PHYSICAL AND CHEMICAL PROPERTIES OF VANADYL PYROPHOSPHATE CATALYSTS OBTAINED VIA DIFFERENT CALCINATION TEMPERATURES

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering

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May 2011

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"PHYSICAL AND CHEMICAL PROPERTIES OF VANADYL PYROPHOSPHATE CATALYSTS OBTAINED VIA DIFFERENT CALCINATION TEMPERATURES"** was prepared by **HII SHIN YI** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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Date : _________________________

Specially dedicated to
my beloved grandmother, mother and father.
Thanks God.

ACKNOWLEDGEMENTS

I would like to thank everyone who had contributed to the successful completion of this project. I would like to express my gratitude to my research supervisor, Dr. Leong Loong Kong for his invaluable advice, guidance and his enormous patience throughout the development of the research.

In addition, I would also like to express my gratitude to my loving parent and friends who had helped and given me encouragement. During the lab works, the postgraduate students helped me to solve the problems. They were very kind to help the undergraduate students to proceed with the final year project. I really appreciated the help from them.

I would like to thank everyone who supported and guided me throughout the synthesis and analysis process. As a result, I had managed to finish my final year project on time.

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ABSTRACT

This report presents the physical and chemical properties of vanadyl pyrophosphate used as catalysts for oxidation to maleic anhydride. The vanadium pyrophosphate catalysts have been calcined in a oxygen (1%)/nitrogen mixture. The effect of calcination temperatures of the oxygen/nitrogen pretreatment was observed. The increasing of the calcination temperatures led to a decrease in the surface area of the catalysts from 15.6 m^2 g^{-1} to 12.3 m^2 g^{-1}, 11.6 m^2 g^{-1} and 6.9 m^2 g^{-1} for calcination temperatures of 380 ^oC, 420 ^oC, 460 ^oC, and 500 ^oC, respectively. The effect of the calcination temperatures on the catalysts morphology can be shown through the scanning electron microscopy. Scanning electron microscopy showed that the characteristic rosette-type of agglomerate increased with the increasing of calcinations temperature of catalysts. Besides, the catalysts were also characterized by X-ray diffraction, redox titration, and inductively coupled plasma-optical emission spectroscopy. The characterization of the catalysts will show the optimum temperature range to get better catalysts which have better selectivity and activity.

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LIST OF SYMBOLS / ABBREVIATIONS

VPO	Vanadium Phophorus Oxide
CO	Carbon monoxide
$VOHPO_4 \cdot 0.5H_2O$	Vanadyl Hydrogen Phosphate Hemihydrate
$VOHPO_4 \cdot 1.5H_2O$	Vanadyl Hydrogen Phosphate Sesquihydrate
$VOPO_4 \cdot 2H_2O$	Vanadyl Phosphate Dihydrate
$(VO)_2P_2O_7$	Vanadyl pyrophosphate
BET	Brunauer, Emmett and Teller
SEM	Scanning Electron Microscope
EDX	Energy-Dispersive X-ray Spectroscopy
XRD	X-ray Diffraction
P/V	Phosphorus to vanadium ratio

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CHAPTER 1

INTRODUCTION

1.1 Catalysis and Catalysts

Catalysts have been used in the making of wine, cheese, and bread in the early year of the human life. The earlier chemists had suggested that to add in small amounts of the foreign source to observe the chemical reaction in 1835 by Berzelius (Fogler, 2006). As a result, a catalytic reaction was denoted. The acceleration rate of the chemical reaction was explained by Ostwald in 1894. There is approximately 85-90% of the products of the chemical industry use catalyst in the catalytic process (I. Chorkendorff, J. W. Niemantsverdriet, 2003).

A catalyst is a substance that affects the rate of a chemical reaction. Catalyst accelerates the chemical reaction but do not change the equilibrium of the reaction. Catalysis is the occurrence, study, and use of catalysts and catalytic processes. In United State, approximately one third of the material gross national product involves a catalytic process. The development and use of catalysts is major part of the present research to improve the catalytic performance. The performance involves the productivity yield and selectivity of the catalyst in the chemical reactions (Fogler, 2006).

The catalysis involves the process of bonding, reaction and separation. The forming of bond between the reactants and catalyst will form before the reaction. Then follow by the separation of the products from the catalyst. This cycle is repeated in the catalytic reaction. Catalysts form from atoms and molecules to large particles such as zeolites (I. Chorkendorff,J. W. Niemantsverdriet, 2003).

