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"I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in term of scope and quality for the award of the degree of Bachelor of Chemical Engineering".

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STUDENT'S DECLARATION

I declare that this report is the result of my own work except as cited in the references and summaries which have been duly acknowledged.

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CATALYTIC WET AIR OXIDATION OF WASTEWATER CONTAINING
ACETIC ACID

by

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Special Dedication to:

My father, Tan Hui Chin,

My mother, Ivy Gan,

My beloved sister and family members,

My supervisor, Dr. Chin Sim Yee

My fellow Lecturers,

My friends

For all your never ending concern, support and faith in me.

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LIST OF ABBREVIATIONS

BET	Brunauer, Emmett and Teller
CWAO	Catalytic Wet Air Oxidation
GC	Gas Chromatography
TOC	Total Organic Carbon
WAO	Wet Air Oxidation
XRD	X–ray Diffraction

PEMANGKIN PENGOKSIDAAN UDARA BASAH AIR SISA MENGANDUNGI ASID ASETIK

ABSTRAK

Air sisa mengandungi asid asetik telah lama dihasilkan oleh industri kimia. Pelupusan sisa ini yang tidak betul telah menjadi masalah yang besar kerana sisa tersebut mencemarkan alam sekitar dan memusnahkan ekosistem akua. Air sisa ini harus dirawat sebelum dilepaskan kea lam sekitar. Antara kaedah rawatan termasuk penggunaan membran dan pengoksidaan udara basah. Kaedah ini mempunyai beberapa batasan. Proses membran terhad oleh kestabilan pelarut dan kestabilan terma dan pengoksidaan udara basah hanya berkesan pada keadaan operasi yang tinggi. Dalam kajian ini, pemangkin pengoksidaan udara basah adalah kaedah yang dicadangkan untuk rawatan. Pemangkin telah disintesis berdasarkan kepada kaedah kebasahan. Eksperimen telah dijalankan dengan mengoksidakan air kumbahan simulasi mengandungi asid asetik dalam reaktor berkelompok. Kajian tindak balas diulangi dengan manipulasi dua operasi parameter yang berbeza. Sampel telah dianalisis menggunakan analisis Jumlah Karbon Organik dan Kromatografi Gas. Pemangkin dicirikan oleh analisis Pembelauan Sinar X dan analisis *Physisorption (BET Method)*. Pemangkin pengoksidaan udara basah menghasilkan penukaran tertinggi pada suhu 80°C. Pemangkin yang mempunyai kawasan permukaan tinggi telah disahkan oleh analisis Pembelauan Sinar X dan *Physisorption*. Penukaran menggunakan pemangkin pengoksidaan udara basah adalah lebih tinggi daripada proses lain seperti yang diramalkan. Kehadiran pemangkin mengurangkan keterukan keadaan operasi dan juga meningkat kadar penukaran.

CATALYTIC WET AIR OXIDATION OF WASTEWATER CONTAINING ACETIC ACID

ABSTRACT

Wastewater containing acetic acid has long been produced by the chemical industry. Improper disposal of the wastewater has become a major problem as it pollutes the environment and destroys aquatic ecosystem. The wastewater has to be treated before it can be released into the environment. Some of the treatment methods include membrane processes and wet air oxidation (WAO). These treatment methods have a few limitations. Membrane processes are limited by their solvent and thermal stability and WAO is only effective at severe operating conditions. In this research, catalytic wet air oxidation (CWAO) is the proposed method for treatment. The catalyst was synthesized according to the wetness method. The experiment was conducted by oxidizing simulated wastewater containing acetic acid in a batch reactor. The reaction study was repeated with the manipulation of two different operating parameters. The sample was analysed using Total Organic Content (TOC) analysis and Gas Chromatography (GC). The catalyst was characterized by X-ray diffraction (XRD) and Physisorption analysis (BET Method). CWAO yielded the highest conversion at the temperature of 80°C. The catalyst with high surface area was confirmed by XRD and BET. The conversion using CWAO was higher than other processes as predicted. The presence of the catalyst reduced the severity of the operating conditions and also increased the conversion rate.

CHAPTER 1

INTRODUCTION

1.1 Background of the Proposed Study

Industrial processes normally produce wastewater and this industrial wastewater is dangerous to be released into the environment. Some wastewater has higher concentration of certain chemicals while some are more dilute. Organic chemicals such as acetic acid are normally found in dilute industrial wastewater. There are many industries that produce wastewater containing acetic acid. Among these industries are the pharmaceutical industry, food and beverage industry (Kumar and Babu, 2008) and polymer manufacturing industry (Shin et al., 2009). Acetic acid is a weak acid and dilute wastewater containing acetic acid is harmful to the environment as it can contaminate and destroy the aquatic ecosystem. Therefore, industrial wastewater must be treated before being released into the environment. By removing the acetic acid from the wastewater, we can, on one hand make full use of our limited resources, and on the other, protect our environment (Yu et al., 2000).

Many methods have been utilized over the years to recover or remove acetic acid from the wastewater. Simple separation techniques such as liquid–liquid extraction, adsorption and distillation have proven to be ineffective (Kumar and Babu, 2008). More advanced methods such as membrane and oxidation methods are more widely used. One of the methods used to remove acetic acid is through wet air oxidation (WAO). WAO is an oxidation process that oxidizes dissolvable or suspended organic compounds as well as reducible inorganic compounds with oxygen or air under the circumstances of high temperature and high pressure in liquid phase. Catalytic wet air oxidation (CWAO) was a new technology developed on the basis of WAO in the 1970s (Zhu et al., 2002). The usage of catalyst can reduce the limitations of WAO by reducing the operating temperature, pressure and also reduce the reaction time.

Previous methods of treatment such as WAO proved ineffective as WAO has limited application due to the conditions of the process; high temperature, pressure and long reaction time (Mikulová et al., 2007). Membrane processes has limited solvent stability (Wee et al., 2008), thermal stability and are prone to fouling (Kumar and Babu, 2008). This indirectly increases the cost of the process. Hence, CWAO is a promising method and catalysts with high activity are needed to ensure higher conversion and a more effective way to remove acetic acid.

1.2 Research Objectives

The objectives of the present study are:

a)   To synthesize and characterize the ruthenium oxide on zirconium oxide and cerium oxide support (RuO_2/ZrO_2-CeO_2) catalyst.

b)   To examine the activity of the synthesized catalyst in the catalytic wet air oxidation of wastewater containing acetic acid.

1.3 Scope of the Study

The scopes of this study are the synthesis of RuO_2/ZrO_2-CeO_2 catalyst using the wetness method and determination of the activity of the synthesized catalyst in oxidizing the wastewater containing acetic acid. The important parameters include concentration of acetic acid in the wastewater, temperature and air flow rate. The analysis methods used to determine the acetic acid concentration are Total Organic Carbon (TOC) analysis and Gas Chromatography (GC). For the catalyst characterization, X–ray diffraction (XRD) and Physisorption analysis (BET Method) are conducted.

1.4   Significance of the Study

The significance of the proposed study is to synthesize the catalyst with high activity in oxidizing the wastewater containing acetic acid. The synthesized catalyst can be used in larger scale operations of treatment of wastewater containing acetic acid. Besides that, the treated wastewater can be safely released into the environment and prevent contamination and destruction of the aquatic ecosystem.

CHAPTER 2

LITERATURE REVIEW

This review discusses about industrial wastewater containing acetic acid, treatment methods and their limitations, catalytic wet air oxidation (CWAO) method and the type of catalyst used in CWAO.

2.1 Industrial Wastewater Containing Acetic Acid

A large number of chemical industries produce huge amounts of wastewater containing various amounts of toxic and hazardous organic compounds. A typical organic compound that is present in wastewater is carboxylic acid such as acrylic acid and acetic acid. Detailed analysis shows that acetic acid is the most commonly found organic acid with significant concentration. Acetic acid is not harmful to

humans if it is dilute, however, it is dangerous to the environment as it can contaminate and destroy the aquatic ecosystem.

There are many industries that produce wastewater containing acetic acid. Among these industries are the pharmaceutical industry, polymer manufacturing industry, food and beverage industry. In a research done by Kumar and Babu (2008), stated that acetic acid is most widely used in the field of food and beverages as an acidulant. They also said acetic acid is used in the synthesis of acetyl cellulose and plastics and also in the food industry, as well as in the printing and dyeing industries.

Slaughter house waste and animal by-products contains ammonia and organic residue which include acetic acid. Animal by-products and slaughter house waste are produced daily and must be dealt with to prevent pollution. The acetic acid in in animal by-products can be treated by means of CWAO, as researched by Frontanier et al. in 2010. Another source of acetic acid waste comes from the silicon wafer manufacturing. The acetic acid is in the wafer etching process. Due to a rapid growth of those industries in Korea, the amount of waste acids generated during etching and cleaning processes is increasing rapidly (Shin et al., 2009).

2.2   Treatment Methods

Before wastewater can be released into the environment, it has to be treated until it meets a standard set by the Department of Environment. Many methods have been utilized over the years to recover or remove acetic acid from the wastewater.

Simple separation techniques such as adsorption and distillation have proven to be ineffective. More advanced methods such as membrane and oxidation methods are more widely used.

2.2.1 Adsorption and Distillation

Adsorption and distillation are well known separation methods. These methods are more focused on removing the acetic acid from the water. Adsorption is another good method to remove acetic acid but the cost associated with regeneration of commercial adsorbents makes adsorption operation very expensive (Kumar and Babu, 2008). Distillation has a disadvantage as it is only effective when the concentration of acetic acid in the wastewater is high (Helsel, 1977).

2.2.2 Membrane Processes

Membrane process is an effective method to recover or remove organic contaminants from wastewater. Basically, membrane process is a form of filtration where wastewater goes through a membrane and the contaminants remain and cleaner water is produced. Ultra filtration, reverse osmosis and pervaporation are some the of membrane processes. The choice of the membrane is a key consideration that defines the type of application (Jullok et al., 2011). Normally, the smallest weight fraction of component in the mixture is to be transported across the

membrane: hydrophilic polymeric membranes are used for the dehydration of organic liquids and hydrophobic polymeric membranes for removal of organics from water streams (Kujawski, 2000). However, polymeric membranes have limitations. Polymeric membrane has limited solvent stability (Wee et al., 2008) and thermal stability. Besides that, another problem with membrane process is the membrane fouling which requires frequent cleaning (Kumar and Babu, 2008).

2.2.3   Wet Air Oxidation

Wet air oxidation (WAO) is defined as the liquid phase oxidation of organic compounds at temperatures (125–320°C) and pressures (0.5–20MPa) below the critical point of water using a gaseous source of oxygen (Mishra et al., 1995). WAO process is also defined as a thermochemical process where several active oxygen species, including hydroxyl radicals, are formed at elevated temperatures (i.e. 200–300°C) and pressures (i.e. 2–20MPa) (Katsoni et al., 2008).

This method works on the principles where low molecular weight pollutant molecules such as acetic acid to carbon dioxide and water if the conditions are severe enough. As a general rule, the oxidation rate increases with an increase in molecular weight of the organic acid (Klinghoffer et al., 1998). Although this method is a well-established technique, it has certain limitations. Severe operating conditions, low oxidation rate of low molecular weight compounds and increased equipment and operating costs (Verenich et al., 2000) are some of the limitations.

Several researches using WAO was conducted and investigated. WAO of long-chain carboxylic acids such as caprylic and oleic acids was determine to be effective where conversions of 90% and greater were achieved in 10 minutes (Sánchez-Oneto et al., 2004). As stated previously, to achieve high conversion or oxidation, operating conditions must be severe (Duprez et al., 2003 and Yang et al., 2010).

2.2.4 Catalytic Wet Air Oxidation

Catalytic wet air oxidation (CWAO) is an improvement over the WAO method with the introduction of a catalyst in the reaction. Introduction of a catalyst into the reaction not only reduces the severity of the operating conditions such as temperature (Wang et al., 2008), but also increases the oxidation rate. Homogeneous and heterogeneous can be used in the reaction, but heterogeneous catalyst are preferred because no catalyst recovery step is required (Klinghoffer et al., 1998). This method overcomes the limitations of membrane and WAO techniques.

Many researches compared the efficiency of WAO and CWAO and how the introduction of catalysts improves the oxidation process. Duprez et al. (2003) concluded that CWAO processes, with homogeneous or heterogeneous catalysts, require milder reaction conditions. Yang et al. (2010) investigated the efficiency of WAO and CWAO in oxidizing of complex and high-loaded industrial wastewater and concluded that CWAO is highly efficient for wastewater treatment.

2.3   Catalyst for Wet Air Oxidation

The usage of catalyst in reactions has long been established in the chemical industry. Catalyst can either promote or inhibit a certain reaction. Catalysts that promotes a reaction is called a *promoter* while catalysts that inhibits a reaction is called an *inhibitor*. There are two types of catalyst, homogeneous catalyst and heterogeneous catalyst. Homogeneous catalysts are catalysts that are in the same phase as the reactants while heterogeneous catalysts are of different phase than the reactants (Fogler, 2006). In catalytic wet air oxidation, the type of catalyst used is heterogeneous catalyst. Heterogeneous catalysts are normally solids and are made from metals. Suitable metals that used in the catalyst ranges from metal oxides (Font et al., 1999 and Hung, 2009), transition metals (Gomes et al., 2005) and noble metals (Barbier Jr. et al., 2010 and Wang et al., 2008).

