkin dimasukkan, 60 °C, 4 jam tindak balas dan 1:6 (asid oleik: etanol) nisbah molar. Kajian menunjukkan bahawa pemangkin layak digunakan bagi pengeluaran biodiesel.

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LIST OF SYMBOLS

%	Percentage
wt	Weight
°C	Degree celcius
h	Hour
w/w	Weight per weight
mol/L	Mol per litre
mL	Mililitre
mg	Miligram
°C/min	Degree celcius per minute
cm^{-1}	Centimeter power -1
°	Degree
α	Alpha
g/molg	Gram per mol gram
mL/min	Mililitre per minute
θ	Theta
cps	Centipose

LIST OF ABBREVIATIONS

PFAD	Palm Fatty Acid Distillate
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Ester
DMAP	Dimethylaminopyridine
PTSA	p-Toluenesulfonic Acid
TGA	Thermogravimetric Analysis
FTIR	Fourier Transform Infrared Spectrometer
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Nowadays, biodiesel is very important to produce the energy source. Biodiesel can be used in any diesel engine when mixed with mineral diesel. The biodiesel industry in Malaysia is at a standstill stage with almost zero production. Many companies in Malaysia were not able to maintain their operations given the high cost of production and the lack of the much needed incentive and subsidies from the Government (U.R. Unnithan, 2010). The high cost of production can be price of oil increase in the world. This problem can be solving by new possible alternative such as biodiesel is on the rise around the world, due to a strong and growing desire.

Biodiesel fuel is the new possible alternative to replace the fossil fuel as the energy source such as in transportation sector. Esterification and transesterification is one of the methods to produce the fuel. Esterification of free fatty acid with alcohol can be produced the fuel. Usually the free fatty acids are found in vegetable oil and animal fats. Oleic acid is a monounsaturated of fatty acid and about 39.2% of oleic acid can be found in palm oil. If free fatty acid higher in the palm oil, the production of biodiesel is lower. Then, the oil can be directly utilized in a transesterification reaction to reduce the free fatty acid in palm oil.

1.2 PROBLEM STATEMENT

Nowadays, whole world has faced a crisis in the crude oil price increase. The sudden crisis in the Middle East has made the world crude oil price increase. The sole depends to crude petroleum and diesel gives us no option left, which could contribute the sudden price increase in all industries.

The price of fossil fuels nowadays is increasing drastically that caused many other expenses to increase. Additionally, the dependencies on foreign countries can create negative impact on economy. With the price of fossil oil increasing each year due to the decreasing supply, it might be wise for Malaysia to adopt and implement the use of renewable fuel resources.

The major shift to Iceland usage of hydrogen in the public transportations an alternative to petroleum and diesel. The small country has gained respect to be the World´s Greenest Country thus set us example how we can actually swift from the traditional fuel to a new and environmentally safe energy.

In 2008 Malaysia gain the 26th spot in the World Greenest Country releases by the Yale EPI Statistic. The National Biofuel Policy that has been launched in that year was seen as a move by many to help our country to reduce environmental pollution. But the implementation of the key point of that respective policy has yet too fat from realization. The result is significant. In the latest ranking released last year, Malaysia drop to 54th rank.

Some of the industry used the homogeneous catalyst in their process or reaction. Homogeneous catalyst usually not environmental friendly, a large amount of waste, corrosive and difficult of being sorted out makes part of the reaction product work up. No homogeneous catalyst yet for cracking process, reformation and ammonia synthesis.

1.3 RESEARCH OBJECTIVE

1.3.1 To develop of supported 12-Tungstophosphoric Acid on Aluminium Oxide catalyst for the esterification of Oleic Acid with Ethanol.

1.3.2 To characterize the developed catalyst

1.3.3 To determine the optimum operating condition of the esterification reaction with Oleic Acid and Ethanol with supported 12-Tungstophosporic Acid.

1.4 SCOPE OF RESEARCH

The scopes of this research are listed as below:-

i. Ratio of xH_3PW/Al_2O_3 where x is varied (5, 10, 15, 25, 40 and 60wt%).

ii. Thermogravimetric Analysis, Fourier Transform Infrared Spectroscopy and X-ray Diffraction will be used to determine the characteristics of catalyst.

iii. The reaction temperature will be varied from 55, 60 and 70°C.

1.5 SIGNIFICANCE OF STUDY

The research will develop catalyst for biodiesel production. The research also to contribute to the reduction of gasoline usage by boosting efficiency of green technology such as biodiesel, bioethanol and biobutanol. The road transport network accounts for 22% of all greenhouse gas emissions and through the use of biodiesel using agriculture raw material some of these emissions will be reduced as the fuel crops absorb the carbon dioxide. The research also used solid catalyst to reduce waste production of biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 BIODIESEL

Biodiesel is non-petroleum-based diesel produce by composed of long-chain free fatty acid with alcohol. Biodiesel produced by the reaction of a vegetable oil with ethyl or methyl alcohol by presence of catalyst. In chemically, biodiesel is called ethyl ester if the ethanol is use for alcohol (T.C.Shean Yaw et al., 2008).

Methyl and ethyl esters of fatty acids (biodiesel) are nontoxic, biodegradable and excellent replacement for petroleum (diesel) (H. Noureddini et all., 2004).

2.2 ESTERIFICATION

Esterification is a chemical process that the reaction between alcohols and carboxylic acids for production of esters. It also looks briefly at making esters from the reactions between acyl chlorides (acid chlorides) and alcohols, and also reactions between acid anhydrides and alcohols (Jim Clark, 2003). The reaction of an alcohol with an acid chloride (R-CO-Cl) or an anhydride (R-CO-O-COR’) produce ester product (R-CO-OR’) is the union of the acyl group (R-C=O-) from the acid, RCO-OH, with the alkoxide group (R'O-) from the alcohol , R'-OH rather than other possible networking.

Chongkhong et al., (2007) studied the production of biodiesel by esterification of palm fatty acid distillate. The palm fatty acid distillate (PFAD) having high free fatty acids (FFA). The scope of study the influence of reaction temperature of 70-100°C, molar ratio of methanol to PFAD of 0.4:1–12:1, quantity of catalyst of 0-5.502% (wt of sulfuric acid/wt of PFAD) and the reaction times of 15-240 min. In their findings, it was observed that optimum conversion was achieved at the molar ratio of 4.3:1. The molar ratio is increasing did not significantly increase the amount of Fatty Acid Methyl Ester (FAME). The rapid formation of FAME was observed within the first 90 min. After 90 min, the conversion rate of FAME was slowly and steady state at the end reaction. Temperature from 70 to 100°C for all molar ratios, the FAME content was increased but the conversion rates were reduced at temperature 90-100°C. The maximum amount of FAME when use 1.834 wt% of H_2SO_4 acid catalyst in the reaction. When increase the amount of catalyst higher than 1.834 wt%, there was no enhancement of FAME content.

Sakthivel et al., (2008) studied an efficient catalyst for the esterification of long-chain fatty acids and alcohols in supercritical carbon dioxide by MCM-48 supported tungstophosphoric acid. The esterification is done by using alcohol and long-chain fatty acids. In their findings, the catalytic activities in *sc*-CO_2 medium were significantly higher than as in mesitylene medium. By loading on MCM-48, HPW gave higher activity for the esterification. With the increase in chain length of acid and alcohols in the esterification in *sc*-CO_2, the yields of esters was increased. The HPW catalyst particularly appropriate useful for the esterification of fatty acids with primary fatty alcohols but the relatively very low yields in the esterification including some short acid and alcohols, secondary alcohols and functional acids. The esterification of long-chain fatty acids and alcohols in sc-CO_2 medium very actively with HPW and MCM-48 supported HPW catalysts.

2.3 CATALYST

Catalyst is a substance for change in rate of a chemical reaction. A catalyst may participate in multiple chemical transformations. Promoter is a substance that increasing the reactivity of catalyst while catalytic poisons is a substance that deactivated catalyst. Catalyst divided by heterogeneous catalyst and homogeneous catalyst. Heterogeneous catalysts such as Palladium on activate charcoal used in the reaction of hydrogen with nitro groups to produce amine groups. Homogeneous catalyst such as DMAP (dimethylaminopyridine) used in solution to catalyst esterification reactions.

2.4 HOMOGENEOUS CATALYST

Vicente et al., (2003) studied a comparison of different homogeneous catalyst system (Integrated biodiesel production). A comparison is made of different basic catalyst which is sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide for methanolysis of sunflower oil. In their findings, the methyl ester concentrations were near 100wt% when used four catalysts. For the methoxide catalysts, biodiesel yields were higher than 98wt% after the separation and purification step while biodiesel yields for sodium and potassium hydroxide were lower namely 85.9 and 91.67 wt%. The biodiesel yields can be higher when a modification of the value for experimental conditions such as temperature and catalyst concentration.

Aranda et al., (2007) studied the acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. In this experiment, used different of homogeneous catalyst such as sulfuric acid, methanesulfonic acid, phosphoric acids were the best catalysts. In their findings, sulfuric and methanesulforic acids were the best catalyst, with conversion higher than 90% at 1 h of reaction for reactant methanol and ethanol. For different alcohols, methanol reaction was faster than ethanol. For effect of water in the reaction medium, inhibition effect can be found in the ethanol reaction. A small amount of catalyst (0.01 w/w) is enough to promote the reaction.

Joseph et al., (2005) studied a green, efficient and reusable catalyst system and reaction medium for Fischer esterification by bronsted acidic ionic liquids. Bronsted acidic ionic liquid containing nitrogen based organic cation 1-methylimidazole and 1-buthyl-3-methylimidazolium and inorganic anions of the type BF4, PF6 and PTSA. In their findings, a maximum 100% conversion and 100% product selectivity was obtained on using PTSA as catalyst over a period of 2 h. For PF6 used in the reaction also gave 100% conversion in 2 h but only 90% selectivity for ester was achieved. In the effect of mole ratio of imidazole and BF4 that on increasing the amount of anion in the ionic liquid, the conversion increases but the selectivity remains the same. The reaction had to be carried out for longer time for complete conversion. When the temperature was increase to 120°C, the conversions also increase.

Tosh et al., (2000) studied the homogeneous esterification of cellulose in the lithium chloride-N, N-dimethylacetamide solvent system: effect of temperature and catalyst. In their findings, LiCL-DMAc was found to be an excellent solvent system for the acetylation of cellulose with acetid=c anhydride in the presence of p-TsCL or pyridine. Pyridine is more active as a catalyst for esterification than p-TsCL. In case of esterification with higher anhydrides, p-TsCL might serve as a better catalyst.

Di Serio et al., (2005) studied the synthesis of biodiesel via homogeneous lewis acid catalyst. In their finding, bivalent cations are catalyst for both transesterification and esterification reactions. Catalytic activities are related to the lewis acid strength of the metals and to the molecular structure of the anion a complex. The best catalytic performances were obtained with cation metals having stability constant with dibenzoilmetane in the range between 8.60 (corresponding to cadium) and 10.23 (corresponding to zinc). Then, the stearates have better performances than acetates.

2.5 HETEROGENEOUS CATALYST

Heterogeneous catalyst was present in a different phase, usually in solid phase. Heterogeneous catalyst has many advantages that main advantage is the relative ease of catalyst separation from the product stream that aids in the creation of continuous chemical processes. Heterogeneous catalyst was typically more tolerance of extreme operation condition. It is to be select for this experiment.

Marchetti et al., (2006) studied the heterogeneous esterification of oil with high amount of free fatty acids. In their experiment, basic resin was use as a heterogeneous catalyst. In their findings, the final conversion follows an endothermic behavior when temperature is changes. Resin should be added during the process at initial FFA amounts changes to increase the final conversion. On the amount catalyst, when more catalyst is added a little higher reaction rate is achieved. In the resin is reused, the final conversion is achieved for 2nd, 3rd, and 4th reuse was less than 25%. They conclude that the resin should to be regenerated after each process and resins are a heterogeneous catalyst is appropriate to perform the esterification with higher conversion.

Joo Kim et al., (2004) studied the transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. In their experiment, $Na/NaOH/\gamma\text{-}Al_2O_3$ is use for heterogeneous base catalyst. In their finding, the activities of the heterogenous base catalysts correlated with their basic strengths. *n*-hexane was the most effective with a loading amount of 5:1 VO to *n*-hexane molar ratio when the co-solvent tested. The ratio optimum methanol to oil loading was found to be 9:1. For different catalyst, the

$Na/NaOH/\gamma\text{-}Al_2O_3$ heterogeneous base catalyst showed almost the same activity under optimized reaction condition compared to the homogeneous NaOH catalyst.

Sejidov et al., (2005) studied the esterification reaction using solid heterogenous acid catalyst under solvent-less condition. In their finding, esterification reaction of phthalic anhydride by 2-ethylexanol in the presence of solid acidic catalyst have been investigated under solvent-less condition. For the best reactivity and efficiency among the investigated heterogenous catalyst is sulfated zirconia. These catalysts are environmentally friendly and cleaner than homogeneous catalyst.

Moo Park et al., (2008) studied the heterogenous catalyst system for the continuous conversion of free fatty acid in used vegetable oils for the production of biodiesel. In their finding, the SO_4/ZrO_2 and WO_3/ZrO_2 catalysts were found to be effective in the esterification of free fatty acid to FAME. When the properties of the catalyst are different, it is difficult to compare batch reaction with packed-bed reactions. Packed-bed reactions have advantages over batch reactions in terms of mass production but have some disadvantages when their activity is considered. For maximize the activity of the catalyst, the optimization of the catalyst pellet size will be needed. For the characterization, the oxidation state of W is mainly related to the catalytic activity of WO_3/ZrO_2.

Table 2.1: Summary for the Homogeneous Catalyst

Author	**Reaction**	**Catalyst**	**Finding**
Vicente et al., (2003)	Esterification (Biodiesel production from sunflower oil)	Sodium Methoxide, Potassium Methoxide, Sodium Hydroxide and Potassium Hydroxide	Biodisel yields were higher when used Methoxide catalyst.
Aranda et al., (2007)	Esterification (Biodiesel production from Palm Fatty Acid)	Sulfuric Acid, Methanesulfonic Acid, phosphoric Acid and Trichloroacetic Acid	Sulfuric and Methanesulfonic Acids were the best catalyst.
Joseph et al., (2005)	Esterification (Acetic acid with Benzyl Alcohol)	Bronsted Acidic ionic liquid (BF4, PF6 and PTSA)	PTSA is the best catalyst than BF4 and PF6.
Tosh et al., (2000)	Esterification (Cellulose in the lithium chloride–*N*,*N*-dimethylacetamide solvent system)	*p*-TsCL and Pyridine	Pyridine is more active as a catalyst for esterification than *p*-TsCL.
Di Serio et al., (2005)	Transesterification and Esterification (Triglycerides (TG) with Methanol)	Lewis Acid catalyst	The best catalytic performances were obtained with cation metals having stability constant.

Table2.2: Summary for Heterogeneous Catalyst

Author	Reaction	Catalyst	Finding
Marchetti et al., (2006)	Esterification (Oil with high amount of free fatty acids)	Basic resin	The basic resin is the best catalyst for esterification reaction.
Joo Kim et al., (2004)	Transesterification (Vegetable oil to biodiesel using heterogenous base catalyst)	Na/NaOH/γ-Al_2O_3	Na/NaOH/γ-Al_2O_3 heterogenous base catalyst showed almost the same activity.
Sejidov et al., (2005)	Esterification (Phthalic Anhydride by 2-Ethylhexanol)	Sulfated Zirconia	Sulfated Zirconia is the best reactivity and efficiency.
Moo Park et al., (2008)	Esterification (Oleic Acid with Methanol)	SO_4/ZrO_2 and WO_3/ZrO_2	The SO_4/ZrO_2 and WO_3/ZrO_2 catalysts were found to be affective in the esterification of free fatty acid to FAME

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

The steps involved in order to obtain experiment of results are catalyst preparation analyze of each of the catalyst involve in order to determine the it's characteristic and perform the activity studies. The general flow of the experiment is illustrated in the figure 3.1.