1.2 Types of Catalysis

1.2.1 Homogeneous Catalysis

Homogeneous catalysis involves process which catalyst is in solution with at least one of the reactants. In homogeneous catalysis, the catalyst and reactants are in the same phase during the reaction. The phase is either in gaseous or liquid commonly (Fogler, 2006). For examples, the decomposition of the ozone layer in the atmosphere. The catalyst in the process is the chlorine atom.

$$Cl + O_2 \rightarrow ClO_3$$
$$ClO_3 \rightarrow ClO + O_2$$
$$ClO + O_2 \rightarrow Cl + O_2$$

Overall equation:

$$O_3 + O \rightarrow Cl + O_2$$

Source: (I. Chorkendorff, J. W. Niemantsverdriet, 2003)

The decomposition of the ozone will occur spontaneously under the sun light. However, the chlorine atom will accelerate the reaction tremendously. Both reactant and catalyst are in the same gas phase. Another example of homogeneous catalysis is the industrial Oxo process for manufacturing normal isobutylaldehyde. The reactant and the catalyst are both in liquid phase. The reaction in liquid phase has been found to accelerate the reaction rate greatly. This is due to the interphase mass transfer limitations can be eliminated (Fogler, 2006).

1.2.2 Heterogeneous Catalysis

Heterogeneous catalysis involves more than one phase. The catalyst used usually is in solid phase. However, the reactants and products are in liquid or gaseous form. The solid phase catalysts are porous and impenetrable to let the catalytic reactions occur at the surface. This is to save the expensive materials such as platinum. Heterogeneous catalysis usually used in the chemical and petrochemical industrial. The reaction for the hydrodesulfurization of heavy petroleum fractions will involve the reacting mixture in both liquid and gaseous forms (Fogler, 2006).

Cleaning of automobile exhaust is a typical example for heterogeneous catalysis. The catalytic reaction begins with the adsorption of CO and O_2 on the surface of platinum. Then the reaction occurs at the surface of the platinum to form carbon dioxide. The stable and unreactive carbon dioxide will be release from the exhaust. Benzene is produced by the heterogeneous catalysis in these days. The dehydrogenation of cyclohexane by using platinum on alumina as the catalyst will form the benzene (I. Chorkendorff, J. W. Niemantsverdriet, 2003).

Heterogeneous catalysis is more economically favourable as the catalysts can be reused for the catalytic process. This will save the industrial cost. Besides, the simple and complete separation of the fluid product mixture from the solid catalyst is much easier compared to the homogeneous catalysis. A heterogeneous catalytic reaction occurs near fluid-solid interface. Therefore, the catalysis can be done for both catalytic and noncatalytic fluid-solid reactions. However, the reactions between gases and liquid are mass-transfer limited (Fogler, 2006).

1.2.3 Biocatalysis

For biocatalysis, enzymes are the nature's catalysts. Enzyme is a large protein which has very shape-specific active site. This will optimally suited to guide reactant molecules in the optimum configuration for reaction. Therefore, enzymes are highly specific and efficient catalysts. For example, enzyme can catalase catalyzes the decomposition of hydrogen peroxide into water and oxygen.

With the discovery of the enzyme, the recombinant DNA technology allows more efficient production. This is due to the enzymes allow biological reactions to occur at the rates necessary to maintain life such as the build up of proteins and DNA. This can be proved when a person who has the breakdown of alcohol to acetaldehyde inside body by the enzyme alcohol dehydrogenase. The acetaldehyde is converted into acetate by aldehyde hydrogenase (I. Chorkendorff, J. W. Niemantsverdriet, 2003).

Biocatalysts do not operate by different scientific principles from organic catalysts. Enzymes can create unusual superior reaction conditions such as low pK_a value or high positive potential for a redox metal ion. Therefore, enzymes have been found to catalyze any reaction of the organic chemistry (I. Chorkendorff, J. W. Niemantsverdriet, 2003).