2.3.1   Metal Oxides and Transition Metals

Metal oxides and transition metals have been used as catalyst in catalytic wet air oxidation. The heterogeneous catalyst that have been used are Cu, Pd, CoO/ZnO, Cu:Mn:La oxides on spinal supports (ZnO, Al_2O_3), copper chromite, iron oxide, Co:Bi complex oxides and Mn/Ce (Klinghoffer et. al., 1998, Gomes et al., 2005, Hung, 2009, Arena et al., 2012). Despite having established the effectiveness of these metals as catalyst, they have also been proven to have some flaws. In a research done by Mikulová et al. (2007), partial leaching of metal ions has been

observed during the reaction, and a recovery step is necessary. This additional recovery step will increase the cost of wastewater treatment and this is undesirable.

2.3.2 Noble Metals

Noble metals are a class of metals that are highly resistant to corrosion and oxidation. Supported noble metals (including Pt, Pd, Ru, and Rh) have been proposed for the CWAO (Mikulová et al., 2007, Barbier Jr. et al., 2010, Wang et al., 2008). Activity wise, Imamura et al. (1988) studied the catalytic effect of noble metals on the wet oxidation of phenols and other model pollutant compounds, and found that ruthenium, platinum and rhodium were more active than homogeneous copper catalyst.

2.3.3 Potential Applications of RuO_2/ZrO_2-CeO_2 Catalyst

This section reviews the potential application of the RuO_2/ZrO_2-CeO_2 catalyst in other reaction systems. As this catalyst is used for CWAO of acetic acid wastewater, this review will give a better insight the potential of this catalyst for the CWAO of other types of wastewater.

2.3.3.1 CWAO of Phenolic Compounds

For the treatment of wastewater containing phenolic compounds such as phenol, noble metal catalyst has been proven to work effectively to remove phenol. Research done by Pintar et al. in 2008 shows that Ru/TiO_2 catalyst not only enables complete removal of phenol, but also removed total organic carbon (TOC) without the formation of carbonaceous deposits. Barbier et al. (2005) also demonstrated the activity order of CeO_2 supported noble metals for the CWAO of phenol as follows:

$$Ru/CeO_2 > Pd/CeO_2 > Pt/CeO_2$$

The introduction of ZrO_2 into the CeO_2 increases the mechanical strength, specific surface area and adsorption capacity of the catalyst. When used in CWAO of phenol, phenol and TOC removal stabilized approximately 100% and 96% respectively (Wang et al., 2008). This shows that the RuO_2/ZrO_2-CeO_2 catalyst can be applied to CWAO of phenolic compounds.

2.3.3.2 CWAO of N-Containing Compounds

Nitrogen-containing compounds are normally present in organic waste and are highly toxic as they can cause acidification of the ecosystem. Some nitrogen-containing compounds such as ammonia and aniline can be treated using CWAO. Aniline is a representative compound of N-containing aromatic compounds and is mainly used as a chemical intermediate in the production of polymers, pesticides, pharmaceuticals, and dyes (Ersöz and Atalay, 2010).

Many researchers have utilized ruthenium catalyst in the CWAO of aniline. Barbier et al. (2005) used a Ru/CeO_2 catalyst while Reddy and Mahajani (2005) used a Ru/SiO_2 catalyst in the CWAO of aniline. As ruthenium is applicable as a catalyst for the conversion of aniline, RuO_2/ZrO_2-CeO_2 has great potential in the reaction of aniline as it may improve on the current reaction rate and conditions.

Ammonia is widely used as a chemical in the manufacture of ammonium nitrate, metallurgy, petroleum refineries, etc. It is known as a key intermediate in the oxidation of N-containing compounds and is not amenable to direct biological treatment due to its toxicity (Ihm and Kim, 2011). Barbier et al. (2002) showed that CWAO is a very effective way to removal of ammonia where ammonia is converted in to elemental nitrogen.

Other research also used ruthenium as a catalyst in the oxidation of ammonia. Ru/TiO_2 was used to remove ammonia (Lee et al., 2005) and it was concluded in that research that ruthenium catalyst was responsible for the oxidation of ammonia and does not affect the selectivity of the formation of nitrogen. RuO_2/ZrO_2-CeO_2 catalyst can be researched to see whether it can oxidize ammonia.

In this research, the researcher is using a ruthenium oxide on zirconium oxide and cerium oxide support (RuO_2/ZrO_2-CeO_2) catalyst. The selection of ruthenium as the catalyst is based on its resistance towards sintering by carbonaceous species during CWAO. Therefore, compared to the platinum catalysts, the equivalent ruthenium materials demonstrate higher resistance against poisoning by carbonaceous species during the CWAO experiments (Gaálová et al., 2010). Ruthenium catalyst has more significant activity compared to platinum catalyst and this is proven in a research done by Perkas et al. (2005).

Table 2.1   Catalyst Type and Their Advantages and Disadvantages.

Catalyst Type	Advantage	Disadvantage
Metal Oxides and Transition Metals	Cost of catalyst is cheaper compared to noble metal catalyst	Partial leaching of metal ion and recovery step is needed (Mikulová et al., 2007)
Noble Metals	High activity (Imamura et al., 1988) , resistant to poisoning by carbonaceous species (Gaálová et al., 2010)	Noble metal catalyst is more expensive than metal oxides and transition metal catalysts

2.4   Catalyst Synthesis Methods

There are many methods to synthesize catalyst and many researchers utilize different methods to synthesize their own type of catalyst, specific to their research. The choice of synthesis methods depends on the final catalyst desired, especially its physical and chemical composition. Generally, the methods may contain the same procedure, but the overall method is unique by itself. In a research conducted by Perego and Villa in 1997, they discussed on the catalyst preparation method. Their paper included on the different methods used to prepare catalysts which are bulk catalyst and support preparation and impregnation method, which will be reviewed in the following subtopics.

2.4.1   Bulk Catalyst and Support Preparation

Bulk catalysts are actually the active substance or the active precursors of the catalyst. Examples of bulk catalyst include silica-alumina for hydrocarbon cracking, Zn-Cr oxide for the conversion of CO-H_2 mixtures to methanol and iron-molybdate for methanol oxidation (Perego and Villa, 1997). Bulk catalysts are further divided into two different types of preparation which are precipitation and sol-gel method. Both these methods have similar steps, but the precipitate that forms separates these two methods.

2.4.1.1 Precipitation Method

Bulk catalyst synthesized using the precipitation method is a simple synthesis method where the active substance is precipitated from a liquid solution and is the base for the catalyst itself. Generally, the precipitate contains the active substance and will slowly become the final, desired catalyst as it progresses.
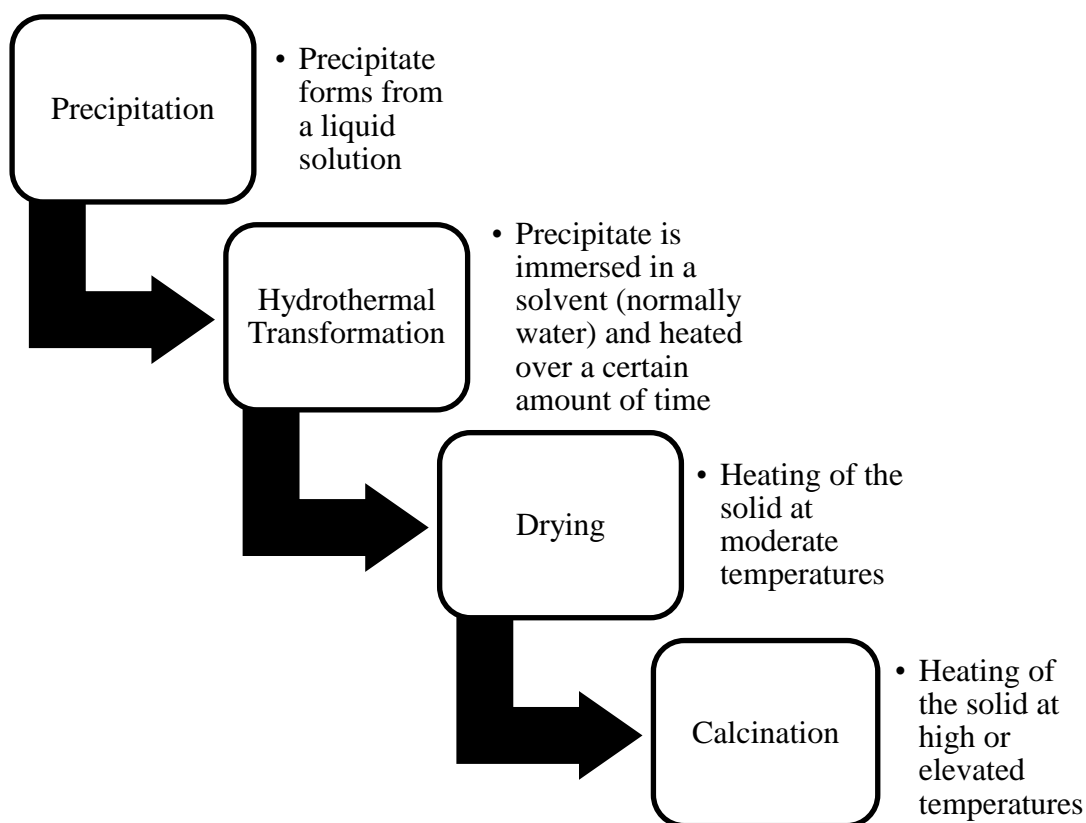
Figure 2.1 General Synthesis Steps for Bulk Catalyst and Support Preparation

Precipitation is the first step and active precursors are normally precipitated from a mixture of metal salts or by pH manipulation. Precipitation is followed by hydrothermal transformation. Hydrothermal transformation is defined as the modification of precipitates, gels or flocculates, induced by temperature, under aging or ripening in the presence of the mother liquor (usually water) (Perego and Villa, 1997). The precipitate is immersed in a solvent and heated at low temperatures, approximately 100 to 300°C.

The next step is drying where the removal of the solvent (usually water) from the solid. The drying does not only remove the solvent from the surface of the solid

but also from the pores of the solid. Finally, the catalyst goes through the calcination step. Calcination is an advanced heat treatment where the previously dried solid is heated at high temperatures. The purpose of calcination is the activation of the catalyst and also the modification of the crystal structure. However, low calcination temperatures may cause poorly crystalline structures (Wang et al., 2008).

Precipitation method was used by Zhu et al. (2002) to synthesize Ce-Cu catalyst in the treatment of H-acid solution. According to Mikulová et al. (2007), CeO_2 support can be prepared via precipitation method. Precipitation method can also be applied to synthesizing $MnCeO_X$ catalyst (Arena et al., 2012).

2.4.1.2 Sol-Gel Method

This method is similar to the precipitation method except for the precipitation step. Instead of a solid precipitate, a gel-like precipitate forms through gelation and flocculation. The following steps are similar to the precipitation method where the sol-gel goes through hydrothermal transformation, drying and calcination. Sol-gel method provides better control of the catalyst surface area, pore volume and pore size distribution.

Sol-gel method differentiates itself from the precipitation method by the way the precipitates form. In precipitation method, the precipitates form based on the solubility concept and it occurs in three steps, supersaturation, nucleation and growth. Supersaturation is generally controlled by temperature and pH whereby manipulating these two parameters the supersaturation region can be achieved.

Precipitating the sol-gel is based on gelation and coagulation/flocculation. Depending on the conditions during the sol-gel formation, two different types of gel may form which are hydrogel and flocculate or gelatinous precipitate.

Sol-gel method has been used to synthesize many different catalysts and supports. Mikulová et al. (2007) synthesized Pt/Ce and Pt/ZrCePr using the sol-gel method. $Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O_2$ support was synthesized using the sol-gel method (Barbier Jr. et al., 2010).

2.4.2 Impregnation Method

The impregnation method is another method used to synthesize catalysts and is also a widely used method. Generally, the support of the catalyst is prepared before the support is immersed into the active precursor. The support may or may not consist of elements that promote the reaction but most supports contain elements that are inert to the reaction. This is due to some elements being leeched as the reaction occurs. Also, supports are generally more resistant to sintering than the active catalyst precursor itself (Perego and Villa, 1997). Support preparation normally follows the precipitation method right up to calcination.

Support selection is crucial and it determines the performance of the catalyst in the reaction. The characteristics which are desirable in the support include:

  i.   inertness

 ii.   mechanical properties (hardness, compressive strength)

iii.   stability (under reaction and regeneration conditions)

iv.   surface area

v.   porosity

vi.   cost

The support is formed from salt solutions and it follows the precipitation method reviewed earlier. However, it must be noted that rapid nucleation and growth in the bulk solution must be avoided since it produces a deposition only outside the support porosity (Perego and Villa, 1997). The formation follows the precipitation method up to the support calcination.

Next, is the impregnation method where the support is contacted with the solution containing the active ingredient. There are three steps for the impregnation which are:

i.   contacting the support with the impregnating solution for a certain period of time

ii.   drying the support to remove the imbibed liquid

iii.   activating the catalyst by calcination, reduction or other appropriate treatment

The impregnation can be conducted in two different and distinctive ways. The first would be the support is contacted in excess solution. The support is dipped into excess solution for a certain period of time for total impregnation. The solid is then drained and dried. The second way would be to contact the support with repeated applications of the solution. The support is contacted with a solution of appropriate concentration, corresponding in quantity to the total known pore volume or slightly less (Satterfield, 1980).