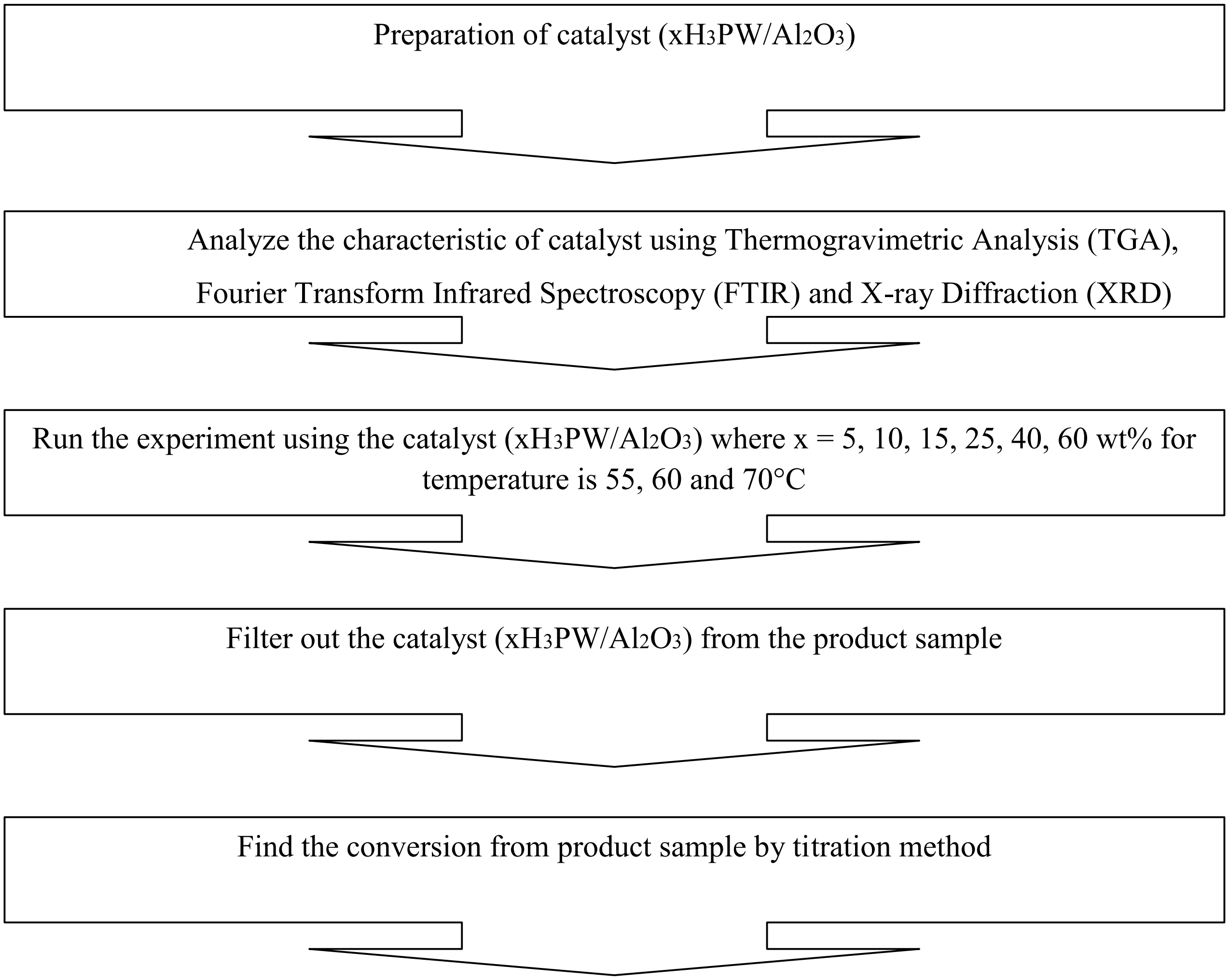


Figure 3.1: Overall Methodology

3.2 MATERIAL

Table 3.1: Material and Function

Material	Function
Oleic Acid	Reactant
Ethanol	Reactant
Aluminium Oxide	Catalyst
12-tungstophosporic Acid	Catalyst
Hydrochloric Acid	Preparation of catalyst
Sodium Hydroxide	Titration solution
Phenolpthalein	Indicator (titration)

3.3 EQUIPMENT/APPARATUS

For the purpose of study, some equipment is required. The equipment required are state below:

1. Thermogravimetric Analysis (TGA)
2. Fourier Transform Infrared Spectroscopy (FTIR)
3. X-ray Diffraction (XRD)
4. Electric Balance Shimadzu (A W220)

3.4 PREPARATION OF xH_3PW/Al_2O_3

Before impregnation procedures, 12-Tungstophosphoric acid will be recrystallized in hydrochloric acid solution (0.1 mol/L). Aluminium Oxide will be used without further purification or treatment. 12-Tungstophosphoric acids in different amounts were dissolved in aqueous solution of HCl (0.1 mol/L). To obtain different mass ratios of H_3PW/Al_2O_3, Aluminium Oxide will be added to 10 mL of each H_3PW solution per gram of Al_2O_3. The samples will be achieved are here after designated xH_3PW/Al_2O_3 where x = 5, 10, 15, 20, 25, 40 and 60 stands for the H_3PW loading (wt%) supported on Al_2O_3. Then, sample will be kept at 80°C and in a constant stirring until overall the liquid has evaporated. The obtained solid will be pulverized and dried at 120°C for 12 h. Finally, all samples will be calcined at 200°C for 4 h in a muffle furnace under static air atmosphere with a 10°C per min heating rate. The solids are hereafter referred by their nominal compositions.

3.5 CHARACTERIZATION OF CATALYST

3.5.1 Thermogravimetric Analysis (TGA)

The Thermogravimetric Analysis (TGA) measurements were carried out using a Shimadzu DT 50 thermal analyzer. The experiments were performed under oxygen, respectively, using 25-50 mg samples and a heating rate of 10 °C/min. The studied temperature range was 25-700 °C.

3.5.2 Fourier Transform Infrared Spectrometer (FTIR)

A Bruker IFS 66 equipment, pellet in KBr and measuring range of 500-1500 cm^{-1} were used to obtain FTIR spectra of the catalyst.

3.5.3 X-ray Diffraction (XRD)

The XRD patterns of the catalysts were obtained by using Phillips PW-1714 difractometer with built-in recorder, Cu Kα radiation and scanning angle from 5-50°.

Table 3.2: Equipment and Function

Equipment	Function
Thermogravimetric Analysis (TGA)	- Determine changes in weight in relation to change in temperature.
Fourier Transform Infrared Spectrometer (FTIR)	- Check H_3PW presence and structural integrity at molecular level.
X-ray Diffraction (XRD)	- Characterize the crystallographic structure, crystallite size (grain size) and preferred orientation in polycrystalline or powder solid samples. - Characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds.

3.6 ESTERIFICATION REACTION

3.6.1 Ratio of xH3PW/Al2O3 where x is varied (5, 10, 15, 25, 40 and 60 wt%)

Firstly, the samples of 1:6 (Oleic Acid : Ethanol) molar ratio and 10wt% of the catalyst (related to oleic acid), will be used following literature previous results and preliminary tests will be fed into the reactor in our laboratory. The reactor used is a lab scale reactor contains a warmer jacket that allows us to set the temperature with an error of ± 0.1°C. Esterification reactions were carried out in a reflux system. Ethanol vapor promptly returned to liquid phase as it reached the condenser, flowing back towards the reaction system that kept at constant stirring under nitrogen atmosphere. The reaction time will be investigated for different xH_3PW/Al_2O_3, pure Aluminium Oxide, pure H_3PW and the mechanical mixture with 20% H_3PW in Al_2O_3. At the end of the reaction period, the reactor system will be shutdown and the products cooled to room temperature. Then, take a sample from reactor into a beaker.

3.6.2 Reaction temperature is varied from 55, 60, 70°C.

The procedure will be repeated for different temperature is 55, 60 and 70°C using catalyst (xH_3PW/Al_2O_3) where x = 25 wt%. At the end of the reaction period, the reactor system will be shutdown and the products cooled to room temperature. Then, take a sample from reactor into a beaker.

3.7 TITRATION PROCESS

The samples will be analyzed by titration procedure for the evaluated of balance acidity. Once the sample will be taken from the reactor, it was separates the catalyst and ethanol. The sample will be centrifuged for 20 min to improve the separation of the phases. A weight amount of the sample will be dissolved in ethanol in order to be able to make the titration analyses. The sample will be added some drops o phenolphthalein as indicator to the system to be able to measure the conversion. The titration will be carried out with a alkaline solution of NaOH. The amount of NaOH used was record and the acidity can be calculated using the following equation:

$$a = \frac{\mathrm{V\ 1000\ Mw\ C}}{\mathrm{W}}$$

Where a is the acidity index, C is the concentration measured by titration (mol/L), W is the weight of the sample (mg), Mw is the molecular weight of the solution (g/molg), V is the volume of solution employed for titration (ml). And using this definition, the conversion of oleic acid was calculated using this equation:

$$x = \frac{ai - at}{ai}$$

Where x the conversion of oleic acid, ai is the initial acidity of the mixture and at is the acidity at a “t” time.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

All result get from the experiment, we combine in this chapter for analyze and discuss. The results include the characteristic of catalyst (xH_3PW/Al_2O_3) and the conversion of Oleic Acid for every parameter which is ratio of catalyst (xH_3PW/Al_2O_3) and temperature.

4.2 CHARACTERIZATION OF ALUMINIUM OXIDE SUPPORT

The characteristic for Aluminium Oxide support include the characteristic by Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD).

4.2.1 Thermogravimetric Analysis (TGA)

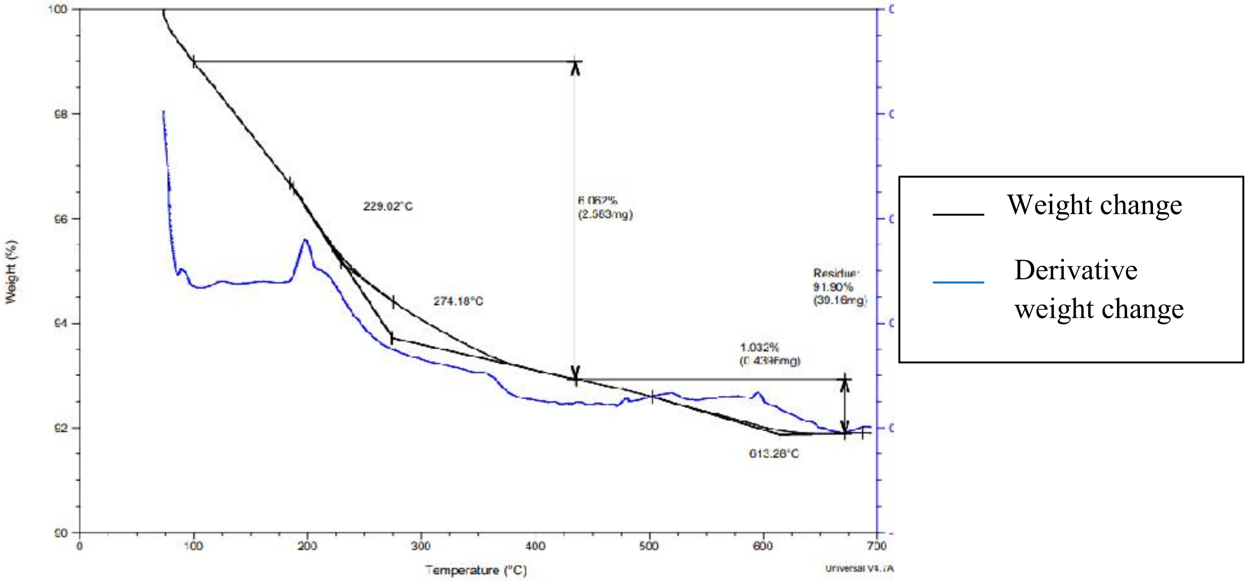


Figure 4.1: Thermogravimetric curves for 12-tungstophosphoric acid supported on alumina catalyst (5 wt%)

TGA analyses of the catalyst were completed with 42.1826 mg samples of catalyst heated at a constant heating rate of 10 °C/min in an atmosphere of oxygen at a constant purge rate of 40 mL/min at the pan. Although other heating rates were examined, 10 °C/min was proven to be a reasonable heating rate while minimizing experimental error. Additional purge rate were not examined because the system used had a fixed purge rate. It was observed that the flow of purge gas promoted pan motion, thus the flow should not substantially exceed the flow rate used. The temperature range employed was 25-700 °C.

Figure 4.1 showed the thermogravimetric plots for 12-tungstophosphoric acid supported on alumina catalyst (5 wt%). The mass of the catalyst start to decrease at approximately after 90 °C and it continues its decrease until 700 °C. The percentage of catalyst could be calculated from the TGA plot of the sample taking into account the first derivative of the weight change of the catalyst mixture.

Figure 4.1 here when the catalyst is analyzed by TGA, we first used the rate of weight loss (derivative weight percentage) to determine the relevant temperatures. It was assumed that inflection points at the lowest rate of weight change values correlated to the temperatures of interest.

In figure 4.1, the initial inflection point is at 274.18 °C and the second inflection point is at 613.28 °C. Thus, the relative weights were 6.062% (2.583 mg) and 1.032% (0.4396 mg). The different relative weight between first and second inflection point is 5.03% and signify catalyst content, which is in good agreement with the actual value of 5 wt%. The initial loss of 6.062 % weight of the sample is attributed to the possible presence of volatile impurities. Then, the residue value at 700 °C is 91.90% (39.16 mg).

4.2.2 Fourier Transform Infrared Spectrometer (FTIR)

Infrared spectroscopy (FTIR) was used to check H_3PW presence and structural integrity at molecular level. Figure 4.2 shows H_3PW Keggin anion displays vibration-absorption bands at ν_{as} (P-O_a) = 1093.14 cm^{-1}, ν_{as} (W=O_t) = 996.17 cm^{-1}, ν_{as} (W-O_c-W) = 939.82 cm^{-1} and ν_{as} (W-O_e-W) = 874.35 cm^{-1}, where a, t, c and e stand for the specific positions (internal, terminal, corner and edge-shared, respectively) of different oxygen atoms in Keggin structure.

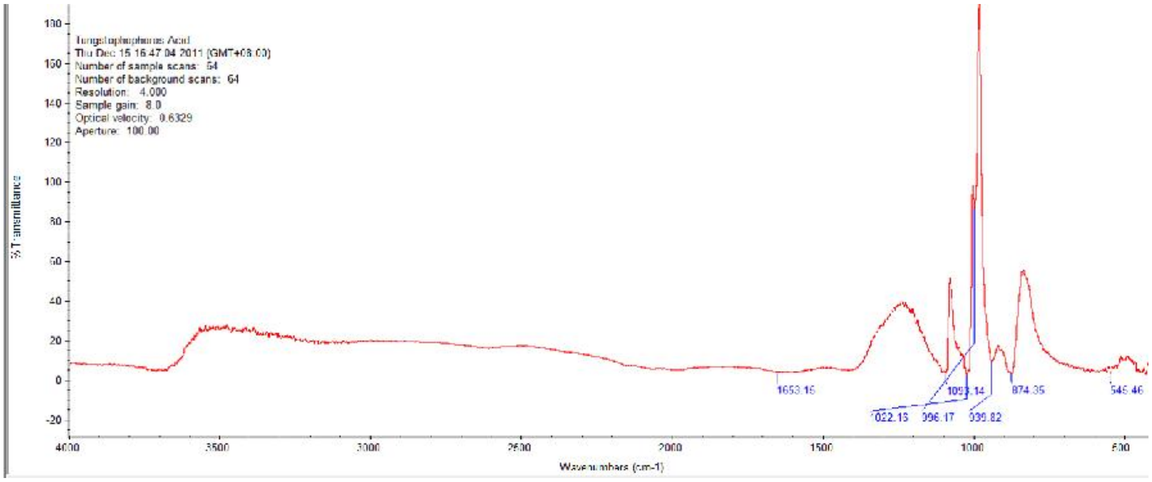


Figure 4.2: FTIR analyses for pure 12-tungstophophoric acid

Figure 4.3 presents FTIR spectra of samples with different amounts of supported H_3PW. We can see that, even at samples with lower amounts of H_3PW (5-15%) the characteristic bands of the Keggin anion, from 800 to 1200 cm^{-1}, show up. This is taken here as instruction that the Keggin structure remains complete throughout the impregnation process.

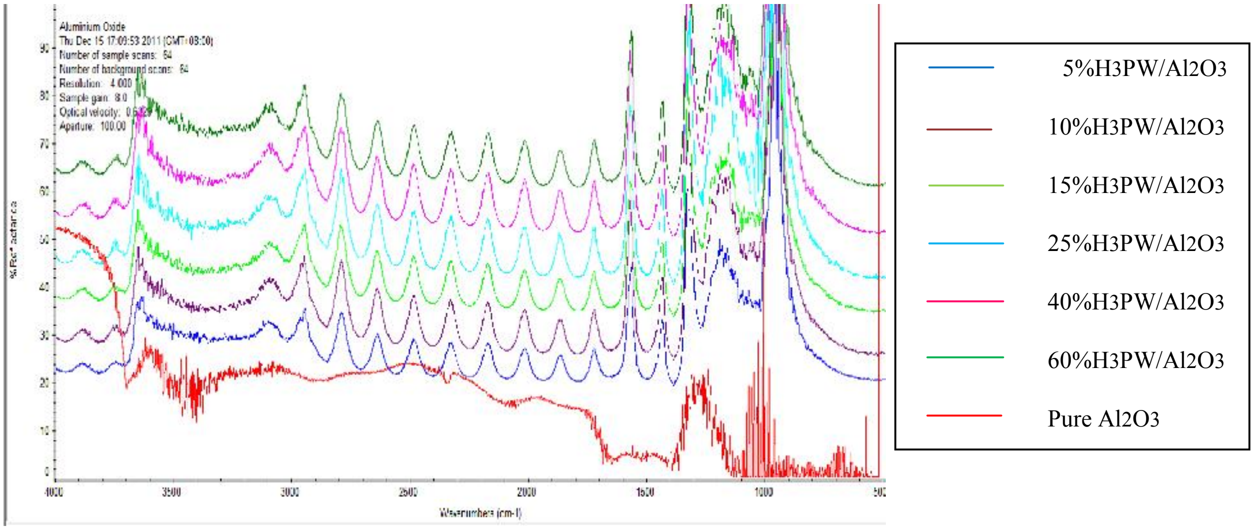


Figure 4.3: FTIR analyses for 5, 10, 15, 25, 40 and 60 wt% of catalyst xH_3PW/Al_2O_3

4.2.3 X-ray Diffraction (XRD)

X-ray diffractograms were collected for xH_3PW/Al_2O_3 samples with: x = 0, 5, 10, 15, 25 and 40%. The number of observed lines in the range $2\theta = 5\text{-}50°$ increases with the amount of H_3PW. Characteristic lines of pure H_3PW are at $2\theta = 10.3°$, 25.3° and 34.6° (Oliveira et al., 2010). Figure 4.4 to 4.8 shows the result to XRD analysis for 5, 10, 15, 25 and 40wt% of H_3PW supported Al_2O_3.

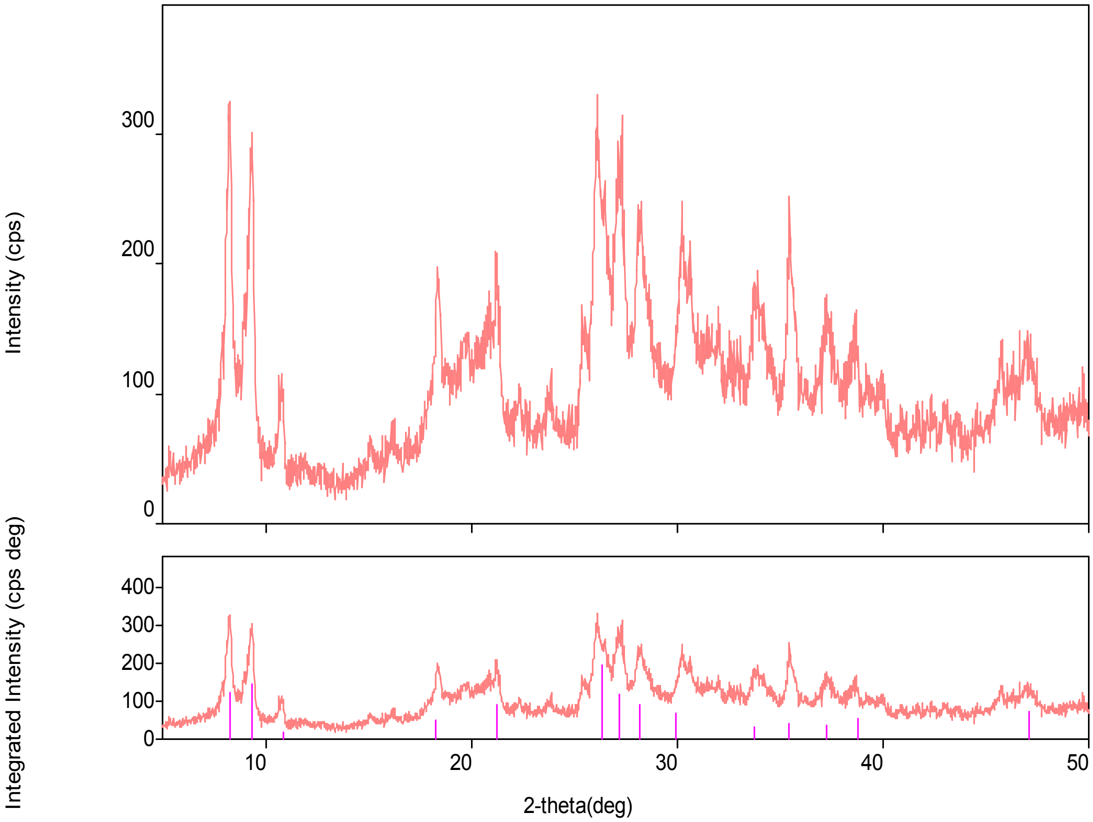


Figure 4.4: XRD analyses for 5%H_3PW/Al_2O_3

Figure 4.4 shows the result XRD analysis for 5%H_3PW/Al_2O_3 the range $2\theta = 5\text{-}50°$. For the figure 4.4 can see that at $2\theta = 10.3°$ (37 cps), 25.3° (129 cps), and 34.6° (76 cps) to presence of crystalline H_3PW.

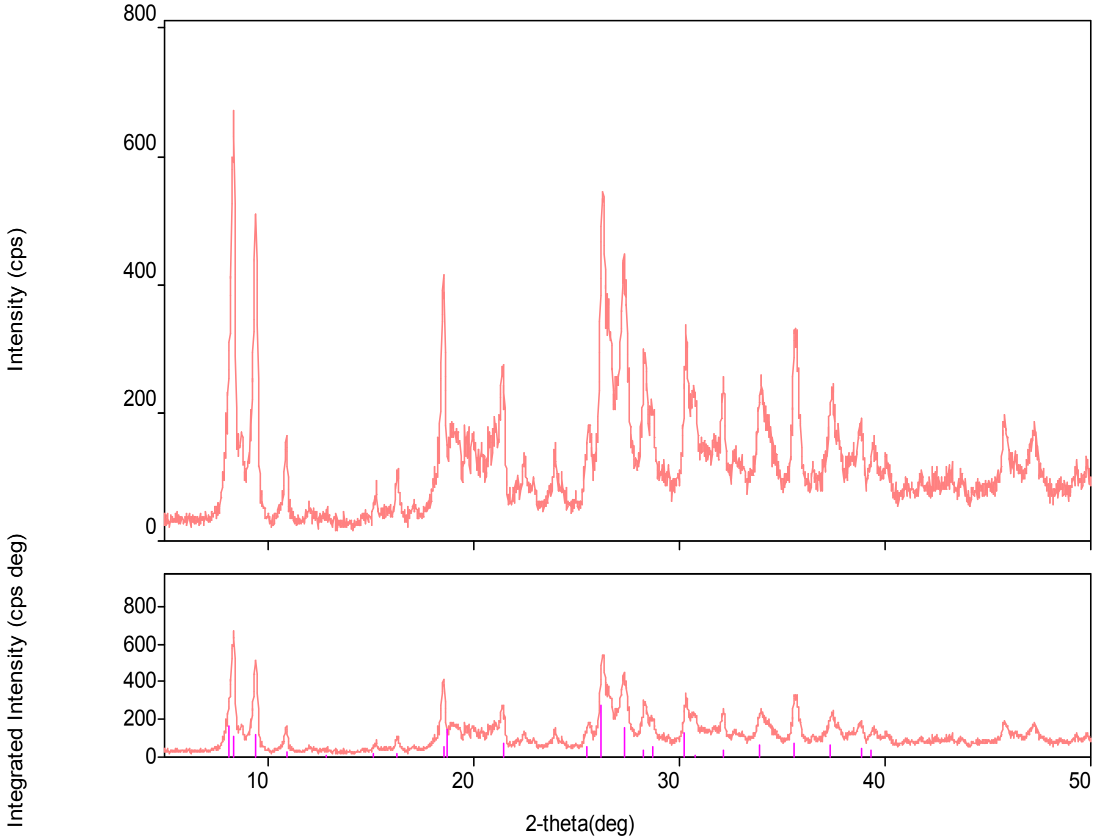


Figure 4.5: XRD analyses for 10%H_3PW/Al_2O_3

Figure 4.5 shows the result XRD analysis for 10%H_3PW/Al_2O_3 the range $2\theta = 5$-50°. For the figure 4.5 can see that at $2\theta = 10.3°$ (290 cps), 25.3° (265 cps), and 34.6° (155 cps) to presence of crystalline H_3PW.

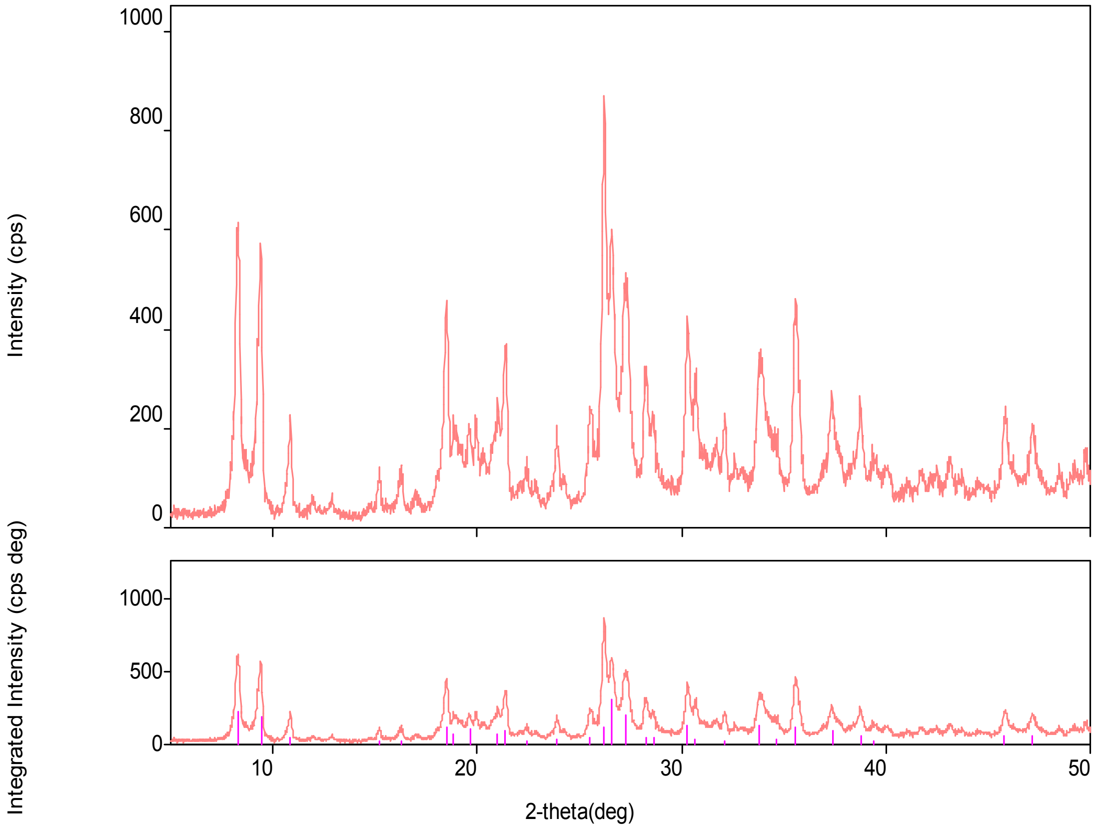


Figure 4.6: XRD analyses for 15%H_3PW/Al_2O_3

Figure 4.6 shows the result XRD analysis for 15%H_3PW/Al_2O_3 the range $2\theta = 5$-50°. For the figure 4.6 can see that at $2\theta = 10.3°$ (341 cps), 25.3° (380 cps), and 34.6° (246 cps) to presence of crystalline H_3PW.