Many catalysts, especially noble metal catalyst are synthesized using impregnation method. Platinum on mesoporous titanium oxide (Pt/TiO_2) catalyst (Perkas et al., 2005) and platinum on alumina monolith (Pt/Al_2O_3) catalyst (Klinghoffer et al., 1998) can be synthesized through impregnation. Wang et al. (2008) synthesized ruthenium catalyst on different supports via impregnation method. Imamura et al. (2003) produced Ru/CeO_2 catalyst using the impregnation method.

CHAPTER 3

METHODOLOGY

3.1   Research Design

This research focuses in the catalytic wet air oxidation (CWAO) of wastewater containing acetic acid. The ruthenium oxide on zirconium oxide and cerium oxide support (RuO_2/ZrO_2-CeO_2) catalyst was synthesized and tested.

The synthesized catalyst was characterized through X-ray diffraction (XRD) and Physisorption analysis (BET Method). The optimal operating conditions will be determined by running the reaction by manipulating different operating variables which are concentration of acetic acid in the wastewater, temperature and air flowrate.

3.2 Materials

3.2.1 Wastewater Containing Acetic Acid

Ethanoic acid, or its IUPAC name, acetic acid, is an organic carboxylic acid with a low molecular weight (60.05 g/mol). It is has a pungent, vinegar–like odour, colourless and is soluble in water. For a 1% acetic acid solution per water, it has a pH of 2 which is an acidic solution. Its ecotoxicology in water (LC50), is 88 parts per million for 96 hours for fathead minnow fish. LC50 is the lethal concentration or dose required to kill half of the test population after a specified testing time. Acetic acid in low concentrations may not cause direct harm to humans but it can contaminate and destroy the aquatic ecosystem (*Material Safety Data Sheet, Acetic Acid MSDS, n.d.*).

3.2.2 Catalyst Reagents

In order to synthesize the RuO_2/ZrO_2-CeO_2 catalyst, the following reagents are required: The amount of reagents above produces only about 7g of catalyst.

i.   50ml of aqueous solution of 0.1mol/L $ZrOCl_2$ and 0.9mol/L $Ce(NO_3)_3$

ii. 1000ml of 0.5mol/L ammonia aqueous solution

iii. 400ml of deionized water

iv. $RuCl_3$ solution

3.2.3 Reagents of GC Analysis

The only reagent needed for sample preparation is the solvent, hexane. The analysis itself requires other solvents and reagents, but it depends on the sample analysed, column used and other relevant factors. For the specific reagents needed, refer to the operating manual.

3.3 Catalyst Preparation

Fifty millilitres of aqueous solution containing 0.1mol/L $ZrOCl_2$ and 0.9mol/L $Ce(NO_3)_3$ were dropped into 1000ml of 0.5mol/L ammonia aqueous solution under vigorous stirring (approximately 800rpm) where precipitations will form. The precipitate will be filtered and dispersed into 400ml of deionized water before being heated and stirred (approximately 500rpm) at 80°C in an airproofing flask with backflow with temperature control for twenty four hours. The resultant slurry is cooled and filtered. The cooled and filtered slurry will be then dried at 300°C for a minimum of 4 hours and then calcined at 400°C for 8 hours. The resultant powder will be immersed in saturated solution of $RuCl_3$ (weight of Ru is calculated to be 2 wt% on metal basis), dried at 100°C for 4 hours and then calcined at 300°C for 8 hours. Using the quantity of the reagents above, about 7g of catalyst will be fabricated.
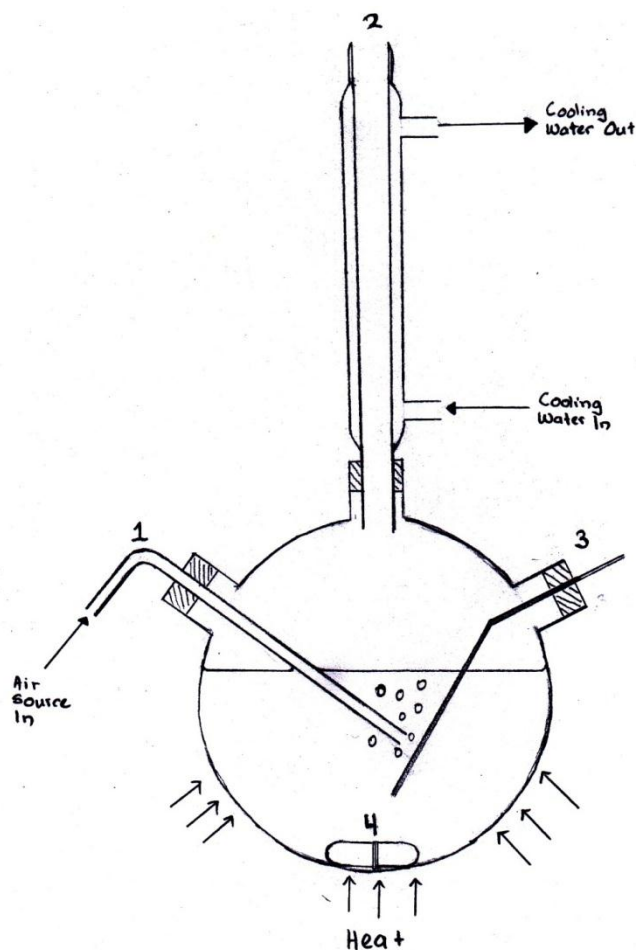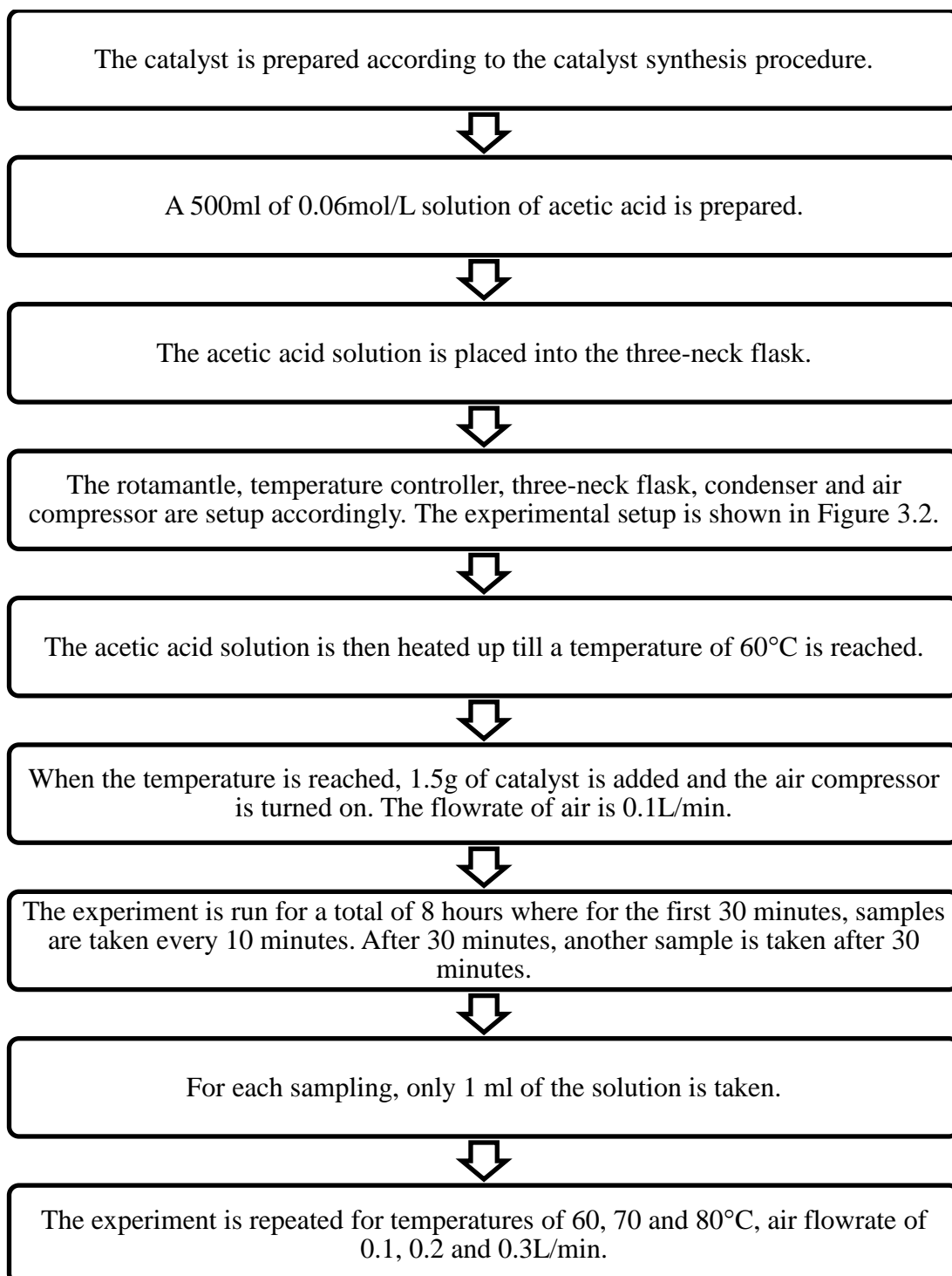
3.4   Catalyst Testing

Figure 3.1   Schematic Diagram of Catalyst Testing Setup.

Figure 3.1 depicts the schematic diagram for catalyst testing. A three-neck flask will be used as a batch reactor for this reaction. Three necks will be used: (1) air source inlet, (2) condenser, to ensure that the solution in the reactor does not dry up by condensing the evaporated water, (3) temperature probe and (4) magnetic bar, for stirring the solution. Heat will be provided via a rotamantle.

Firstly, in order to control the temperature of the reaction, a temperature controller is used. This is an electronic temperature controller connected to the

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heating source. To detect the temperature, a temperature probe is used. The temperature is set in the controller and the probe will detect the temperature of the solution. If the temperature does not reach the set point, the heat will be turned on until it reaches the set point. Also, the use of a temperature controller eliminates the need for a thermometer to indicate the temperature and provides automatic control of the temperature.

A rotamantle is used instead of the conventional combination of heating mantle and overhead stirrer. A rotamantle is a heating mantle with a built in magnetic stirrer and this eliminates the need for an overhead stirrer. Hence, the final experimental setup consists of a rotamantle, temperature controller, air inlet source and condenser connected to a three-neck flask. The setup is also depicted in Figure 3.2. The experimental procedures involved for testing the catalyst in catalytic wet oxidation of wastewater containing acetic acid are as follows:
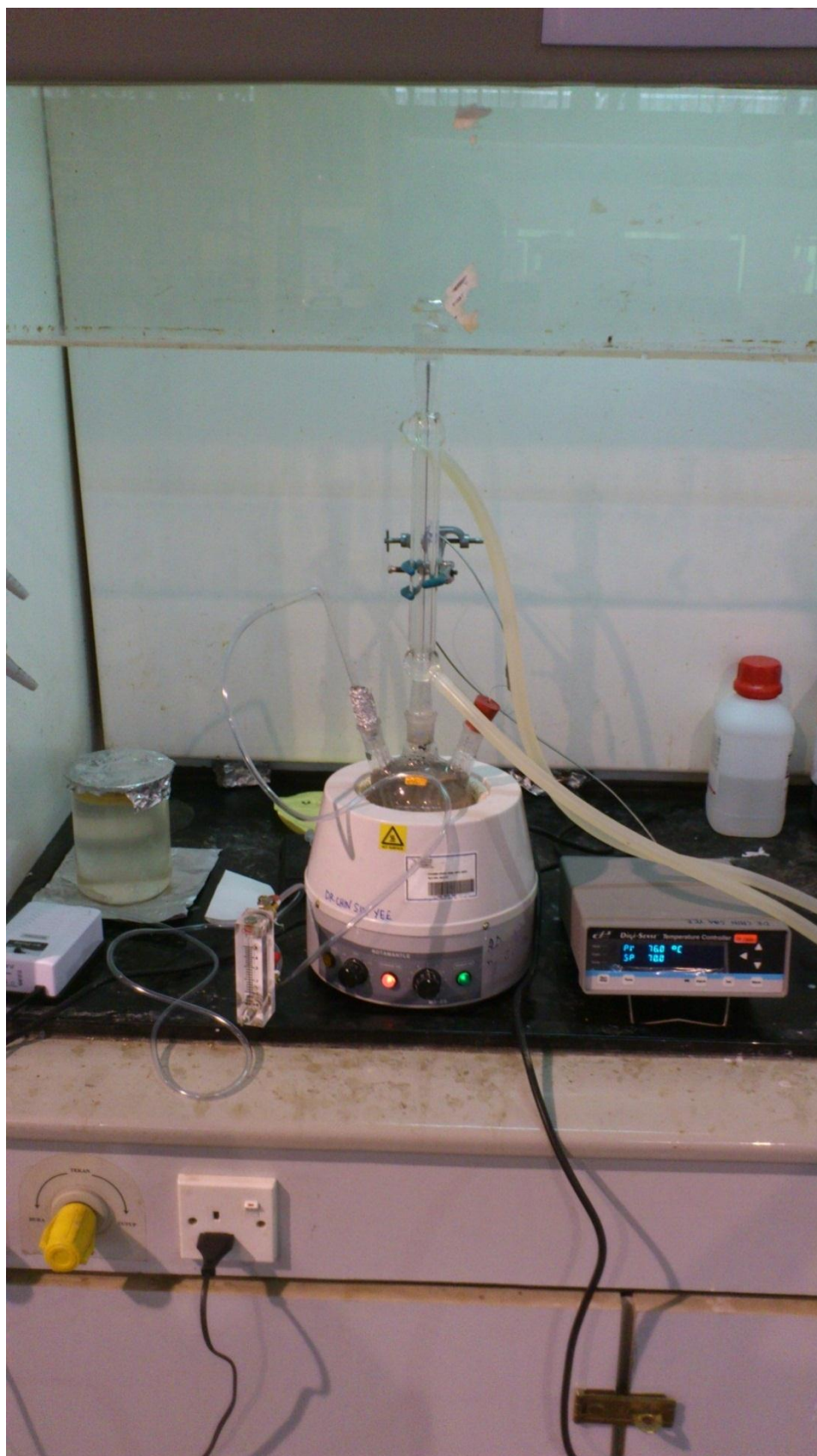
The catalyst is prepared according to the catalyst synthesis procedure.

⬇

A 500ml of 0.06mol/L solution of acetic acid is prepared.

⬇

The acetic acid solution is placed into the three-neck flask.

⬇

The rotamantle, temperature controller, three-neck flask, condenser and air compressor are setup accordingly. The experimental setup is shown in Figure 3.2.

⬇

The acetic acid solution is then heated up till a temperature of 60°C is reached.

⬇

When the temperature is reached, 1.5g of catalyst is added and the air compressor is turned on. The flowrate of air is 0.1L/min.

⬇

The experiment is run for a total of 8 hours where for the first 30 minutes, samples are taken every 10 minutes. After 30 minutes, another sample is taken after 30 minutes.

⬇

For each sampling, only 1 ml of the solution is taken.

⬇

The experiment is repeated for temperatures of 60, 70 and 80°C, air flowrate of 0.1, 0.2 and 0.3L/min.

Figure 3.2   Experimental Setup (from left: Air Compressor, Flowmeter,

Rotamantle with Three-Neck Flask, Condenser and Temperature Controller).

3.5   Analysis Methods

Catalyst characterization analysis was conducted using X-ray diffraction (XRD) and Physisorption analysis (BET Method). In order to determine the conversion of the reaction, Total Organic Carbon (TOC) and Gas Chromatography (GC) were used to check the concentration of acetic acid.

Table 3.1   Analytical Methods and their Purpose.

Analytical Method	Purpose
XRD	Used for catalyst characterization, analyses the crystalline structure and size of the catalyst crystal
Physisorption analysis (BET Method)	Used for catalyst characterization, analyses the surface characteristics of the catalyst (surface area)
TOC and GC	Used to determine the concentration of acetic acid in the wastewater after the reaction; can calculate/determine the conversion

3.5.1   XRD and BET Analysis Method

XRD was conducted with Cu rays at 30kV and 15mA. Samples were degassed at 300°C for 12 hours before the BET analysis was conducted. BET surface was estimated via N_2 adsorption at 77K.

3.5.2   Gas Chromatography (GC) Analysis

GC analysis provides a more detailed analysis of the sample and the remaining concentration of acetic acid after the reaction. Before the samples can be injected into the GC, the samples must be prepared for analysis. The most important steps in preparing the samples are dilution in a solvent and filtration of the samples before injection. Filtration is important as it prevents the malfunction of the GC column.
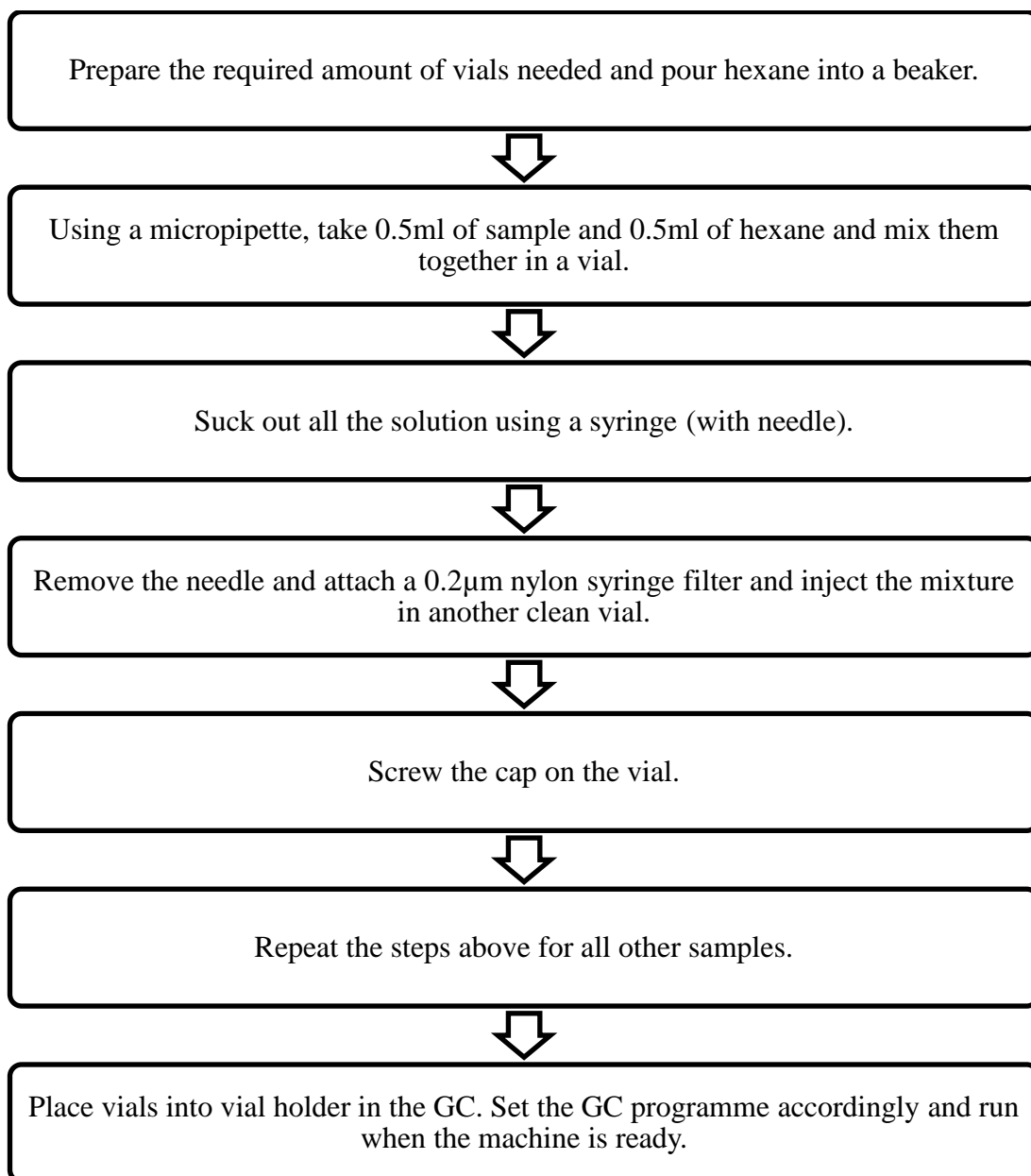
3.5.2.1 GC Specifications and Operating Conditions

The GC column used was purchased from Agilent Technologies. The column is primarily used for the detection of acrylic acid. However, acetic acid can also be used to detect acetic acid. Table 4.2 describes the technical specification and operating conditions.

Table 3.2   GC Column Specifications and Operating Conditions.

Column	DB 200
Column Size	30m x 0.53mm, 1.00µm
Carrier	Helium at 34.5cm/s, Measured at 35°C
Oven Temperature	35°C for 5 mins, 35 – 200°C at 10°/min
Detector	FID, 250°C

3.5.2.2 GC Analysis Procedure

Prepare the required amount of vials needed and pour hexane into a beaker.

⬇

Using a micropipette, take 0.5ml of sample and 0.5ml of hexane and mix them together in a vial.

⬇

Suck out all the solution using a syringe (with needle).

⬇

Remove the needle and attach a 0.2µm nylon syringe filter and inject the mixture in another clean vial.

⬇

Screw the cap on the vial.

⬇

Repeat the steps above for all other samples.

⬇

Place vials into vial holder in the GC. Set the GC programme accordingly and run when the machine is ready.

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Catalyst Characterization

4.1.1   X-ray Diffraction (XRD)

The synthesized catalyst was sent for XRD analysis and the results obtained were compared to the previous work done by Wang et al. (2008). The XRD pattern for two samples of the synthesized catalyst is shown in Figure 4.1 and Figure 4.2. Both samples were synthesized using the same methodology, but were synthesized as two different batches. Both XRD patterns were compared with the XRD pattern obtained from the work done by Wang et al. (2008).
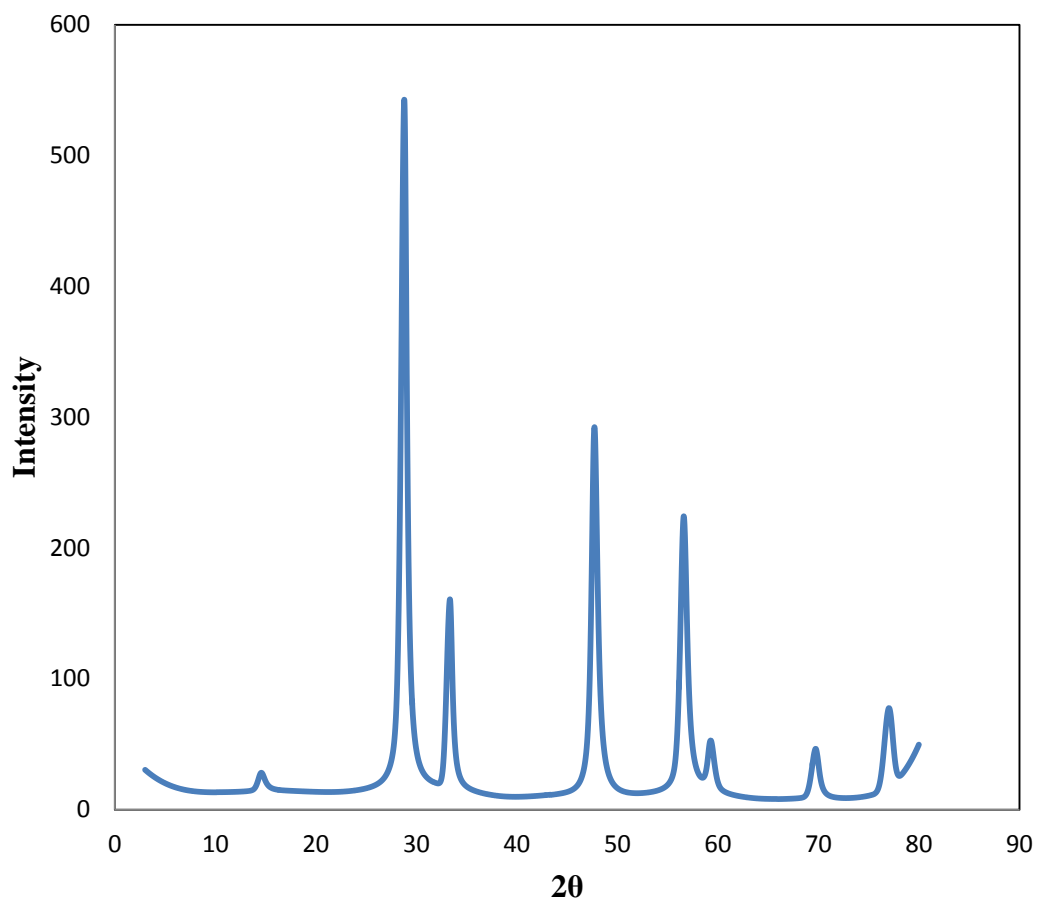
Figure 4.1   XRD Pattern for Sample 1 of the Synthesized RuO_2/ZrO_2-CeO_2
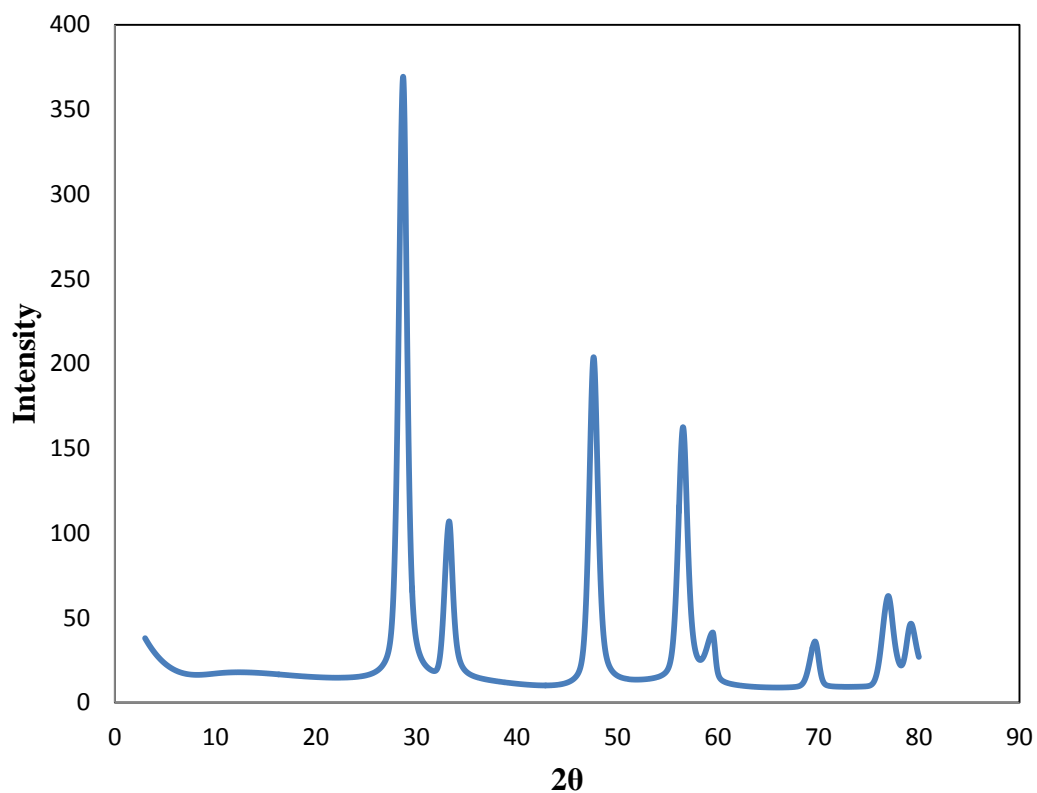
Catalyst.