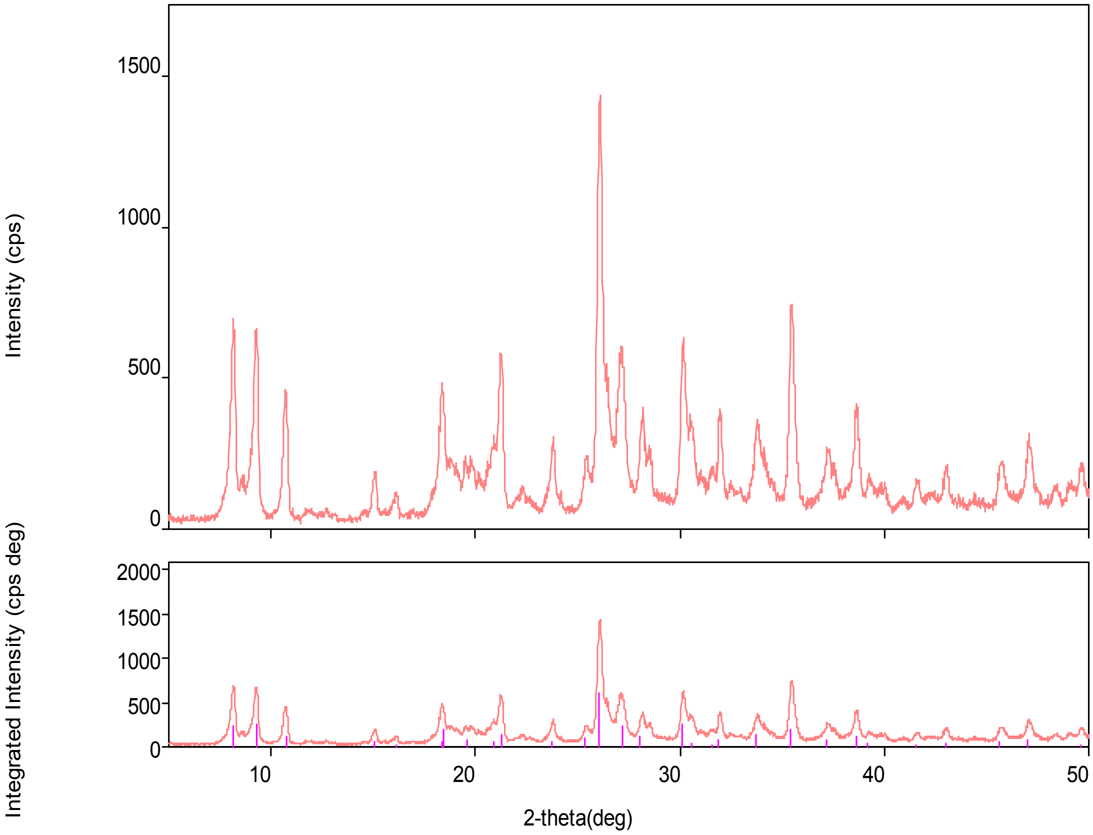


Figure 4.7: XRD analyses for 25%H_3PW/Al_2O_3

Figure 4.7 shows the result XRD analysis for 25%H_3PW/Al_2O_3 the range $2\theta = 5$-50°. For the figure 4.7 can see that at $2\theta = 10.3°$ (404 cps), 25.3° (845 cps), and 34.6° (433 cps) to presence of crystalline H_3PW.

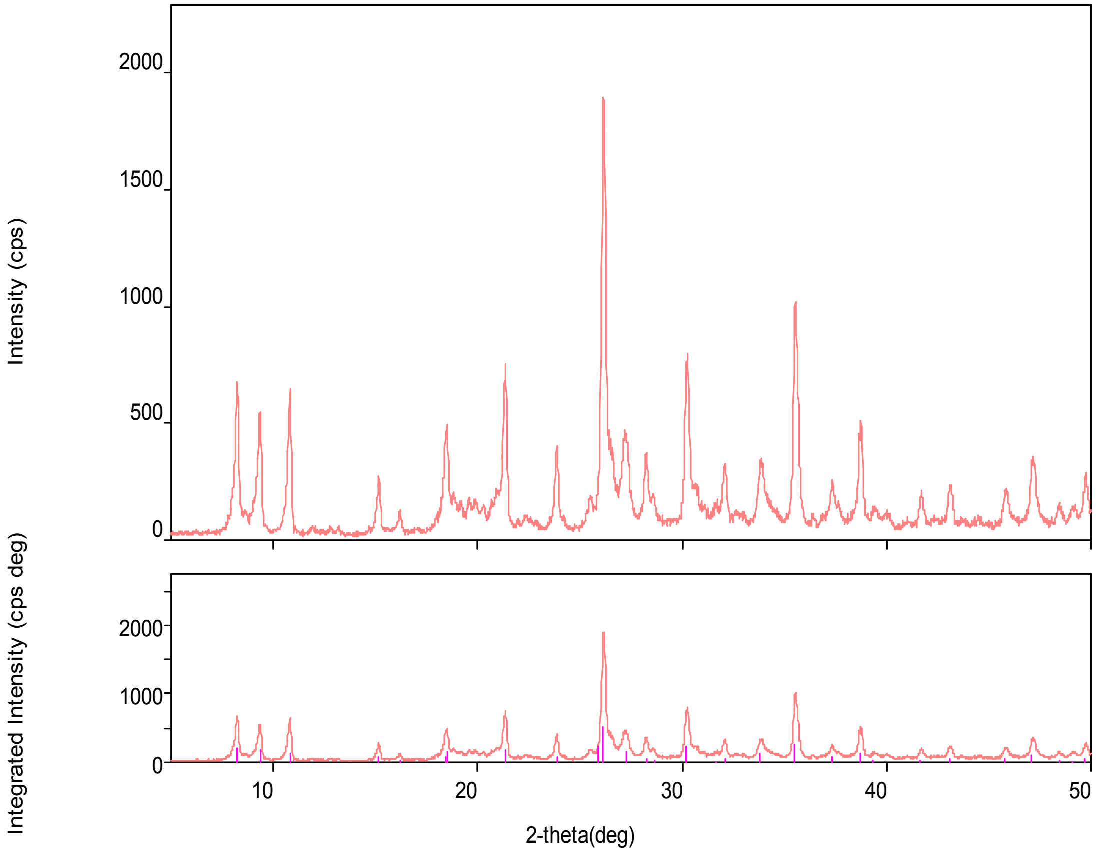


Figure 4.8: XRD analyses for 40%H_3PW/Al_2O_3

Figure 4.8 shows the result XRD analysis for 40%H_3PW/Al_2O_3 the range $2\theta = 5$-50°. For the figure 4.8 can see that at $2\theta = 10.3°$ (309 cps), 25.3° (1199 cps), and 34.6° (632 cps) to presence of crystalline H_3PW.

Table 4.1: Summary for XRD analysis

Ratio Catalyst, xH_3PW/Al_2O_3 (wt%)	2θ (°)		
	10.3	25.3	34.6
	Intensity (cps)		
5	37	129	76
10	290	265	155
15	341	380	246
25	404	845	433
40	309	1199	632

Table 4.1 shows the summary for XRD analysis for every catalyst. From table 4.1, this intensity increased monotonically as the amount of H_3PW increased with x-value in xH_3PW/Al_2O_3. For example at 25.3°, $5\%H_3PW/Al_2O_3$ displayed a 129 cps, $15\%H_3PW/Al_2O_3$ showed 380 cps and $40\%H_3PW/Al_2O_3$ reached 1199 cps. Line at 25.3° gets better defined, pointing to the presence of crystalline H_3PW.

Crystallites average sizes of H3PW were determined through Scherrer’s equation applied to the line at 25.3°. Its intensity and independence of alumina lines influence makes this line a natural choice in this case. The results were 56.7, 89.2, 90.9, 168.4 and 255.5 nm, for 5, 10, 15, 25 and 40 wt%. From this result, these data shows that the higher concentration of H_3PW leads to bigger crystal size and points to a more efficient H_3PW dispersion on alumina’s surface.

4.3 ESTERIFICATION REACTION OF OLEIC ACD WITH ETHANOL

Esterification reactions strength look simple, but they have low equilibrium constants and need the addition of a catalyst. The addition of a catalyst is one method to obtain high yields. Commonly, esterification reaction is carry out under Bronsted acid catalysts. Since both support and supported oxide have intrinsic Bronsted acidity, they were tested for this reaction.

4.3.1 Effect of Catalyst Ratio (xH_3PW/Al_2O_3)

For the first parameter we used the effect of catalyst ratio (xH_3PW/Al_2O_3), where x = 5, 10, 15, 25, 40 and 60 wt%. All experiment run at 60 °C. Table 4.2 and figure 4.9 shows the result of the conversion of oleic acid versus catalyst ratio.

Table 4.2: Effect of Catalyst Ratio (xH_3PW/Al_2O_3)

Catalyst Ratio (wt%)	Conversion, X (%)
0	20
5	39
10	53
15	70
25	79
40	80
60	81

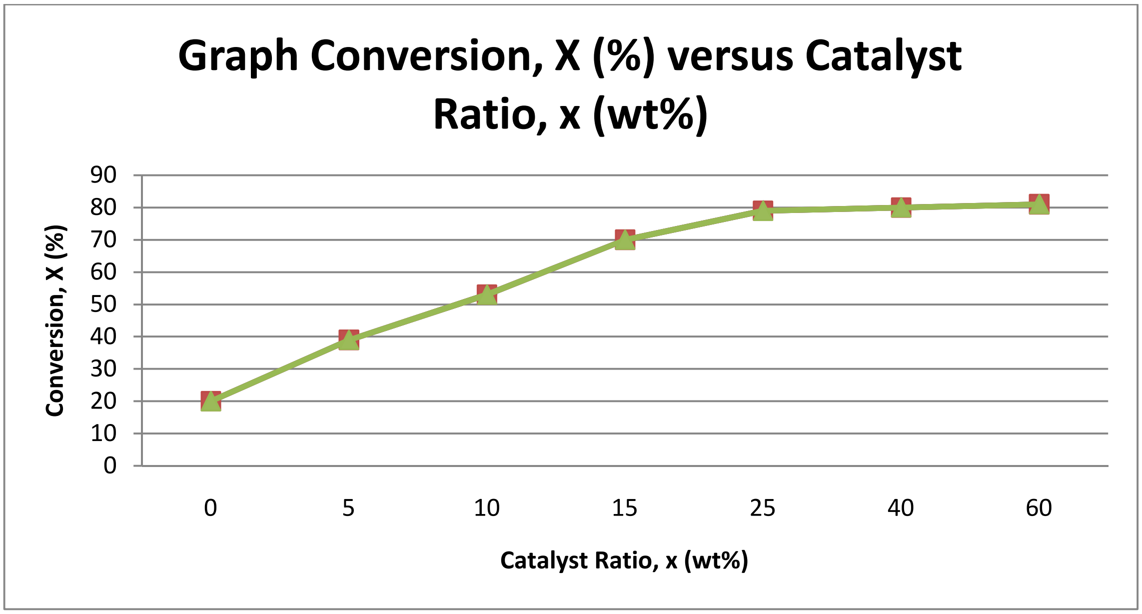


Figure 4.9: Graph Conversion (%) versus Catalyst Ratio (wt%)

In figure 4.8 shows the conversion for oleic acid versus different amount of xH_3PW/Al_2O_3 in a period of 4 hour was measured using 1:6 acids to alcohol molar ratio. For pure alumina (x=0), the observed conversion was 20%. From figure 4.8, we can see that the conversion increased monotonically as the amount of H_3PW increased with x-value in xH_3PW/Al_2O_3 samples. For example, $5\%H_3PW/Al_2O_3$ displayed a 39%, $25\%H_3PW/Al_2O_3$ showed 79% and $60\%H_3PW/Al_2O_3$ reached 81%. Then, the result show that $25\%H_3PW/Al_2O_3$ is very fast to achieve the higher conversion compare the others catalyst ratio. It is because $25\%H_3PW/Al_2O_3$ catalyst is optimum to convert oleic acid to produce the ethyl oleate. When $40\%H_3PW/Al_2O_3$ and $60\%H_3PW/Al_2O_3$ used, the conversion of oleic acid is equilibrium. $25\%H_3PW/Al_2O_3$ catalyst is the best catalyst to convert oleic acid to ethyl oleate. Then, we continue the experiment using only $25\%H_3PW/Al_2O_3$ catalyst for different reaction temperature to get the higher conversion with temperature.

4.3.2 Effect of reaction time for 25%H_3PW/Al_2O_3 catalyst

The reaction was run at 60 °C for 25%H_3PW/Al_2O_3 catalyst for 6 hour reaction. At 1 hour reaction, we take some of sample from the reactor to check it conversion. This method was repeated to 6 hour reaction. The result was shows in table 4.3 and figure 4.10.

Table 4.3: Result for Effect of Reaction Time

Time (hr)	**Conversion, X (%)**
1	25
2	40
3	58
4	80
5	82
6	84

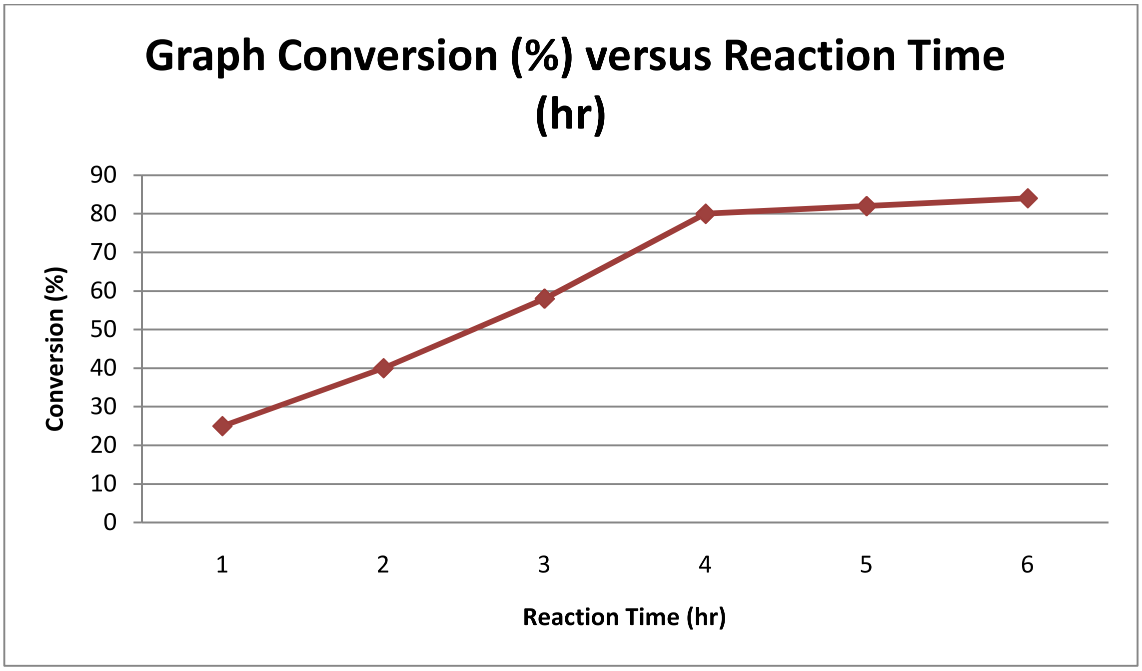


Figure 4.10: Graph Conversions (%) versus Reaction Time (hr)

Figure 4.10 shows the conversion of oleic acid versus reaction time was measured using 1:6 acids to alcohol molar ratio. At 1 hour reaction, the conversion is very low (25%) that means the reaction inside the reactor is not complete. It needed more time to react. At 2 and 3 hour reaction, the conversion is low (40% and 58%) and the reaction slowly increased from 2 hour to 3 hour reaction. For 4 hour reaction, the conversion increased very fast and it achieve at 80% conversion that means the reaction inside the reactor is complete. For 5 and 6 hour reaction, the conversion increased very slowly and it achieve at 82% and 84% conversion. At this time, the reactions almost achieve equilibrium mean that oleic acid in equilibrium with ethyl oleate. So, the reaction is slowly and the conversion increased slowly. From this result, we can conclude that the best reaction time for this reaction at 4 hour.

4.3.3 Effect of temperature for 25%H_3PW/Al_2O_3 catalyst

The reaction was run under different reaction temperature which is 55, 60 and 70 °C for 25%H_3PW/Al_2O_3 catalyst for 4 hour. The result was shows in table 4.3 and figure 4.9.