Figure 4.2 XRD Pattern for Sample 2 of the Synthesized RuO_2/ZrO_2-CeO_2 Catalyst.

Figure 4.3 shows the XRD pattern of the RuO_2/ZrO_2-CeO_2 synthesized in a research conducted by Wang et al. (2008). The XRD pattern of Wang's catalyst is highlighted in a red box.

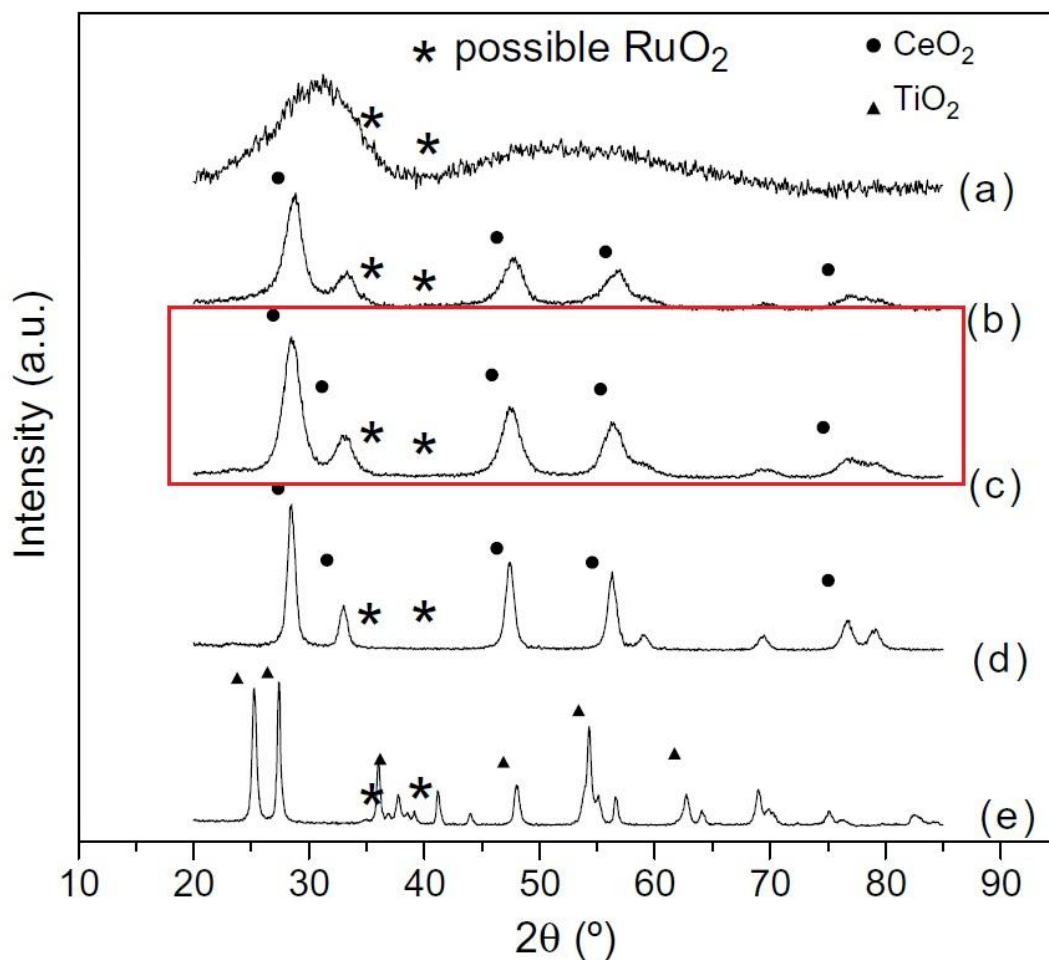**Figure 4.3**   XRD pattern of (a) RuO_2/ZrO_2, (b) $RuO2/TiO_2–CeO_2$, (c) $RuO_2/ZrO_2–CeO_2$, (d) RuO_2/CeO_2 and (e) RuO_2/TiO_2 (Wang et al., 2008).

The pattern highlighted in Figure 4.3 shows the peaks of the catalyst and the possible RuO_2 and the support which is CeO_2. The pattern also shows that the catalyst has a proper crystalline structure. The XRD pattern of Sample 1 and 2 was compared with the XRD pattern of Wang's catalyst and is illustrated in Figure 4.4.
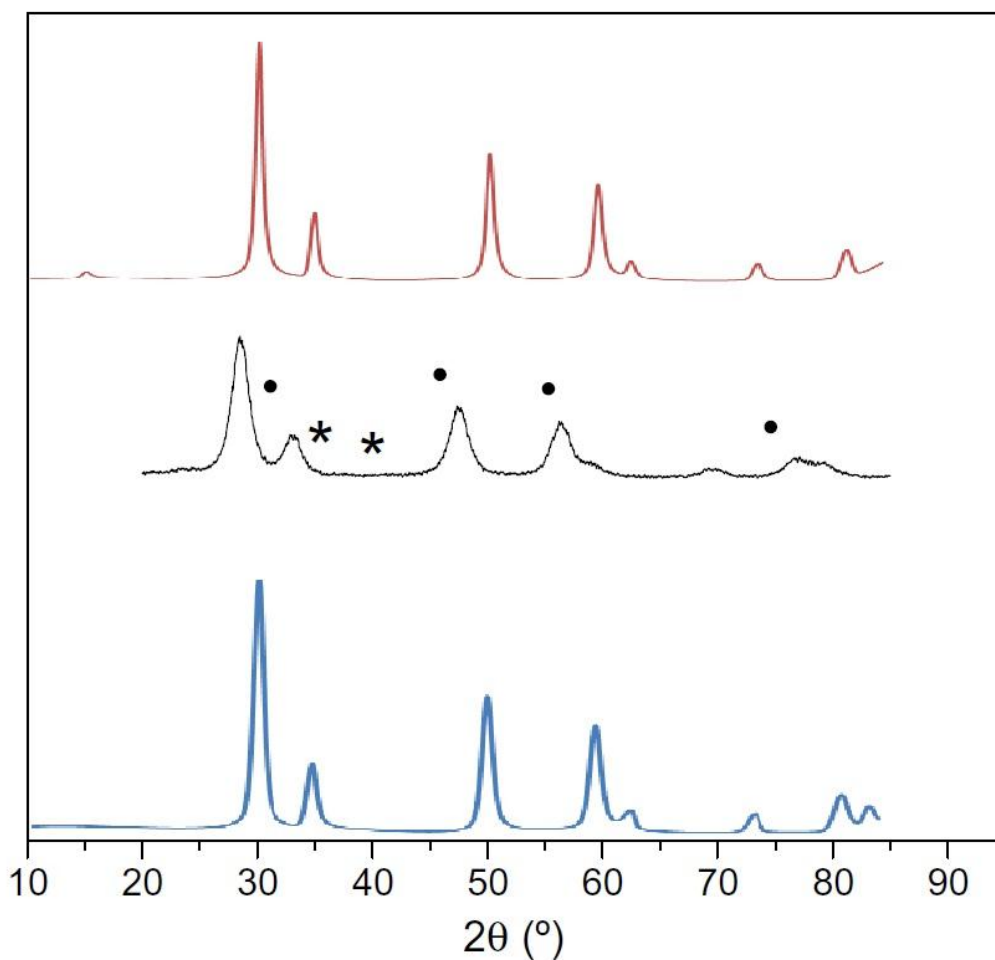
Figure 4.4   Comparison of XRD Pattern of Sample 1 (Red), Sample 2 (Blue) and

Catalyst from Wang et al. (Black).

As shown in Figure 4.4, the peaks of all the analysed samples which are in red and blue are similar to the peaks of the catalyst from Wang et al., illustrated in black. Each peak of the samples analysed have the same 2θ value with the one obtained from research. With that said, the catalyst synthesized is proven to be $RuO_2/ZrO_2\text{-}CeO_2$ catalyst as all peaks are the same. Additionally, both synthesized catalyst have properly crystallined structure as the XRD pattern shows. Poorly crystallined structures will register a 'rough' pattern instead of a smooth pattern. As

both catalyst samples register a smooth pattern, it can be concluded that both samples have properly crystallined structures.

All peaks of the XRD pattern are of CeO_2. No peaks are attributed to Ru and ZrO_2. For Ru, no discernable peaks were observed because of the low content of Ru (Wang et al, 2008). The content of Ru is only 2.5wt% on the metal basis. As for ZrO_2, introduction of ZrO_2 into the CeO_2 lattice induced a structural modification after calcination at high temperature; the formation of a solid solution of composition $Ce_XZr_{1-X}O_2$ (Leitenburg et al., 2000).

4.1.2 Physisorption Analysis (BET Method)

BET analysis was conducted to determine the surface area of the synthesized catalyst. The first catalyst sample was analysed using the unknown surface method of analysis. The surface area calculated was $111.39m^2/g$. The adsorption isotherm and BET plot of the first sample is shown in Figure 4.5 and Figure 4.6 respectively.
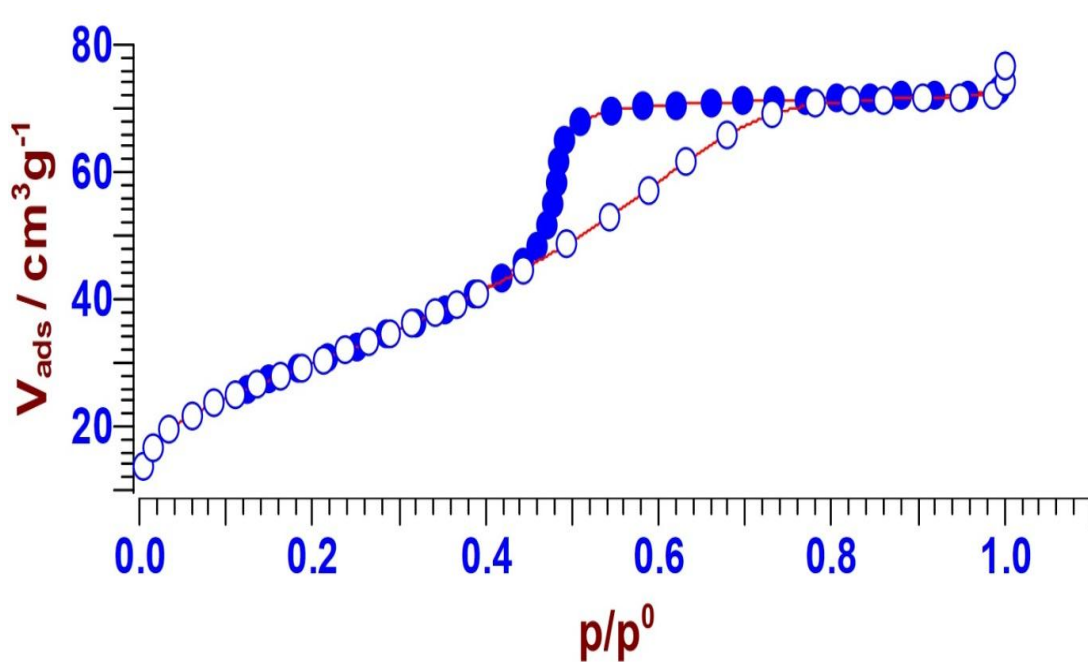
Figure 4.5   Adsorption Isotherm for Catalyst Sample 1.

Figure 4.5 shows the adsorption isotherm for sample 1 of the synthesized catalyst. The isotherm follows the type IV isotherm. Type IV isotherm deviates largely from the Langmiur isotherm. When the first point of inflection is reached, the monolayer adsorption has been completed. In other words, the intermediate flat region in the isotherm corresponds to monolayer formation. After the monolayer formation, is the multilayer formation. The multilayer is indicated by the low slope region in the isotherm.

The area where the blue point and white points in the isotherm separate is known as the hysteresis. Hysteresis indicates the capillary condensation in meso and macropores. The hysteresis will indicate the size of the pores. Larger hysteresis indicates mesopores while smaller hysteresis indicates large pores or voids.
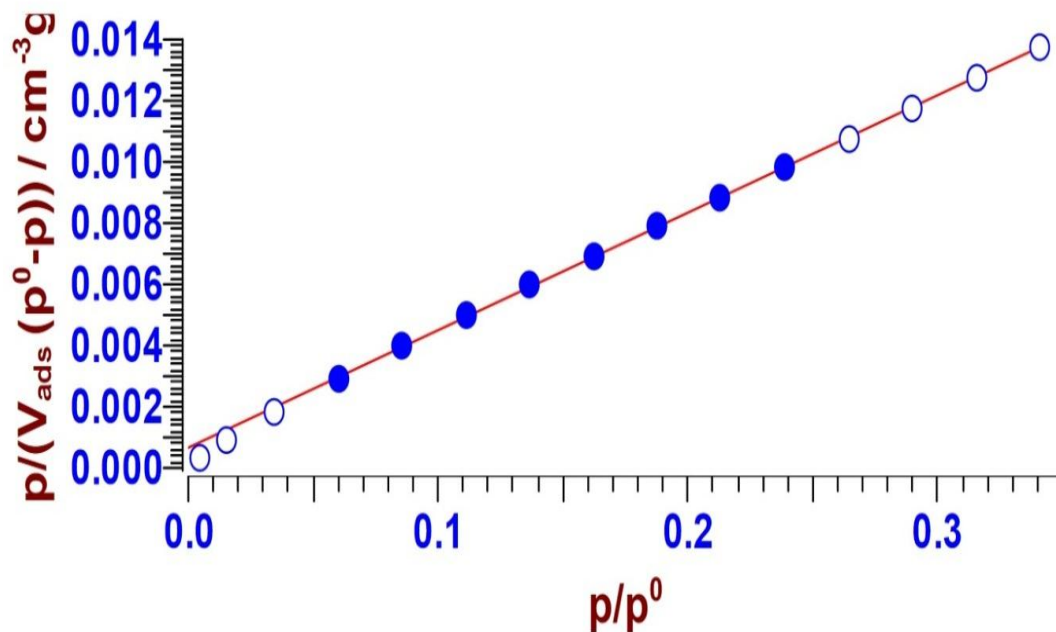
Figure 4.6   BET Plot of Catalyst Sample 1.

From the BET plot, the distribution of the points produces a straight line with a R^2 of 0.9998. Hence, the catalyst has a good pore distribution which contributes to a high surface area. The analysis also shows that the catalyst is nano-sized as the catalyst has an average pore diameter of 1.9249nm. The BET plot for the second catalyst is shown in Figure 4.6 and the summary of the BET analysis for both catalyst samples are shown in Table 4.1.

The second catalyst sample was analysed using the mesoporous surface method of analysis. Selection of this method is based on the first catalyst BET surface area. Mesoporous catalyst has a surface area of approximately 40 to 200m^2/g. The first catalyst sample has a surface area between 40m^2/g and 200m^2/g. Therefore, selection the mesoporous method of analysis will yield a more accurate analysis. The surface area calculated for sample 2 was 95.988m^2/g. Figure 4.7 and Figure 4.8

shows the adsorption isotherm and the BET plot of sample 2 of the synthesized catalyst.
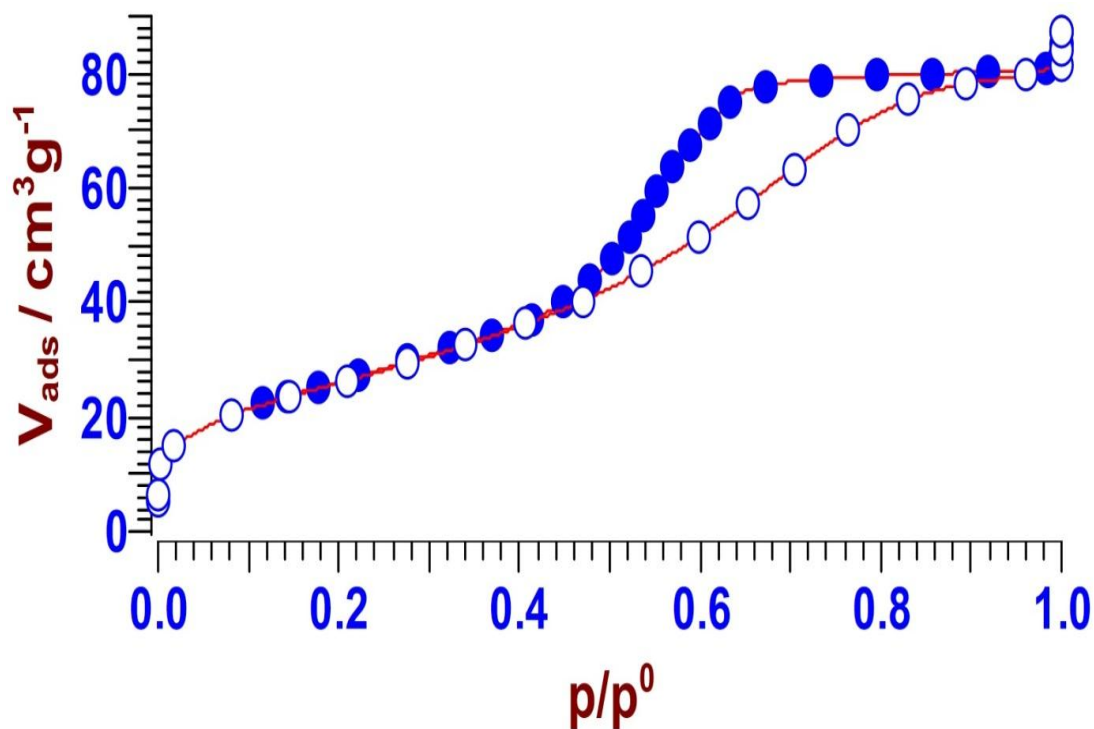

Figure 4.7   Adsorption Isotherm for Catalyst Sample 2.

Figure 4.7 shows the adsorption isotherm for sample 2 of the synthesized catalyst. The isotherm is similar with the isotherm of sample 1. The catalyst has multilayers and the hysteresis indicates that the catalyst is mesoporous.
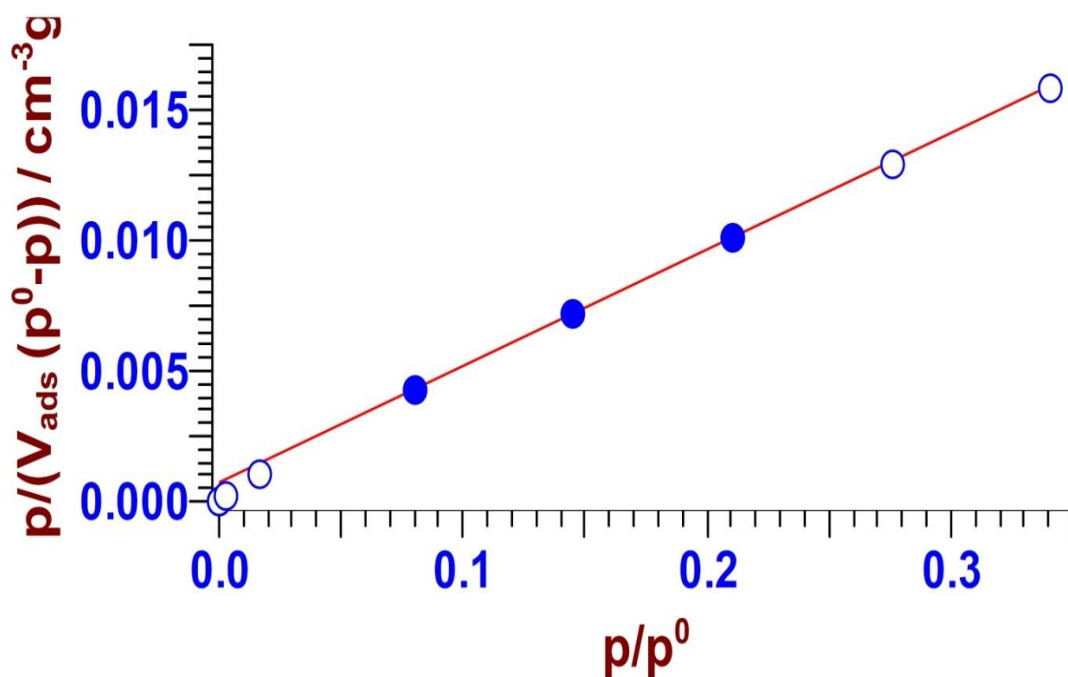
Figure 4.8   BET Plot of Catalyst Sample 2.

From the BET plot, the distribution of the points produces a straight line with a R^2 of 0.9999. Hence, the catalyst has a good pore distribution which contributes to a high surface area. The analysis also shows that the catalyst is nano-sized as the catalyst has an average pore diameter of 2.2676nm. Therefore, the synthesized catalyst is mesoporous with high surface area and high pore volume.

Table 4.1   Summary of BET Analysis for Both Catalyst Samples.

Catalyst	Surface Area, m^2/g	Average Pore Diameter, nm
Sample 1	111.39	1.9249
Sample 2	95.988	2.2676

From the research work done by Wang et al. (2008), their catalyst has a surface area of $114.0m^2/g$. From Table 4.1, the surface areas of both samples are close to the surface area of the catalyst from Wang's research. Hence, based on the XRD and BET analysis, it can be deduced that the catalyst synthesized is indeed a RuO_2/ZrO_2-CeO_2 catalyst and compared to the catalyst synthesized and analysed by other researchers, the catalyst is very similar in terms of crystalline structure and surface area.

4.2   Catalyst Activity

4.2.1   Temperature Effect

The WAO was conducted at temperatures of 60, 70 and 80°C while maintaining the concentration of acetic acid at 0.06mol/L and air flow rate of 0.1L/min. The samples were taken periodically and analysed using GC. The conversion versus time for all runs are shown in Figure 4.7, 4.8 and 4.9.
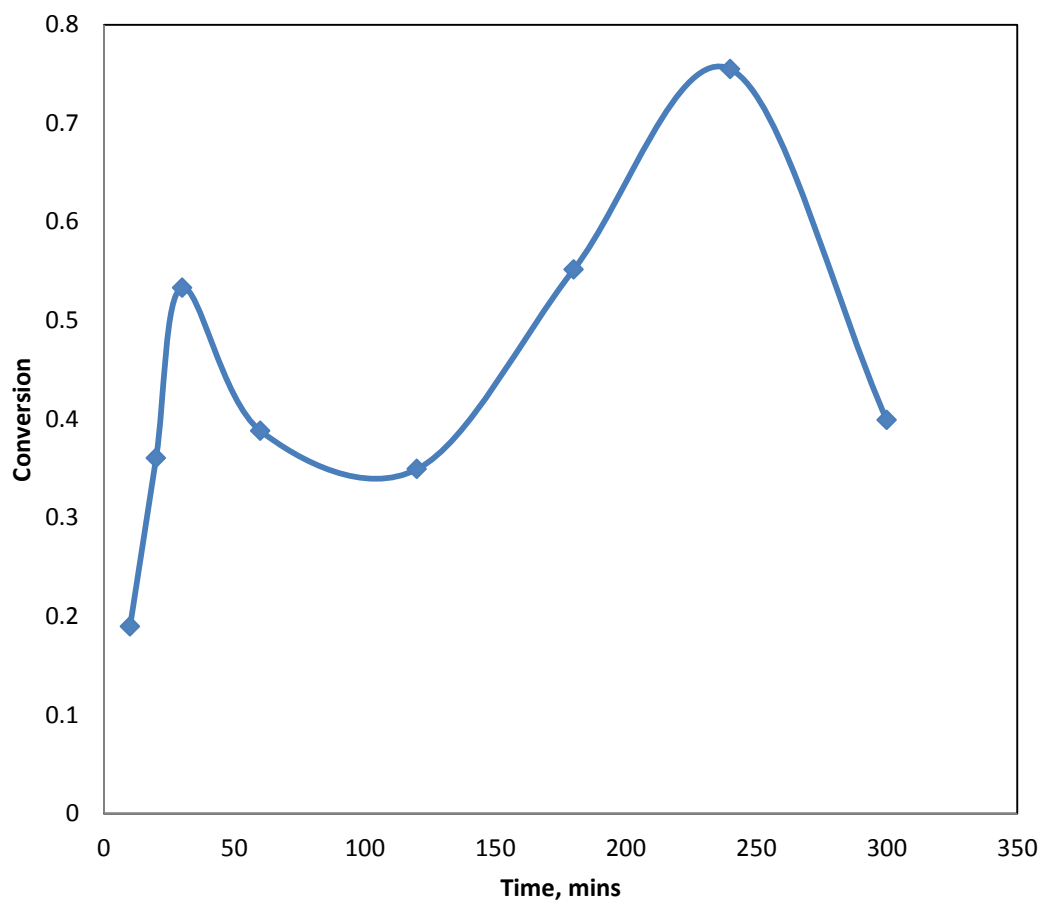
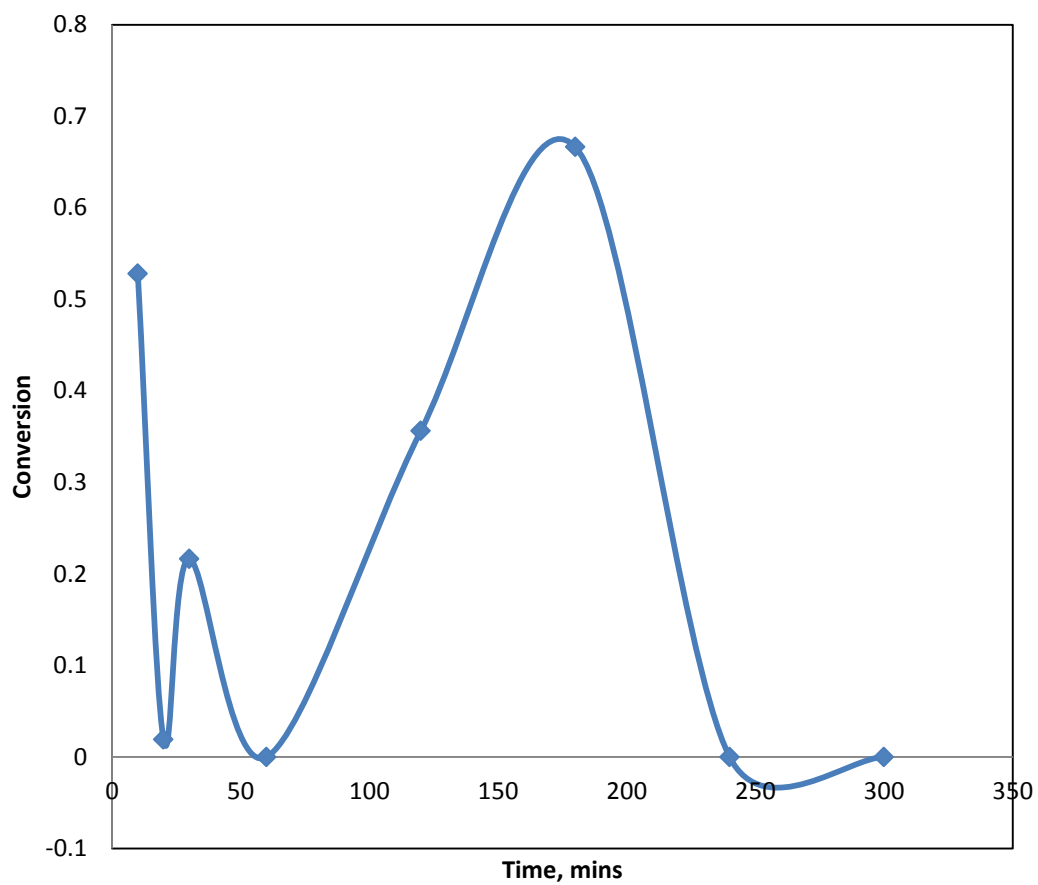**Figure 4.7**   Conversion Versus Time for Reaction Run at 60°C.