Table 4.4: Result for Effect of Temperature

Temperature (°C)	**Conversion, X (%)**
55	70
60	79
70	80

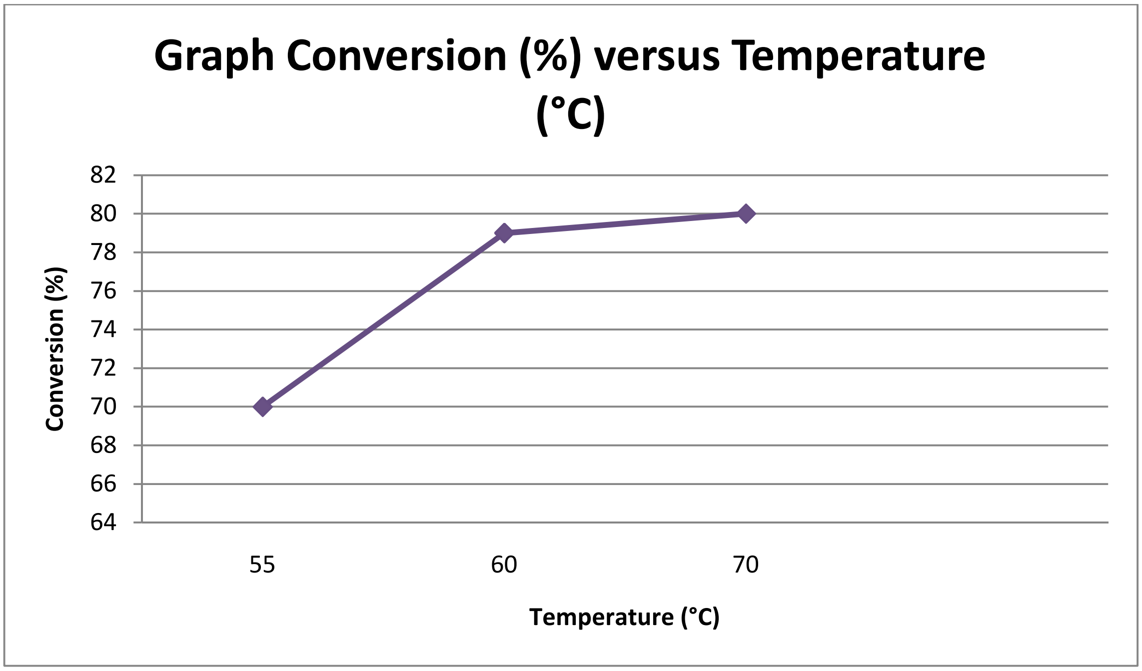


Figure 4.11: Graph Conversions (%) versus Temperature (°C)

Figure 4.11 shows the conversion for oleic acid versus different reaction temperature (55, 60 and 70 °C) in a period of 4 hour was measured using 1:6 acids to alcohol molar ratio. The result shows that at temperature 55 °C, the conversion of oleic acid is 70%. That means at this temperature the conversion is very lower than 60 and 70 °C. At 60 °C, the conversion increased too fast is 79%. Lastly, at 70 °C the conversion is 80%. When the temperature increases, the conversion also increases. From Arrhenius equation, if temperature increases, rate constant also increase in the reaction and kinetic energy in the reaction then the conversion also increase. From the result, we can conclude that the best temperature for this reaction is 60 °C.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 INTRODUCTION

Ester of organics acids and alcohols form an industrially important class of substances. They are mainly produced as components of esterification reactions. These are reversible and slow chemical reactions at room temperature, where the reactants, an alcohol and an acid, yield an ester and water as the equilibrium of the reaction is shifted towards the products (Ulmann's Encyclopedia of Industrial Chemistry, 2001). The esterification reaction of long chain carboxylic acid such as oleic acid is interesting in the context of biodiesel.

5.2 CONCLUSION

Acid catalyzed heterogeneous esterification reaction of oleic acid with ethanol was studied using a batch reactor. The present work demonstrates that 12-tungstophosphoric acid (H_3PW) supported on Al_2O_3 surface can be achieved by the acidic of 0.1 mol/L hydrochloric acid with impregnation method at different coverage layers.

The characteristic of catalyst was done by Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectrometer (FTIR) and X-ray Diffraction (XRD). Thermogravimetric analysis results showed that the initial weight loss at 274.18 °C and second weight loss at 613.28 °C. From this result, the initial loss is attributed to the possible presence of volatile impurities.

X-ray diffraction results showed that a considerable quantity of material (5-40 wt%, calcined at 200 °C for 4 h) can be obtained without the decomposition of Keggin structure. X-ray average crystal size determinations for different H_3PW to alumina concentrations were consistent with the picture of H_3PW dispersion on alumina's surface. X-ray results showed that the lower concentration of H_3PW leads to smaller crystal size and points to a more efficient H_3PW dispersion on alumina's surface.

From esterification reaction result on this study can be concluded that 25%H_3PW/Al_2O_3 is the most active catalyst for the esterification of oleic acid with ethanol reaching 80% conversion at 4 h reaction with 1:6 (oleic acid:ethanol) molar ratio and 10 wt% of the catalyst.

5.3 RECOMMENDATION

For get the good results, equipment is an important. During this research, the equipment used for characteristic the catalyst such as TGA, FTIR and X-ray. This is equipment not enough to check the characteristic of catalyst. Thus, it is recommended that the equipment which is Brunauer-Emmet-Teller isotherms (BET) is using in this research to measure the specific surface area of the catalyst.

For improve this research, it is recommended that used the effect of other parameter which is pressure and ratio of oleic acid with ethanol. Many parameter used in this research can get more operating condition for esterification reaction. Then, more information about the esterification can get from this.

In the chemical reaction, the higher conversion is an important to get high product from the reaction. In this research, the higher conversion is 80%. Thus, it is recommended that to change alumina with other metal oxide which is zirconia. Based on the reference, zirconia is a best metal oxide for supported with 12-tungstophosphoric acid to produce solid catalyst for esterification reaction.

REFERENCES

Y. Liu, E. Lotero, J. G. Goodwin Jr. 2006. Effect of carbon chain length on esterification of carboxylic acids with methanol using acid catalysis: *Journal of Catalysis.* **243**: 221–228.

B. Tosh, C. N. Saikia, N. N. Dass,. 2000. Homogeneous esterification of cellulose in the lithium chloride – N,N-dimethylacetamide solvent system: effect of temperature and catalyst: *Carbohydrate Research.* **327**: 345 – 352.

D. A. G. Aranda, R. T. P. Santos, N. C. O. Tapanes, A. L. Dantas Ramos, O. Auqusto C. Antunes,. 2008. Acid-Catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids: *Catal Lett (2008).* **122**: 20–25.

P. Chand, Ch. Venkat Reddy, J. G. Verkade, T. Wang, and D. Grewell. 2009. Thermogravimetric quantification of biodiesel produced via alkali catalyzed transesterification of soybean oil: *Energy Fuels.* **23** (2): 989-992.

C. F. Oliveira, L. M. Dezaneti, F. A. C. Garcia, J. L. de Macedo, J. A. Dias, S. C. L. Dias, K. S. P. Alvim. 2009. Esterification of oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia: *Applied Catalysis A: General.* **372**: 153–161.

F. Tataroglu Sejidov, Y. Mansoori, N. Goodarzi. 2005. Esterification reaction using solid heterogeneous acid catalysts under solvent-less condition: *Journal of Molecular Catalysis A: Chemical.* **240**: 186–190.

G. Vicente, M. Martiınez, J. Aracil. 2003. Integrated biodiesel production: a comparison of different homogeneous catalysts systems: *Bioresource Technology.* **92**: 297–305.

H. J. Kim, B. Seung Kang, M. Ju Kim, Y. Moo Park, D. Keun Kim, J. Suk Lee, K. Young Lee. 2004. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst: *Catalysis Today*. **93–95**: 315–320.

J.M. Marchetti, V.U. Miguel, A.F. Errazu. 2006. Heterogeneous esterification of oil with high amount of free fatty acids: *Fuel.* **86**: 906–910.

M. Di Serio, R. Tesser, M. Dimiccoli, F. Cammarota, M. Nastasi, E. Santacesaria. 2005. Synthesis of biodiesel via homogeneous Lewis acid catalyst: *Journal of Molecular Catalysis A: Chemical.* **239**: 111–115.

M. Abdollahi-Alibeik, Z. Zaghaghi, I. Mohammadpoor-Baltork. 2008. Alumina supported 12-tungstophosphoric acid as an efficient and reusable catalyst for synthesis of 1,5-benzodiazepines: *Journal of the Chinese Chemical Society.* **55**: 1-4.

T. Joseph, S. Sahoo, S.B. Halligudi. 2005. Bronsted acidic ionic liquids: A green, efficient and reusable catalyst system and reaction medium for Fischer esterification: *Journal of Molecular Catalysis A: Chemical.* **234**: 107–110.

Y. Moo Park, D. Won Lee, D. Keun Kim, J. Suck Lee, K. Young Lee. 2008. The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel: *Catalysis Today.* **131**: 238–243.

E. Lopez-Salinas, J.G. Hernandez-Cortez, Ma. A. Cortes-Jacome, J. Navarretea, Ma.E. Llanos, A.Vazquez, H. Armendariz, T.Lopez. 1998. Skeletal isomerization of 1-butene on 12-tungstophosphoric acid supported on zirconia: *Applied Catalysis A: General*. **175**: 43-53.

A. C. Carmo Jr., L. K.C. de Souza, C. E. F. da Costa, E. Longo, J. R. Zamian, G. N. da Rocha Filho. 2009. Production of biodiesel by esterification of palmitic acid over mesoporous aluminosilicate Al-MCM-41: *Fuel*. **88**: 461–468.

H. Duc Hanh, N. The Dong, K. Okitsu, R. Nishimura, Y. Maeda. Biodiesel production by esterification of oleic acid with short-chain alcohols under ultrasonic irradiation condition: *Renewable Energy*. **34**: 780–783.

P. Madhusudhan Rao, A. Wolfson, M.V. Landau, M. Herskowitz. Efficient immobilization of 12-tungstophosphoric acid catalyst at the surface of silica support grafted with alumina: *Catalysis Communications*. **5**: 327–331.

L.R. Pizzio, P.G. Vázquez, C.V. Cáceres, M.N. Blanco. Supported Keggin type heteropolycompounds for ecofriendly reactions: *Applied Catalysis A: General*. **256**: 125–139.

T. A. Peters, N. E. Benes, A. Holmen, J. T. F. Keurentjes. 2006. Comparison of commercial solid acid catalysts for the esterification of acetic acid with butanol: *Applied Catalysis A: General*. **297**: 182–188.

J.H. Sepu´lveda, J.C. Yori, C.R. Vera. Repeated use of supported $H_3PW_{12}O_{40}$ catalysts in the liquid phase esterification of acetic acid with butanol: *Applied Catalysis A: General*. **288**: 18–24.

APPENDIX A

Figure A.1: Thermogravimetric Analysis (TGA)

Figure A.2: Fourier Transform Infrared Spectroscopy (FTIR)

APPENDIX B

Figure B.1: Esterification Reaction Process

Figure B.2: Esterification Reaction with Batch Reactor

Figure B.3: Product with Catalyst

Figure B.4: Process Filtration the Catalyst

Figure B.5: Catalyst (xH_3PW/Al_2O_3)

APPENDIX C

Figure C.1: Titration Process

Figure C.2: After Titration

APPENDIX D

Result from characteristic of catalyst (xH_3PW/Al_2O_3) using Thermogravimetric Analysis (TGA)

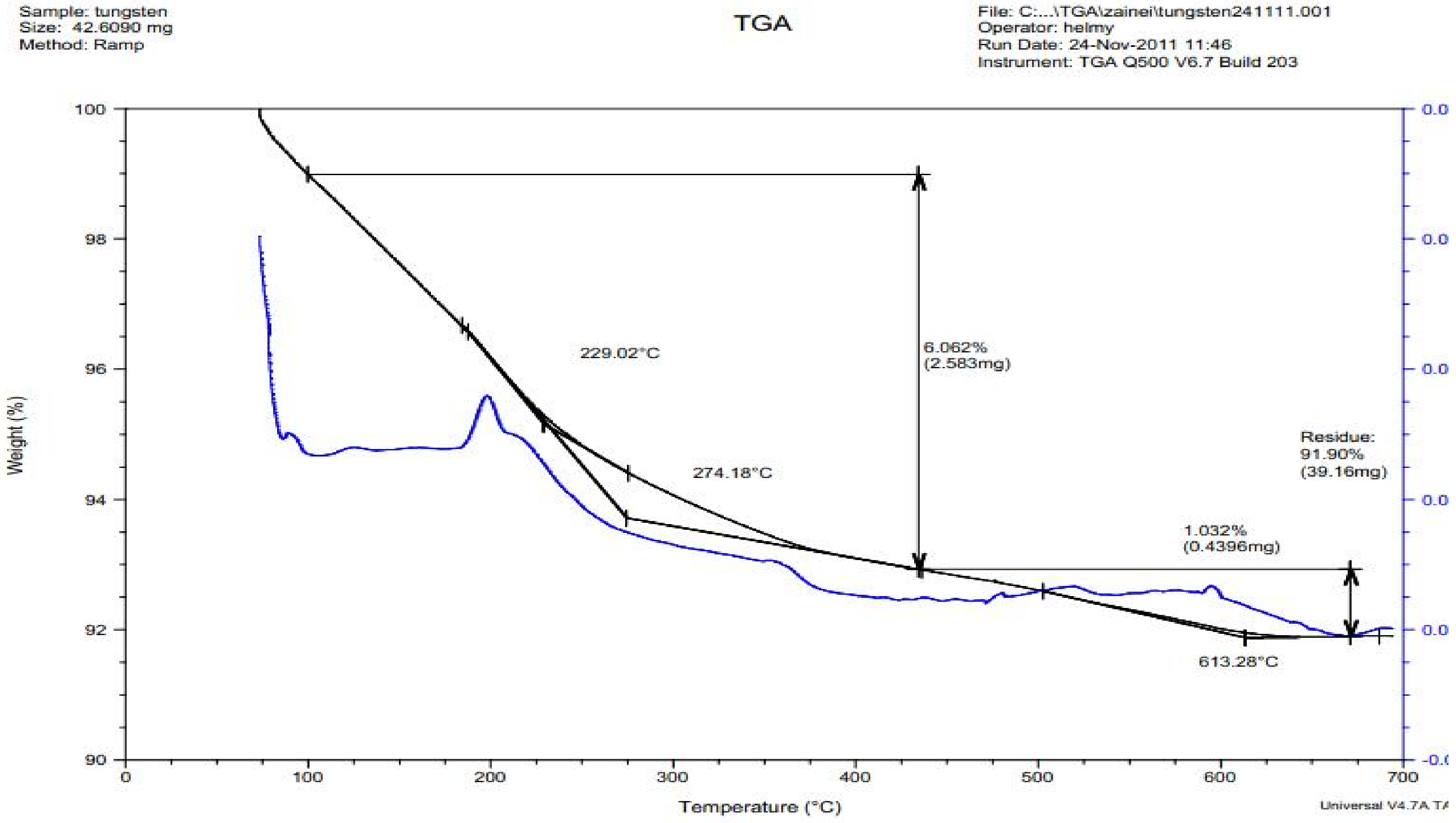


Figure D.1: TGA result for 5%H_3PW/Al_2O_3

APPENDIX E

Results from characteristic of catalyst (xH_3PW/Al_2O_3) using Fourier Transform Infrared Spectroscopy (FTIR).