Figure 4.8   Conversion Versus Time for Reaction Run at 70°C.
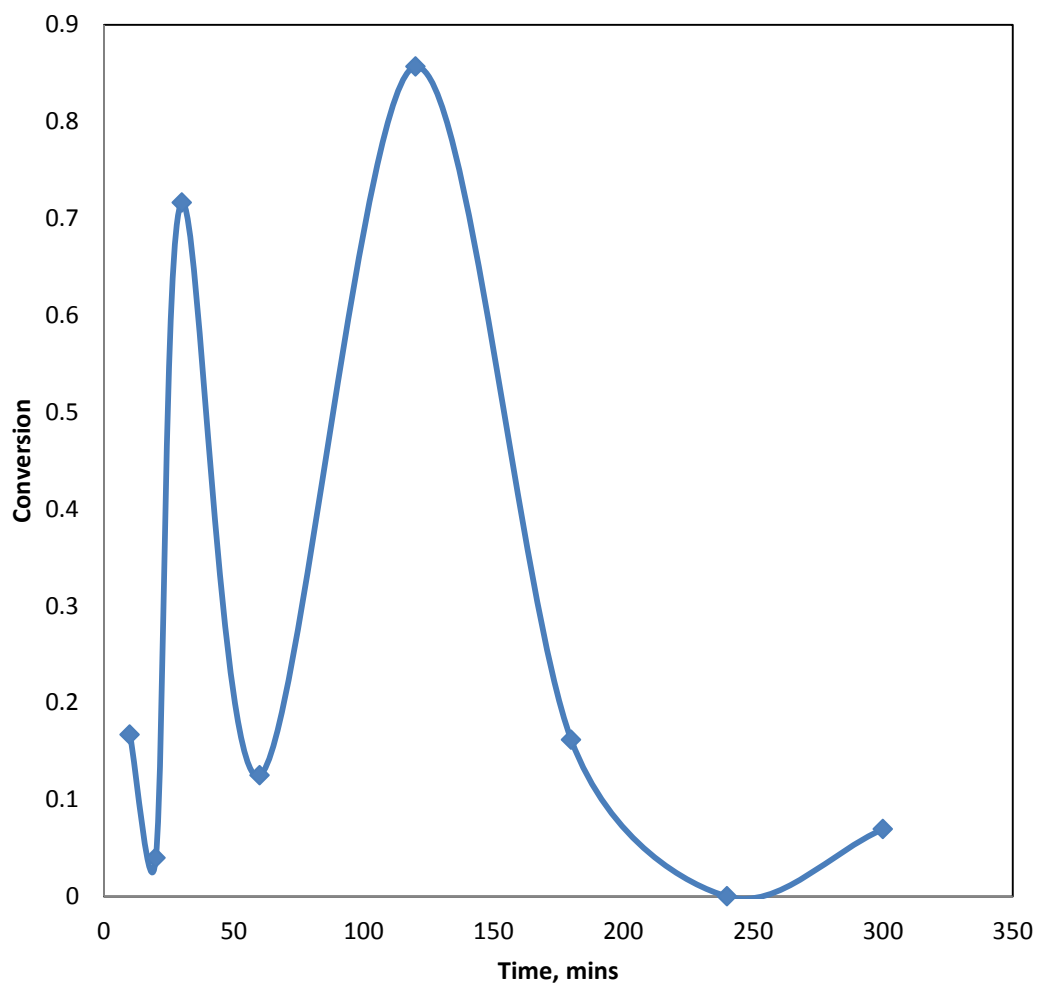
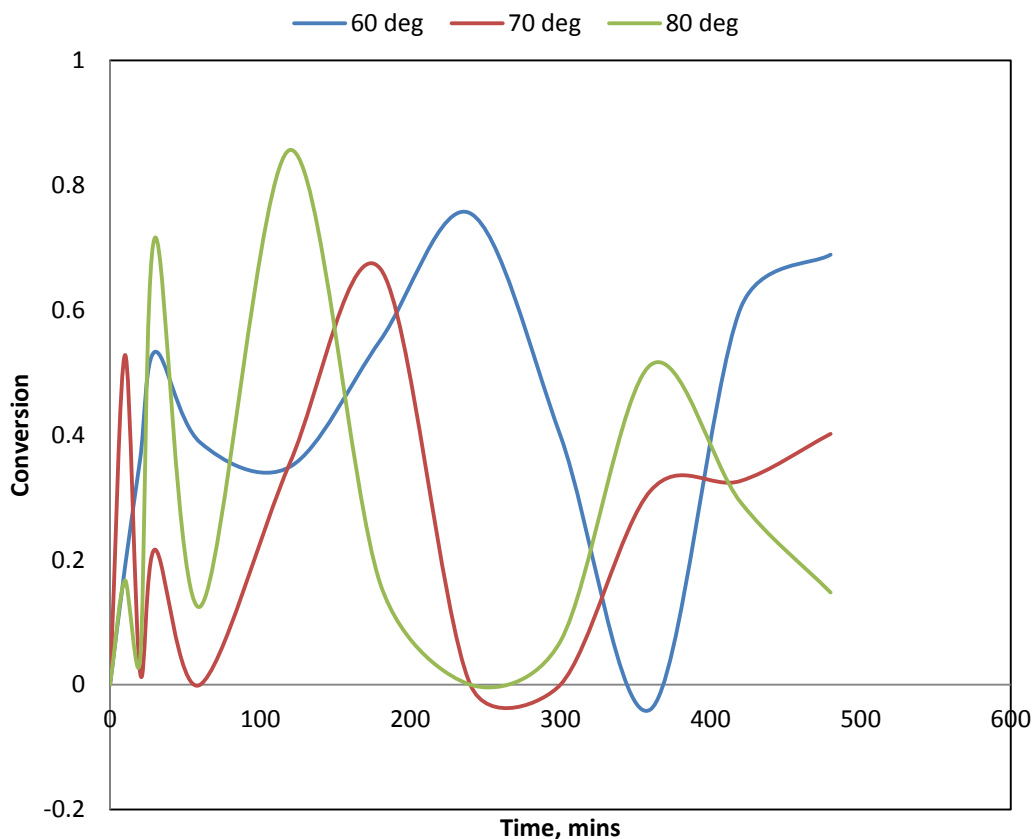**Figure 4.9**   Conversion Versus Time for Reaction Run at 80°C.

Figure 4.10   Comparison of the Conversion of Acetic Acid at Different

Temperatures.

Figures 4.7, 4.8 and 4.9 shows the fluctuating conversion of the acetic acid throughout the reaction period for temperature of 60°C, 70°C and 80°C respectively. Figure 4.10 shows the comparison of all conversions at different temperatures. Steady state of the reaction could not be achieved after running the reaction for 6 hours. The possible explanation of this fluctuation would be the formation of formic acid as an intermediate product (Barbati et al., 2011) before the all carboxylic acids were converted to CO_2. However, further explanation would be partial oxidation of the metallic ruthenium.

Surface oxidation of the catalyst takes place the fastest during the start of the oxidation run. Since steady state could not be achieved, it can be concluded that the oxidation of the metallic Ru takes place throughout the entire reaction run (Pintar et al., 2008). The highest peaks or highest conversion for all runs at different temperatures was achieved after a minimum of 100 minutes. At 60°C, the highest conversion was achieved after 200 minutes. As the temperature is increased, the highest conversion requires lesser time to achieve where at 80°C, the highest conversion was achieved after 100 minutes.

Increasing the temperature increases the conversion and the conversion rate. This based on two theories: Collision Theory and Arrhenius Theory. For any specific reaction, the rate of reaction has a rate constant. Arrhenius Theory says that the rate constant follow the temperature of reaction and any changes in the reaction temperature affects the rate constant. Arrhenius Theory is based on the kinetics of the Collision Theory.

Following the Collision Theory, as temperature increases, molecules have more energy to move about and thus increases the frequency of a successful collision. A successful collision contains enough energy to overcome the energy barrier. This energy is known as the activation energy. Once the energy barrier has been overcome, the product will form. So, increasing temperature will increase the conversion rate.

From the reaction study, at 80°C the conversion is highest compared to the conversion at other temperatures. Also, the time needed to achieve the highest conversion is lesser than compared to the reaction run at lower temperatures. This result agrees with both the Collision and Arrhenius Theory even though the

conversion did not reach steady state. As mentioned previously, the fluctuating conversion resulted from formation of intermediate compound and partial oxidation of the catalyst.

4.2.2   Air Flow Rate Effect

The CWAO was conducted with different air flow rates which are 0.1L/min, 0.2L/min and 0.3L/min while maintaining the concentration of acetic acid at 0.06mol/L and temperature of 80°C. The samples were taken periodically and analysed using GC. The conversion versus time for all runs are shown in Figure 4.11, 4.12 and 4.13.
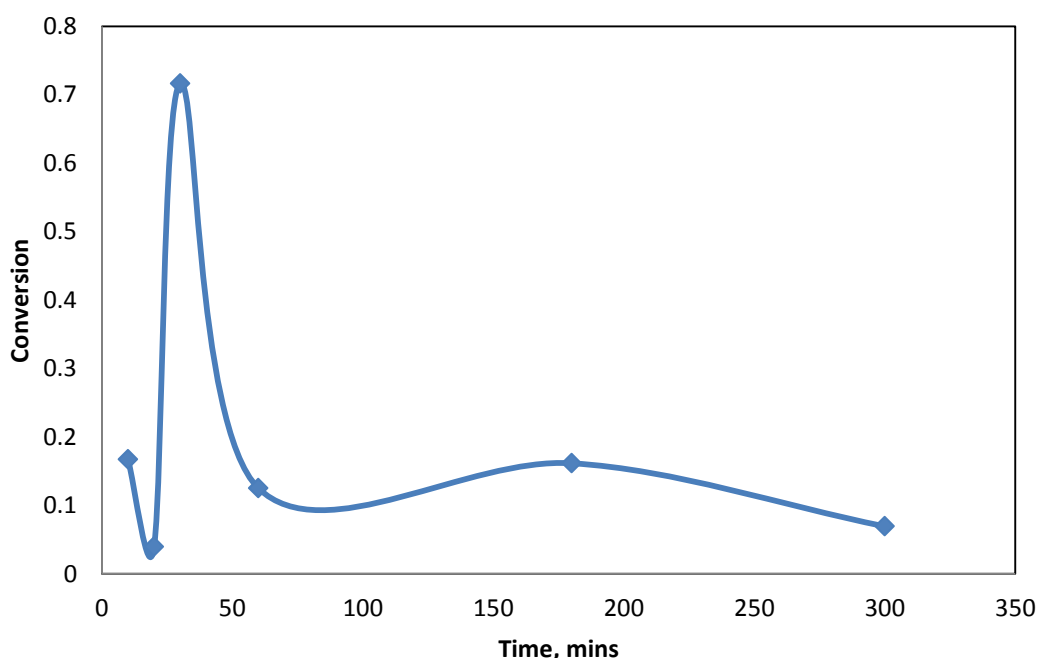