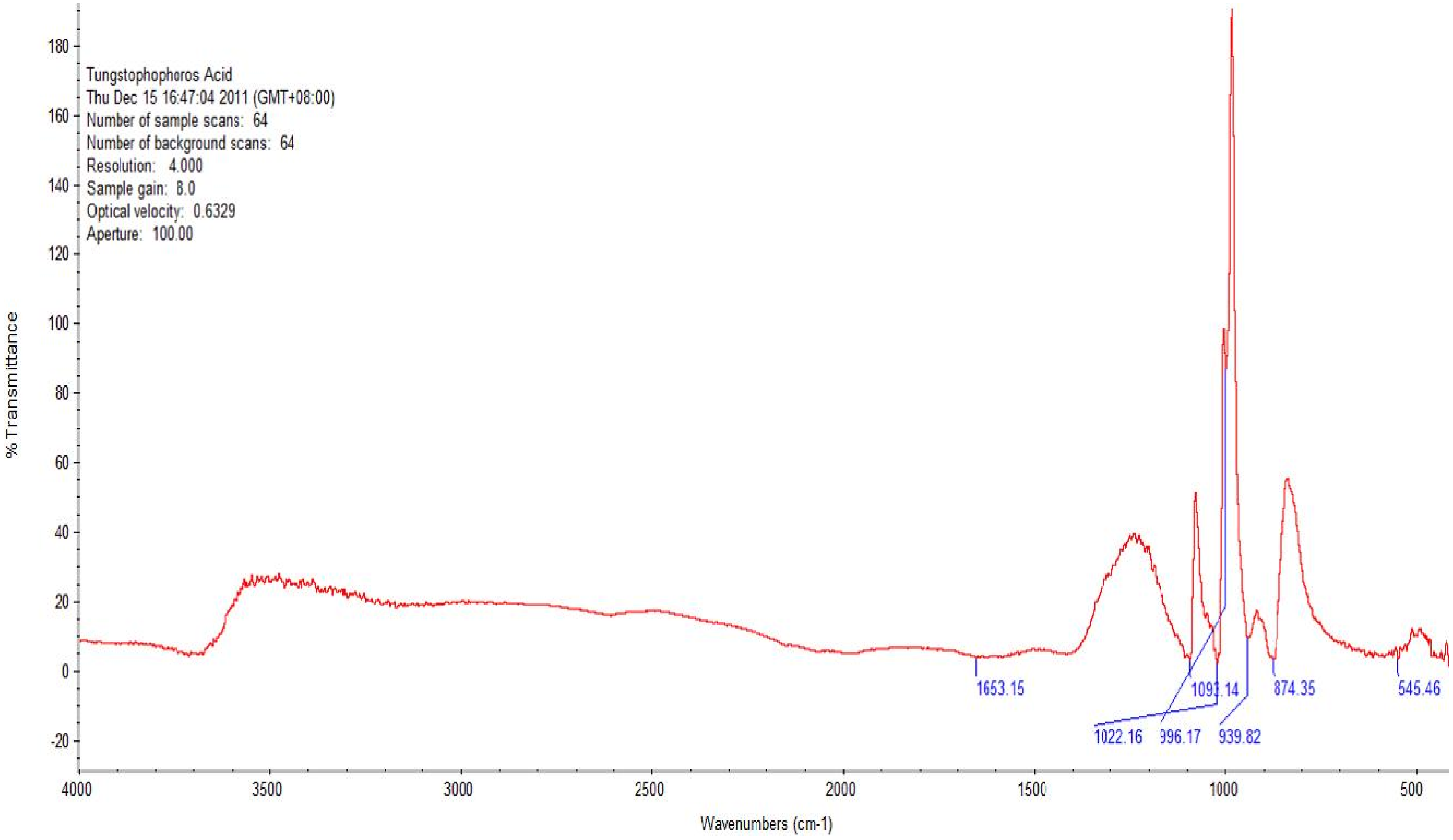


Figure E.1: FTIR results for pure 12-Tungstophosphoric Acid

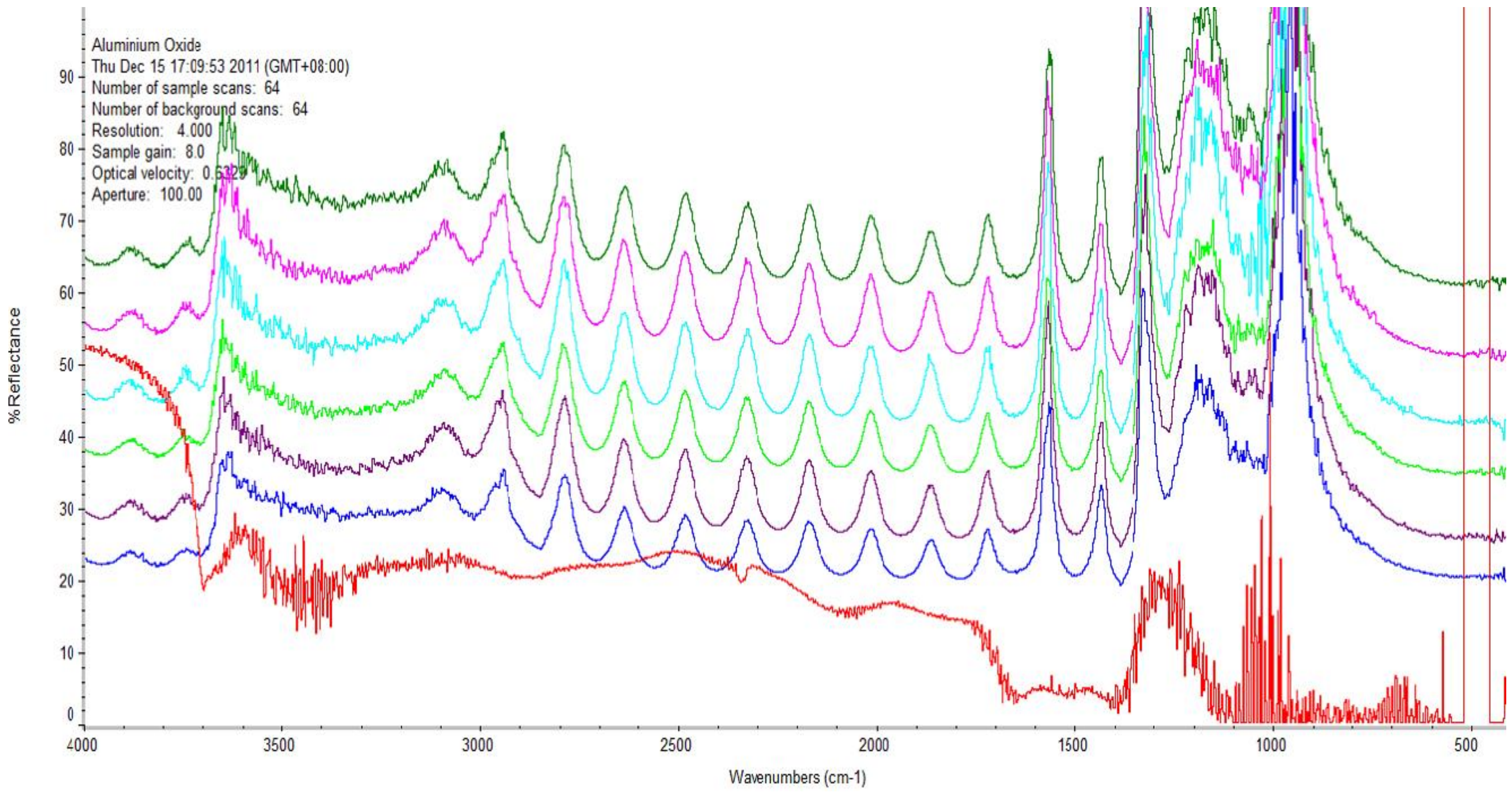


Figure E.2: FTIR result for catalyst (xH_3PW/Al_2O_3), where x= 5, 10, 15, 25, 40 and 60 wt%

APPENDIX F

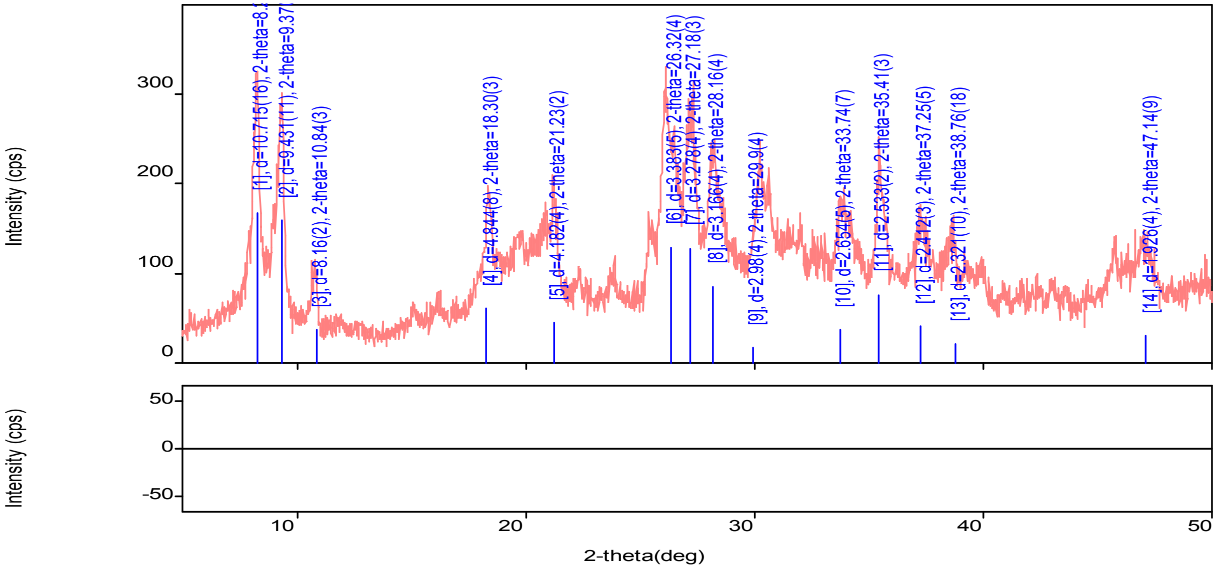
Results from characteristic of catalyst (xH_3PW/Al_2O_3) using X-ray Diffraction (XRD).

Analysis Results

General Information

Analysis date	12/21/2011 4:00:38 PM		
Sample name	XRD Analysis	Measured time	12/7/2011 8:07:05 AM
File name	1-Sample 5%.raw	Operator	administrator
Comment	FKKSA		

Measurement profile



Measurement Condition

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	5-50 deg
Incident monochromator	-	Incident slit	-
Receiving monochromator	-	Vertical divergence slit	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

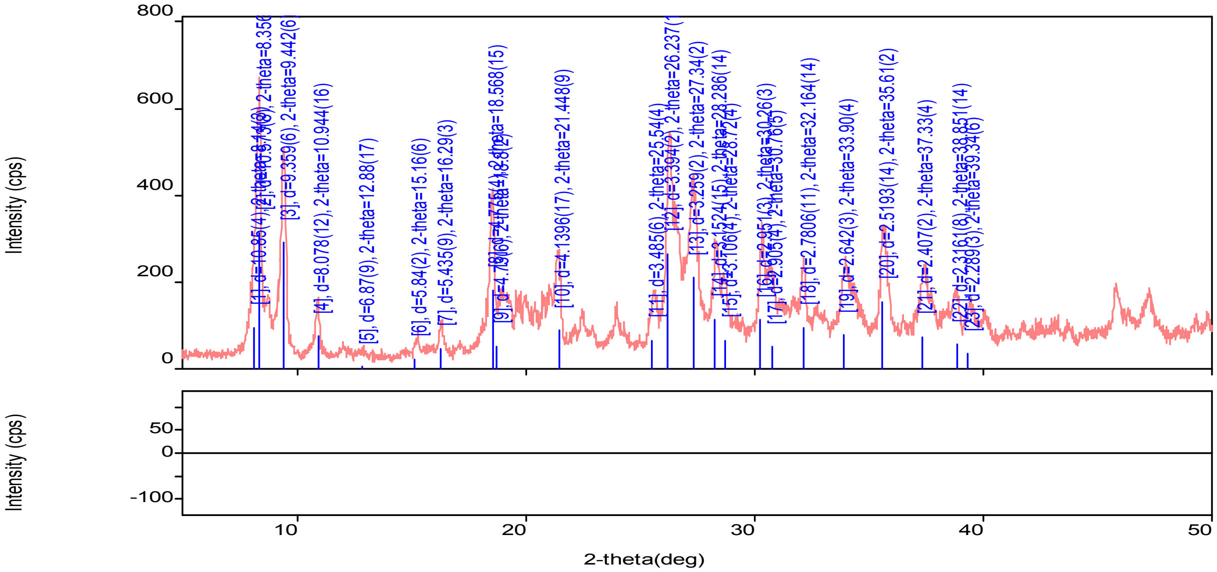
2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phase name
8.245(12)	10.715(16)	167(13)	81(3)	0.315(15)	264(13)	Unkno
9.370(11)	9.431(11)	159(13)	95(3)	0.385(17)	216(10)	Unkno
10.84(3)	8.16(2)	37(6)	11.6(14)	0.29(3)	291(29)	Unkno
18.30(3)	4.844(8)	61(8)	32(2)	0.40(4)	210(20)	Unkno
21.23(2)	4.182(4)	45(7)	60(4)	0.88(7)	96(8)	Unkno
26.32(4)	3.383(5)	129(11)	131(8)	0.95(7)	89(6)	Unkno
27.18(3)	3.278(4)	128(11)	78(8)	0.57(6)	150(15)	Unkno
28.16(4)	3.166(4)	85(9)	60(3)	0.66(4)	129(8)	Unkno
29.9(4)	2.98(4)	17(4)	44(4)	2.4(6)	36(9)	Unkno
33.74(7)	2.654(5)	37(6)	20(2)	0.52(6)	166(19)	Unkno
35.41(3)	2.533(2)	76(9)	28.4(17)	0.35(3)	248(18)	Unkno
37.25(5)	2.412(3)	41(6)	24(3)	0.56(5)	158(15)	Unkno
38.76(18)	2.321(10)	21(5)	36(3)	1.64(18)	54(6)	Unkno
47.14(9)	1.926(4)	30(5)	50(4)	1.56(10)	58(4)	Unkno

Analysis Results

General Information

Analysis date	12/21/2011 4:02:16 PM		
Sample name	XRD Analysis	Measured time	12/7/2011 9:44:14 AM
File name	1-Sample 10%.raw	Operator	administrator
Comment	FKKSA		

Measurement profile



Measurement Condition

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	5-50 deg
Incident monochromator	-	Incident slit	-
Receiving monochromator	-	Vertical divergence slit	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