Figure 4.11   Conversion Versus Time for Reaction Run at Air Flow Rate of 0.1L/min.
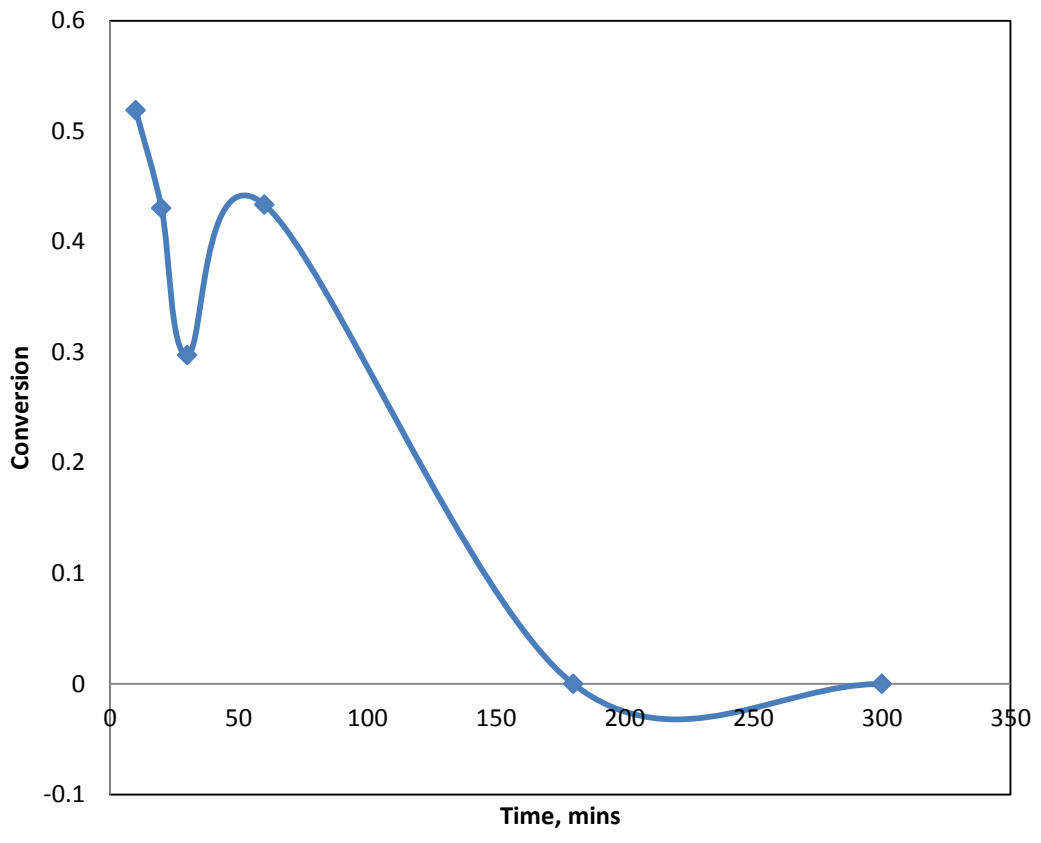
Figure 4.12   Conversion Versus Time for Reaction Run at Air Flow Rate of
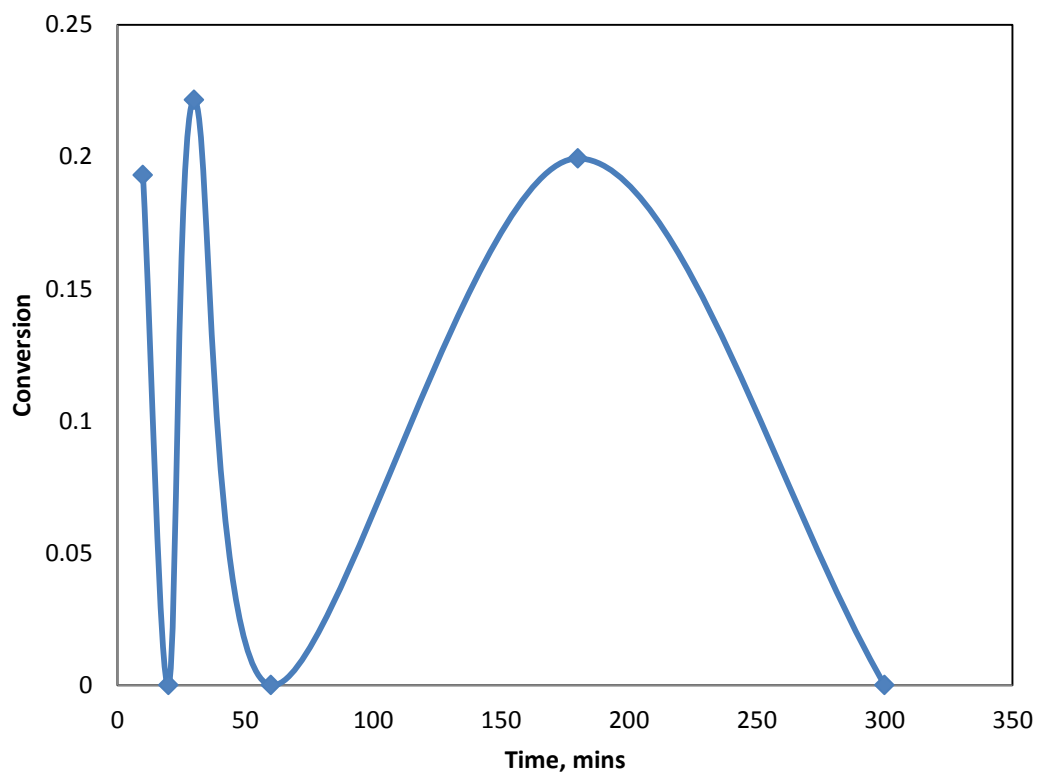
0.2L/min.

Figure 4.13   Conversion Versus Time for Reaction Run at Air Flow Rate of
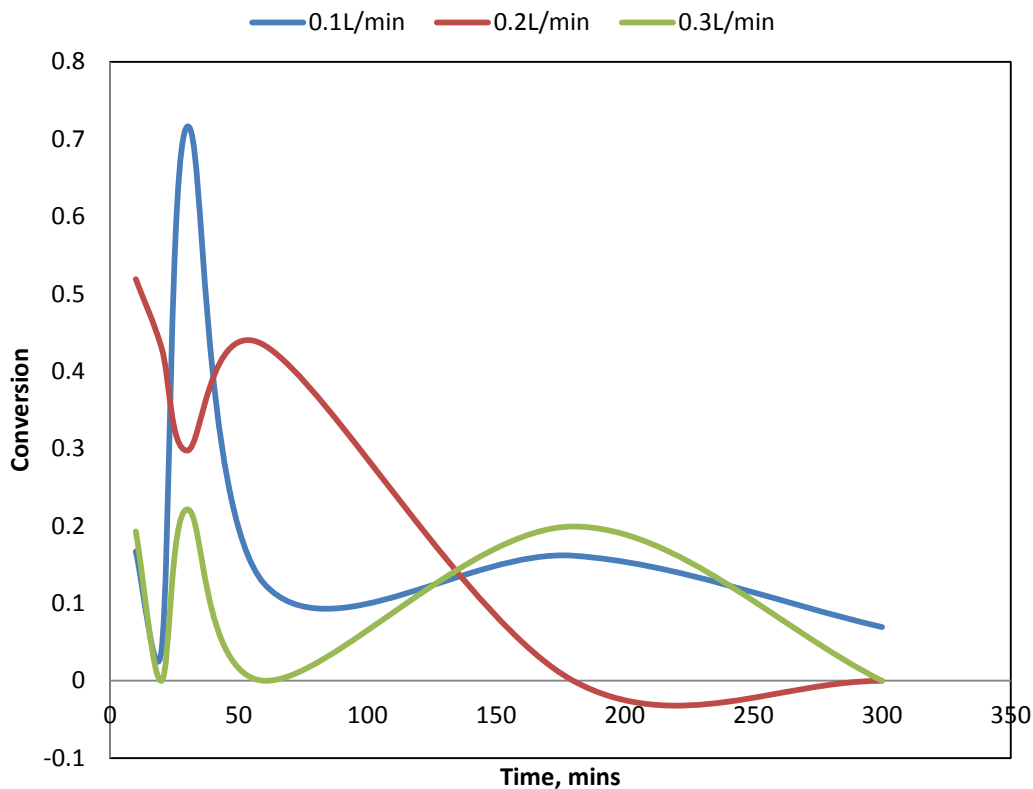
0.3L/min.

Figure 4.14   Comparison of the Conversion of Acetic Acid at Different Air Flow Rates.

Figures 4.11, 4.12 and 4.13 shows the fluctuating conversion of the acetic acid throughout the reaction period for air flow rate of 0.1L/min, 0.2L/min and 0.3L/min respectively. Figure 4.14 shows the comparison of all conversions at different temperatures. Steady state of the reaction could not be achieved after running the reaction for 6 hours. Theoretically, increasing the air flow rate should increase the conversion. However, from Figure 4.14, as the air flow rate was increased, the conversion decreases.

This could be due to the bubbling of the air into the acetic acid solution. The increased air flow rate increases the bubbling of air into the solution. The bubbling may have decreased the contact time between the solution and the catalyst. This influences the mass transfer between the solution and the catalyst.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1   Conclusion

This research details on the synthesis of a high activity catalyst (RuO_2/ZrO_2–CeO_2) and the activity study of said synthesized catalyst. The catalyst was characterized via XRD and physisorption analysis and the results show that the catalyst has high surface area of $95.988m^2/g$ to $111.39m^2/g$. The physisorption analysis also shows that the catalyst is a mesoporous catalyst.

From the activity study, the increase in temperature increases the conversion and the conversion rate. Reaction run at 80°C yielded the highest conversion of 86% at slightly over 100 minutes. Increasing the air flow rate theoretically should increase the conversion. However, the increase in the air flow rate from 0.1L/min to 0.3L/min records a decrease in conversion.

The conversion for both parameters fluctuates throughout the reaction period and does not reach steady state. This is because of the formation of formic acid as an

intermediate product and partial oxidation of metallic ruthenium. Also, the increased air flow rate may have affected the mass transfer process which affected the conversion.

5.2   Recommendations

Further understanding and improvement of this research can be undertaken by following the suggested steps. Firstly, the reaction study should be conducted in a closed system instead of an open system as used in the research. Utilizing a closed system will eliminate external factors that may influence the reaction process.

Next, the catalyst synthesis process should be optimized by including other processes such as washing and decanting. Optimizing the synthesis process will help improve the performance of the catalyst by removing organic contaminants during the synthesis process. Besides that, other parameters should be included into the reaction study. Parameters such as concentration of acetic acid, reaction pressure and catalyst amount should be included as it will provide a more detailed activity study of the reaction.

Finally, the catalyst can be applied to the real industrial wastewater to determine the real activity and effectiveness of the catalyst. The data can be compared and further optimization can be conducted.

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APPENDIX A

Example of Gas Chromatography Analysis Result for Reaction Run at 80°C for 1 hour.
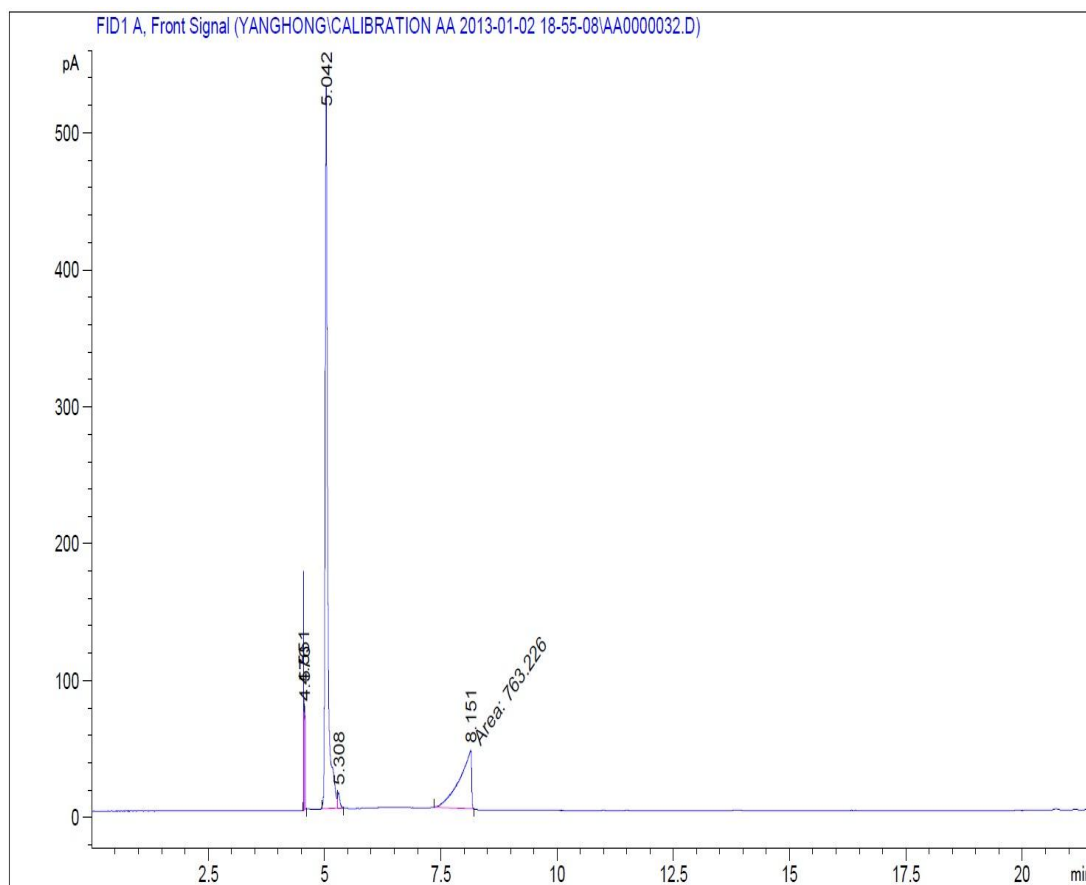
APPENDIX B

Example of XRD Analysis Result for Catalyst Sample 1.