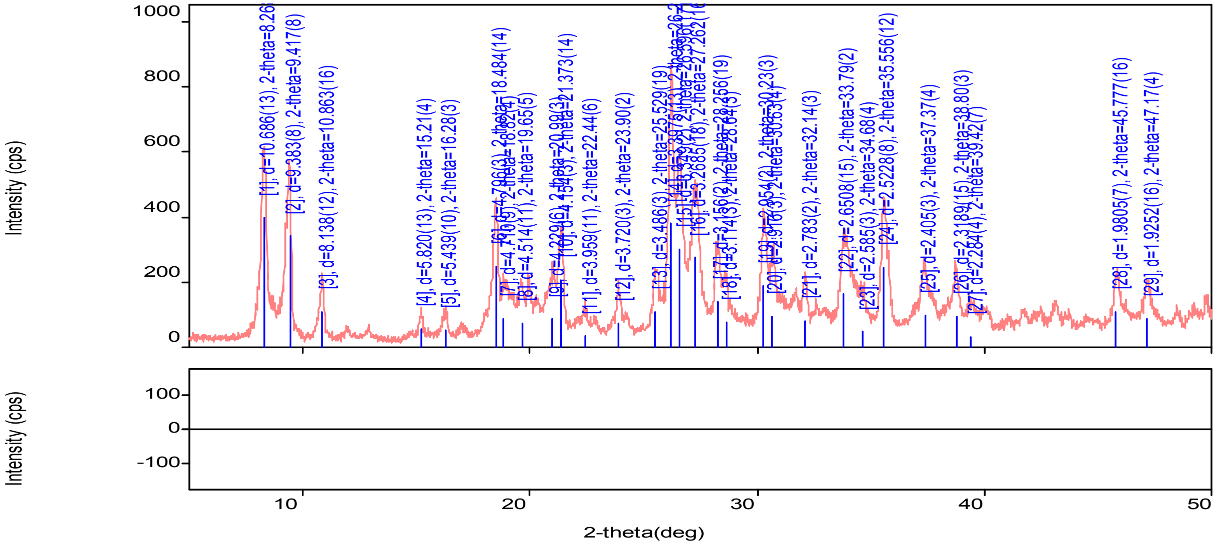
2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phase name
8.14(3)	10.85(4)	95(10)	111(4)	1.05(6)	79(4)	Unknow
8.356(7)	10.573(8)	314(18)	75(3)	0.211(8)	395(14)	Unknow
9.442(6)	9.359(6)	290(17)	82(3)	0.249(6)	334(8)	Unknow
10.944(16)	8.078(12)	75(9)	18.7(11)	0.223(14)	374(23)	Unknow
12.88(17)	6.87(9)	5(2)	5.6(11)	1.0(2)	88(21)	Unknow
15.16(6)	5.84(2)	22(5)	12.6(19)	0.39(9)	214(51)	Unknow
16.29(3)	5.435(9)	46(7)	10.2(10)	0.19(2)	442(53)	Unknow
18.568(15)	4.775(4)	182(14)	39(2)	0.199(12)	422(26)	Unknow
18.8(2)	4.73(6)	52(7)	98(5)	1.79(11)	47(3)	Unknow
21.448(9)	4.1396(17)	88(9)	49(3)	0.52(3)	161(10)	Unknow
25.54(4)	3.485(6)	66(8)	38(6)	0.47(8)	182(31)	Unknow
26.237(17)	3.394(2)	265(16)	183(9)	0.56(3)	153(7)	Unknow
27.34(2)	3.259(2)	210(14)	101(7)	0.42(2)	204(12)	Unknow
28.286(14)	3.1524(15)	114(11)	26.3(18)	0.173(17)	496(48)	Unknow
28.72(4)	3.106(4)	65(8)	38(5)	0.54(6)	160(18)	Unknow
30.26(3)	2.951(3)	113(11)	88(6)	0.52(9)	165(27)	Unknow
30.76(5)	2.905(4)	51(7)	5(4)	0.08(8)	1025(918)	Unknow
32.164(14)	2.7806(11)	95(10)	23.7(15)	0.170(18)	507(54)	Unknow
33.90(4)	2.642(3)	77(9)	45(3)	0.55(3)	158(9)	Unknow
35.61(2)	2.5193(14)	155(12)	49(2)	0.299(15)	292(14)	Unknow
37.33(4)	2.407(2)	73(9)	44(2)	0.57(3)	155(9)	Unknow
38.851(14)	2.3161(8)	56(7)	30(3)	0.46(4)	190(19)	Unknow
39.34(6)	2.289(3)	35(6)	27(3)	0.53(9)	167(30)	Unknow

Analysis Results

General Information

Analysis date	12/21/2011 4:29:31 PM		
Sample name	XRD Analysis	Measured time	12/7/2011 10:56:21 AM
File name	1-Sample 15%.raw	Operator	administrator
Comment	FKKSA		

Measurement profil



Measurement Condition

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	5-50 deg
Incident monochromator	-	Incident slit	-
Receiving monochromator	-	Vertical divergence slit	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

Peak List

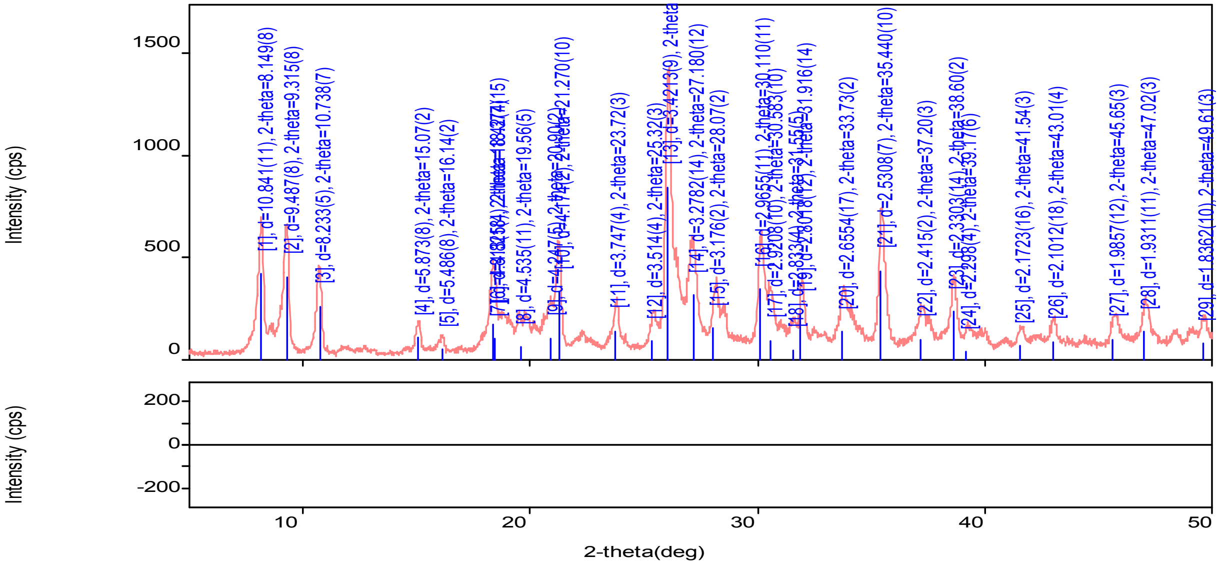
2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phase name
8.268(10)	10.686(13)	397(20)	151(4)	0.252(11)	330(15)	Unknow
9.417(8)	9.383(8)	341(18)	125(3)	0.241(13)	345(18)	Unknow
10.863(16)	8.138(12)	109(10)	28.3(15)	0.239(13)	349(19)	Unknow
15.21(4)	5.820(13)	57(8)	13.7(12)	0.16(3)	515(104)	Unknow
16.28(3)	5.439(10)	53(7)	17.8(14)	0.25(3)	338(43)	Unknow
18.484(14)	4.796(3)	249(16)	81(5)	0.255(15)	330(19)	Unknow
18.82(4)	4.710(9)	88(9)	45(9)	0.45(8)	189(32)	Unknow
19.65(5)	4.514(11)	74(9)	75(10)	0.84(10)	100(12)	Unknow
20.99(3)	4.229(6)	87(9)	45(6)	0.39(5)	218(26)	Unknow
21.373(14)	4.154(3)	208(14)	67(6)	0.25(2)	340(31)	Unknow
22.44(6)	3.959(11)	34(6)	14.8(15)	0.28(6)	306(71)	Unknow
23.90(2)	3.720(3)	74(9)	24.2(17)	0.26(2)	332(29)	Unknow
25.529(19)	3.486(3)	110(10)	36(3)	0.28(2)	304(22)	Unknow
26.208(10)	3.3975(13)	380(19)	76(5)	0.178(10)	479(27)	Unknow
26.596(17)	3.349(2)	302(17)	206(7)	0.61(2)	140(5)	Unknow
27.262(16)	3.2685(18)	275(17)	139(4)	0.439(17)	194(7)	Unknow
28.256(19)	3.156(2)	141(12)	34(8)	0.21(3)	398(49)	Unknow
28.64(3)	3.114(3)	78(9)	28(8)	0.33(11)	261(88)	Unknow
30.23(3)	2.954(2)	190(14)	89(9)	0.34(4)	250(26)	Unknow
30.63(4)	2.916(3)	96(10)	24(6)	0.18(6)	478(150)	Unknow
32.14(3)	2.783(2)	82(9)	15.2(15)	0.17(2)	496(70)	Unknow
33.79(2)	2.6508(15)	163(13)	85(13)	0.48(6)	181(23)	Unknow
34.68(4)	2.585(3)	48(7)	21(13)	0.4(2)	214(126)	Unknow
35.556(12)	2.5228(8)	246(16)	81(2)	0.309(9)	282(8)	Unknow
37.37(4)	2.405(3)	98(10)	66(3)	0.51(4)	171(15)	Unknow
38.80(3)	2.3189(15)	95(10)	37(3)	0.34(3)	261(23)	Unknow
39.42(7)	2.284(4)	33(6)	13(2)	0.31(8)	284(71)	Unknow
45.777(16)	1.9805(7)	109(10)	42.7(16)	0.285(16)	316(17)	Unknow

Analysis Results

General Information

Analysis date	12/21/2011 4:32:23 PM		
Sample name	XRD Analysis	Measured time	12/7/2011 3:49:46 PM
File name	1-Sample 25%.raw	Operator	administrator
Comment	FKKSA		

Measurement profil



Measurement Condition

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	5-50 deg
Incident monochromator	-	Incident slit	-
Receiving monochromator	-	Vertical divergence slit	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

Peak List

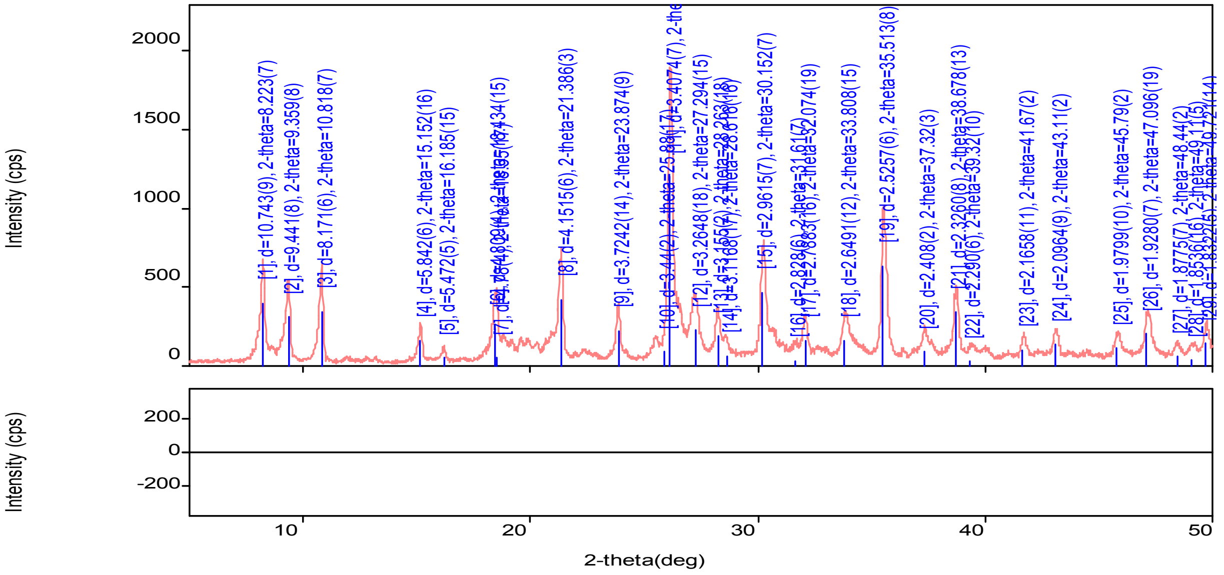
2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phasename
8.149(8)	10.841(11)	419(20)	160(3)	0.280(10)	297(10)	Unknown,
9.315(8)	9.487(8)	404(20)	175(3)	0.284(9)	293(10)	Unknown,
10.738(7)	8.233(5)	260(16)	73.6(19)	0.261(6)	319(8)	Unknown,
15.07(2)	5.873(8)	108(10)	35.7(14)	0.21(2)	390(36)	Unknown,
16.14(2)	5.486(8)	50(7)	17.3(13)	0.25(3)	330(37)	Unknown,
18.374(15)	4.825(4)	173(13)	41(4)	0.215(18)	391(33)	Unknown,
18.42(7)	4.813(18)	103(10)	135(7)	1.18(8)	71(5)	Unknown,
19.56(5)	4.535(11)	63(8)	58(8)	0.83(12)	102(14)	Unknown,
20.90(2)	4.247(5)	104(10)	41(5)	0.37(3)	228(20)	Unknown,
21.270(10)	4.174(2)	332(18)	98(5)	0.272(14)	311(15)	Unknown,
23.72(3)	3.747(4)	140(12)	44(3)	0.26(2)	330(31)	Unknown,
25.32(3)	3.514(4)	90(9)	63(9)	0.46(8)	184(31)	Unknown,
26.022(7)	3.4213(9)	845(29)	406(9)	0.328(9)	260(7)	Unknown,
27.180(12)	3.2782(14)	315(18)	161(6)	0.382(17)	223(10)	Unknown,
28.07(2)	3.176(2)	153(12)	79(3)	0.481(17)	178(6)	Unknown,
30.110(11)	2.9655(11)	346(19)	177(8)	0.352(19)	244(13)	Unknown,
30.583(10)	2.9208(10)	94(10)	30(6)	0.23(4)	379(73)	Unknown,
31.55(5)	2.833(4)	48(7)	18(4)	0.28(10)	303(110)	Unknown,
31.916(14)	2.8018(12)	221(15)	50(5)	0.172(16)	502(48)	Unknown,
33.73(2)	2.6554(17)	137(12)	87(3)	0.60(2)	145(5)	Unknown,
35.440(10)	2.5308(7)	433(21)	138(3)	0.299(7)	292(7)	Unknown,
37.20(3)	2.415(2)	99(10)	57(3)	0.51(3)	172(9)	Unknown,
38.60(2)	2.3303(14)	235(15)	76(4)	0.24(2)	373(38)	Unknown,
39.17(6)	2.298(4)	38(6)	25(3)	0.52(10)	168(31)	Unknown,
41.54(3)	2.1723(16)	68(8)	18.2(17)	0.17(5)	521(149)	Unknown,
43.01(4)	2.1012(18)	87(9)	28(2)	0.24(4)	364(58)	Unknown,
45.65(3)	1.9857(12)	100(10)	44(2)	0.32(4)	284(32)	Unknown,
47.02(3)	1.9311(11)	137(12)	50(3)	0.31(3)	296(25)	Unknown,
49.61(3)	1.8362(10)	79(9)	16(2)	0.17(4)	549(122)	Unknown,

Analysis Results

General Information

Analysis date	12/21/2011 4:36:57 PM		
Sample name	XRD Analysis	Measured time	12/7/2011 2:55:41 PM
File name	1-Sample 40%.raw	Operator	administrator
Comment	FKKSA		

Measurement profile



Measurement Contiditon

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	5-50 deg
Incident monochromator	-	Incident slit	-
Receiving monochromator	-	Vertical divergence slit	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

Peak List

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phase name
8.223(7)	10.743(9)	396(20)	131(3)	0.231(8)	360(13)	Unknow
9.359(8)	9.441(8)	309(18)	114(3)	0.252(9)	330(12)	Unknow
10.818(7)	8.171(6)	343(19)	91(2)	0.230(7)	363(11)	Unknow
15.152(16)	5.842(6)	161(13)	44.6(14)	0.185(14)	452(35)	Unknow
16.185(15)	5.472(5)	50(7)	15.8(9)	0.230(17)	365(27)	Unknow
18.434(15)	4.809(4)	237(15)	60(4)	0.190(16)	443(37)	Unknow
18.55(17)	4.78(4)	53(7)	102(7)	1.47(14)	57(5)	Unknow
21.386(3)	4.1515(6)	422(21)	127(5)	0.222(12)	380(21)	Unknow
23.874(9)	3.7242(14)	223(15)	55.5(19)	0.203(9)	418(18)	Unknow
25.88(17)	3.44(2)	91(10)	160(16)	1.27(12)	67(6)	Unknow
26.131(5)	3.4074(7)	1199(35)	346(8)	0.216(5)	394(10)	Unknow
27.294(15)	3.2648(18)	228(15)	101(6)	0.37(2)	229(13)	Unknow
28.263(18)	3.155(2)	189(14)	42(7)	0.19(2)	451(53)	Unknow
28.616(16)	3.1168(17)	63(8)	19(7)	0.26(10)	331(126)	Unknow
30.152(7)	2.9615(7)	467(22)	154(4)	0.251(10)	343(13)	Unknow
31.61(7)	2.828(6)	31(6)	6(2)	0.17(8)	513(252)	Unknow
32.074(19)	2.7883(16)	161(13)	35(4)	0.193(15)	448(35)	Unknow
33.808(15)	2.6491(12)	163(13)	83(3)	0.364(16)	238(11)	Unknow
35.513(8)	2.5257(6)	632(25)	169(4)	0.248(6)	351(8)	Unknow
37.32(3)	2.408(2)	89(9)	46(3)	0.41(3)	211(15)	Unknow
38.678(13)	2.3260(8)	339(18)	89(2)	0.196(14)	449(31)	Unknow
39.32(10)	2.290(6)	29(5)	16(3)	0.50(9)	175(32)	Unknow
41.67(2)	2.1658(11)	99(10)	20.8(13)	0.189(17)	469(43)	Unknow
43.11(2)	2.0964(9)	136(12)	34.2(16)	0.20(2)	456(46)	Unknow
45.79(2)	1.9799(10)	111(11)	36.5(14)	0.25(3)	359(39)	Unknow
47.096(19)	1.9280(7)	203(14)	69(3)	0.27(2)	333(25)	Unknow
48.44(2)	1.8775(7)	59(8)	9.8(9)	0.16(2)	585(81)	Unknow
49.11(5)	1.8536(16)	38(6)	7.9(11)	0.19(4)	469(105)	Unknow
49.721(14)	1.8322(5)	142(12)	27.2(15)	0.189(15)	508(41)	Unknow

APPENDIX G

Equation and Calculation for Conversion

$M1 \; x \; V1 = M2 \; x \; V2$

M1= molar concentration of Acid (mol/L)

M2= molar concentration of NaOH (mol/L)

$M1 = \frac{M2 \; x \; V2}{V1}$

V1= volume of Acid (mol/L)

V2= volume of NaOH (mol/L)

$$a = \frac{V \; 1000 \; Mw \; C}{W}$$

V = volume of solution employed for titration (ml)

Mw = molecular weight of the solution (g/mol)

C = concentration sample measured by titration (mol/L)

W = weight of the sample (mg)

$$X = \frac{ai - at}{ai}$$

X = conversion of Oleic Acid

ai = initial acidity of mixture

at = acidity at a “t” time

A.1- Ratio catalyst (5, 10, 15, 25, 40, 60 wt%), 60°C, 4hr

(a)0 wt% of catalyst ratio:

$$M1i = \frac{(0.1\ x\ 0.0181)}{0.0261}$$

= 0.069 mol/L

$$ai = \frac{(18.1\ x\ 1000\ x\ 40\ x\ 0.069)}{18070}$$

= 2.76

$$M1t = \frac{(0.1\ x\ 0.0161)}{0.0261}$$

= 0.062 mol/L

$$at = \frac{(16.1\ x\ 1000\ x\ 40\ x\ 0.062)}{18070}$$

= 2.21

$$X = \frac{2.76 - 2.21}{2.76}\ x\ 100\%$$

= 20%

(b) 5 wt% of catalyst ratio:

$$M1i = \frac{(0.1\ x\ 0.0201)}{0.026}$$

= 0.08 mol/L

$$ai = \frac{(20.1\ x\ 1000\ x\ 40\ x\ 0.08)}{18064}$$

= 3.56

$$M1t = \frac{(0.1\ x\ 0.0162)}{0.026}$$

= 0.06 mol/L

$$at = \frac{(16.2\ x\ 1000\ x\ 40\ x\ 0.06)}{18064}$$

= 2.15

$$X = \frac{3.56 - 2.15}{3.56}\ x\ 100\%$$

= 39%

(c) 10 wt% of catalyst ratio:

$$M1i = \frac{0.1\ x\ 0.0238}{0.0265}$$

= 0.09 mol/L

$$ai = \frac{23.8\ x\ 1000\ x\ 40\ x\ 0.09}{19058}$$

= 4.50

$$M1t = \frac{0.1\ x\ 0.0163}{0.0265}$$

= 0.062 mol/L

$$at = \frac{16.3\ x\ 1000\ x\ 40\ x\ 0.062}{19058}$$

= 2.12

$$X = \frac{4.50 - 2.12}{4.50}\ x\ 100\%$$

= 53%

(d) 15 wt% of catalyst ratio:

$$M1i = \frac{0.1\ x\ 0.0252}{0.0282}$$

= 0.09 mol/L

$$ai = \frac{25.2\ x\ 1000\ x\ 40\ x\ 0.09}{22060}$$

= 4.11

$$M1t = \frac{0.1\ x\ 0.0137}{0.0282}$$

= 0.05 mol/L

$$at = \frac{13.7\ x\ 1000\ x\ 40\ x\ 0.05}{22060}$$

= 1.24

$$X = \frac{4.11 - 1.24}{4.11}\ x\ 100\%$$

= 70%

(e) 25 wt% of catalyst ratio:

$$M1i = \frac{0.1\ x\ 0.0263}{0.029}$$

= 0.09 mol/L

$$ai = \frac{26.3\ x\ 1000\ x\ 40\ x\ 0.09}{25084}$$

= 3.77

$$M1t = \frac{0.1\ x\ 0.0125}{0.029}$$

= 0.04 mol/L

$$at = \frac{12.5\ x\ 1000\ x\ 40\ x\ 0.04}{25084}$$

= 0.80

$$X = \frac{3.77 - 0.80}{3.77}\ x\ 100\%$$

= 79%

(f) 40 wt% of catalyst ratio:

$$M1i = \frac{0.1\ x\ 0.0269}{0.0301}$$

= 0.09 mol/L

$$ai = \frac{26.9\ x\ 1000\ x\ 40\ x\ 0.09}{26011}$$

= 3.72

$$M1t = \frac{0.1\ x\ 0.0124}{0.0301}$$

= 0.04 mol/L

$$at = \frac{12.4\ x\ 1000\ x\ 40\ x\ 0.04}{26011}$$

= 0.76

$$X = \frac{3.72 - 0.76}{3.72}\ x\ 100\%$$

= 80%

(g) 60 wt% of catalyst ratio:

$$M1i = \frac{0.1\ x\ 0.0274}{0.0323}$$

= 0.085 mol/L

$$ai = \frac{27.4\ x\ 1000\ x\ 40\ x\ 0.085}{26823}$$

= 3.47

$$M1t = \frac{0.1\ x\ 0.0119}{0.0323}$$

= 0.037 mol/L

$$at = \frac{11.9\ x\ 1000\ x\ 40\ x\ 0.037}{26823}$$

= 0.66

$$X = \frac{3.47 - 0.66}{3.47}\ x\ 100\%$$

= 81%

A.2- Catalyst Ratio (25 wt%), 4hr:

(a) 55°C:

$$M1i = \frac{0.1\ x\ 0.019}{0.028}$$

= 0.068 mol/L

$$ai = \frac{19.0\ x\ 1000\ x\ 40\ x\ 0.068}{24242}$$

= 2.13

$$M1t = \frac{0.1\ x\ 0.0103}{0.028}$$

= 0.037 mol/L

$$at = \frac{10.3\ x\ 1000\ x\ 40\ x\ 0.037}{24242}$$

= 0.63

$$X = \frac{2.13 - 0.63}{2.13}\ x\ 100\%$$

= 70%

(b) 60°C:

$$M1i = \frac{0.1\ x\ 0.0263}{0.029}$$

= 0.09 mol/L

$$ai = \frac{26.3\ x\ 1000\ x\ 40\ x\ 0.09}{25084}$$

= 3.77

$$M1t = \frac{0.1\ x\ 0.0125}{0.029}$$

= 0.04 mol/L

$$at = \frac{12.5\ x\ 1000\ x\ 40\ x\ 0.04}{25084}$$

= 0.80

$$X = \frac{3.77 - 0.80}{3.77}\ x\ 100\%$$

= 79%

(c) 70°C:

$$M1i = \frac{0.1\ x\ 0.0263}{0.030}$$

= 0.088 mol/L

$$ai = \frac{26.3\ x\ 1000\ x\ 40\ x\ 0.088}{25842}$$

= 3.58

$$M1t = \frac{0.1\ x\ 0.0118}{0.030}$$

= 0.039 mol/L

$$at = \frac{11.8\ x\ 1000\ x\ 40\ x\ 0.039}{25842}$$

= 0.71

$$X = \frac{3.58 - 0.71}{3.58}\ x\ 100\%$$

= 80%

A.3- Catalyst Ratio (25 wt%), 60°C

(a) 1 hour:

$$M1i = \frac{0.1 \ x \ 0.0125}{0.010}$$

= 0.125 mol/L

$$ai = \frac{12.5 \ x \ 1000 \ x \ 40 \ x \ 0.125}{8924}$$

= 7.00

$$M1t = \frac{0.1 \ x \ 0.0108}{0.010}$$

= 0.108 mol/L

$$at = \frac{10.8 \ x \ 1000 \ x \ 40 \ x \ 0.108}{8924}$$

= 5.23

$$X = \frac{7.00 - 5.23}{7.00} \ x \ 100\%$$

= 25%

(b) 2 hour:

$$M1i = \frac{0.1\ x\ 0.0155}{0.010}$$

= 0.155 mol/L

$$ai = \frac{15.5\ x\ 1000\ x\ 40\ x\ 0.155}{8940}$$

= 10.75

$$M1t = \frac{0.1\ x\ 0.0120}{0.010}$$

= 0.120 mol/L

$$at = \frac{12.0\ x\ 1000\ x\ 40\ x\ 0.120}{8940}$$

= 6.44

$$X = \frac{10.75 - 6.44}{10.75}\ x\ 100\%$$

= 40%

(c) 3 hour:

$$M1i = \frac{0.1\ x\ 0.0176}{0.010}$$

= 0.176 mol/L

$$ai = \frac{17.6\ x\ 1000\ x\ 40\ x\ 0.176}{8946}$$

= 13.85

$$M1t = \frac{0.1\ x\ 0.0114}{0.010}$$

= 0.114 mol/L

$$at = \frac{11.4\ x\ 1000\ x\ 40\ x\ 0.114}{8946}$$

= 5.81

$$X = \frac{13.85 - 5.81}{13.85}\ x\ 100\%$$

= 58%

(d) 4 hour:

$$M1i = \frac{0.1\ x\ 0.0208}{0.010}$$

= 0.208 mol/L

$$ai = \frac{20.8\ x\ 1000\ x\ 40\ x\ 0.208}{8947}$$

= 19.34

$$M1t = \frac{0.1\ x\ 0.0092}{0.010}$$

= 0.092 mol/L

$$at = \frac{9.2\ x\ 1000\ x\ 40\ x\ 0.092}{8947}$$

= 3.78

$$X = \frac{19.34 - 3.78}{19.34}\ x\ 100\%$$

= 80%

(e) 5 hour:

$$M1i = \frac{0.1\ x\ 0.0243}{0.010}$$

= 0.243 mol/L

$$ai = \frac{24.3\ x\ 1000\ x\ 40\ x\ 0.243}{8946}$$

= 26.40

$$M1t = \frac{0.1\ x\ 0.0103}{0.010}$$

= 0.103 mol/L

$$at = \frac{10.3\ x\ 1000\ x\ 40\ x\ 0.103}{8946}$$

= 4.74

$$X = \frac{26.40 - 4.74}{26.40}\ x\ 100\%$$

= 82%

(f) 6 hour:

$$M1i = \frac{0.1\ x\ 0.026}{0.010}$$

$= 0.260$ mol/L

$$ai = \frac{26.0\ x\ 1000\ x\ 40\ x\ 0.260}{8946}$$

$= 30.23$

$$M1t = \frac{0.1\ x\ 0.0105}{0.010}$$

$= 0.105$ mol/L

$$at = \frac{10.5\ x\ 1000\ x\ 40\ x\ 0.105}{8946}$$

$= 4.93$

$$X = \frac{30.23 - 4.93}{30.23}\ x\ 100\%$$

$= 84\%$

Table A.1: Data from Experiment for Ratio catalyst (5, 10, 15, 25, 40, 60 wt%), 60°C, 4hr

Catalyst Ratio (wt%)	Product		NaOH		
	Volume of Sample (ml)	Weight of Sample (mg)	Initial Volume (ml)	Final Volume (ml)	**Conversion, X (%)**
0	26.1	18070	16.1	18.1	20
5	26.0	18064	16.2	20.1	39
10	26.5	19058	16.3	23.8	53
15	28.2	22060	13.7	25.2	70
25	29.0	25084	12.5	26.3	79
40	30.1	26011	12.4	26.9	80
60	32.3	26823	11.9	27.4	81

Table A.2: Data from Experiment for Catalyst Ratio (25 wt%), 4hr

Temperature (°C)	Product		NaOH		
	Volume of Sample (ml)	Weight of Sample (mg)	Initial Volume (ml)	Final Volume (ml)	**Conversion, X (%)**
55	28	24242	10.3	19.0	70
60	29	25084	12.5	26.3	79
70	30	25842	11.8	26.3	80

Table A.3: Data from Experiment for Catalyst Ratio (25 wt%), 60°C

Time (hr)	Product		NaOH		**Conversion, X (%)**
	Volume of Sample (ml)	Weight of Sample (mg)	Initial Volume (ml)	Final Volume (ml)	
1	10	8924	10.8	2.5	25
2	10	8940	12.0	15.5	40
3	10	8946	11.4	17.6	58
4	10	8947	9.2	20.8	80
5	10	8946	10.3	24.3	82
6	10	8946	10.5	26.0	84

APPENDIX H

Scherrer's equation:

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

K is the shape factor,

λ is the x-ray wavelength,

β is the line broadening at half the maximum intensity (FWHM) in radians,

θ is the Bragg angle,

τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size.

E1. Crystalline size for 2θ = 25.3°:

(a) 5%H_3PW/Al_2O_3

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

$$= \frac{0.94\ x\ 1}{0.017\ x \cos 12.65}$$

= 56.7 nm

(b) 10%H_3PW/Al_2O_3

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$

$$= \frac{0.94\ x\ 1}{4.35x10\hat{}-3\ x\cos 12.65}$$

= 89.2 nm

(c) 15%H_3PW/Al_2O_3

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$

$$= \frac{0.94\ x\ 1}{0.0106\ x\cos 12.65}$$

= 90.9 nm

(d) 25%H_3PW/Al_2O_3

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$

$$= \frac{0.94\ x\ 1}{0.00572\ x\cos 12.65}$$

= 168.4nm

(d) 40%H_3PW/Al_2O_3

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$

$$= \frac{0.94\ x\ 1}{0.00377\ x \cos 12.65}$$

= 255.5 nm