1.3 Reaction of the catalysts

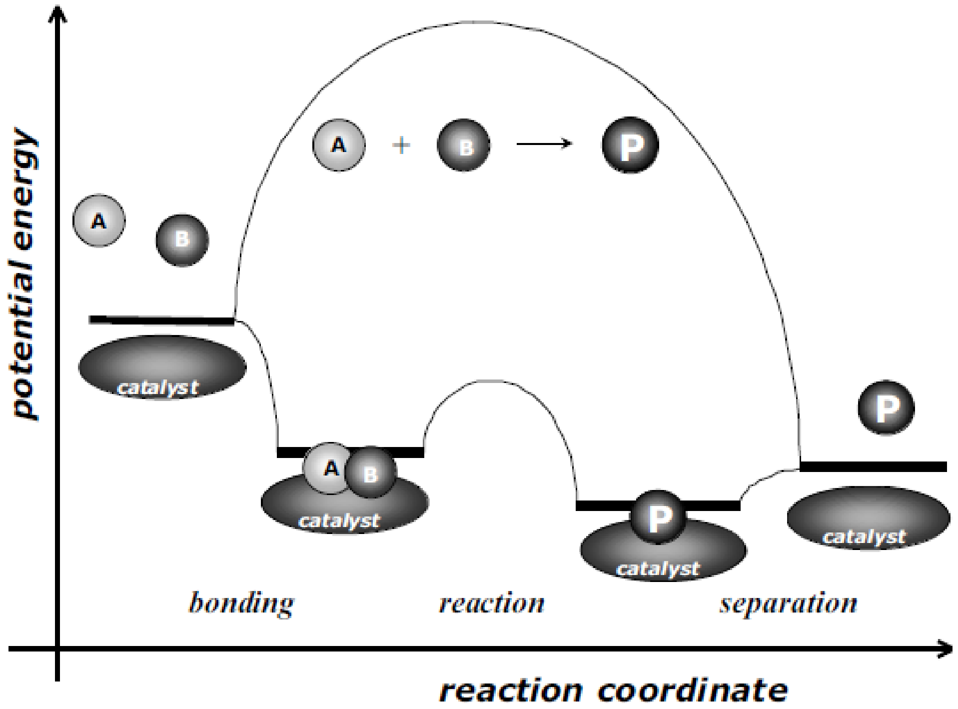


Figure 1.1: Potential energy of a catalytic reaction and uncatalyzed reaction

The energy diagram illustrates that the catalyst will decrease the activation energy of the catalytic reaction compared to the uncatalyzed reaction. From the figure 1.1, it shows that the catalyst does not affect the equilibrium of the reaction. Moreover, the reaction is thermodynamically unfavourable. The forward and reverse reaction of the reaction is same with the catalyst (I. Chorkendorff, J. W. Niemantsverdriet, 2003).

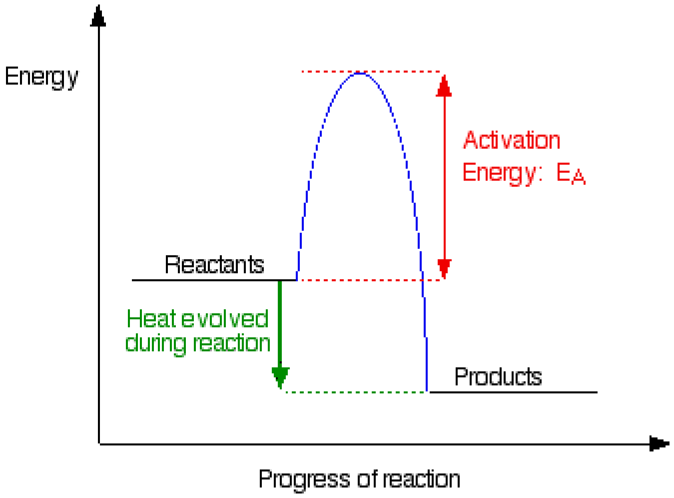


Figure 1.2: Activation energy of the catalytic reaction

Activation energy is the minimum energy required for a reaction to occur. The figure 1.2 shows the energy profile for the exothermic reaction. Activation energy is involved in breaking the original bonds and forming the new bond. This process need the energy as the activation energy is a barrier to the reaction. When the particles collide with less energy than the activation energy, no reaction will occur. In other words, the boding between reactants and catalyst is important to form the products. Either too strong or weak bonding between the reactants and catalyst will not obtain the desired products (Clark, 2002).

1.4 Catalyst Properties

A catalyst which has the porous surface will result a large area for the reaction to occur. This kind of catalyst is called porous catalyst. However, there is different size of pores in catalysts. Despite of that, some pores will only admit small molecules but prevent the large molecules to enter the catalyst. This type of pores is called molecular sieves. For example, zeolites are a natural substance which has the sieves to form the selective catalysts. The pores will affect the residence time of the reactants which allows the desired molecules to react only (Fogler, 2006).

For the reaction which has the pressure drop and heat removal limitation, the monolithic catalysts will be used. As not all the catalytic reaction need a porous structure catalyst, the porous catalyst would be wasted. For the catalyst which consists of minute particles of an active material dispersed over a less active substance called a support. Normally the active material is the pure metal. On the other hand, the unsupported catalyst is used with the addition of the active substance. The promoters will increase the activity of the catalytic reaction (Fogler, 2006).

1.5 Importance of Catalysis

The catalysis is important as the temperature, concentration, pressure and contact time can be controlled during the catalytic reaction. By increase the temperature and pressure of the reactor, the reactions will proceed at a reasonable rate of production. There are thermodynamic limitations for certain production. Moreover, the reaction which needs higher temperatures can be proceed by using the catalyst. Without catalyst, the reaction would not be possible for chemical industry. Nevertheless, catalysts can accelerate the reactions and enable the reaction to be carried out under the most favourable thermodynamic condition. For a industrial factory, catalyst are important to reduce the investment and the operation costs of the process. Then the plant will obtain high quality product and profit (I. Chorkendorff, J. W. Niemantsverdriet, 2003).

1.6 Problem Statements

Vanadium phosphate oxide catalysts (VPO) is one of the most extensively studied heterogeneous catalysts. This is due to VPO catalysts are very useful for the oxidation of an alkane commercially. However, there are many ways to transform the maleic anhydrate from the VPO catalysts. In most industry, the oxidation of *n*-butane to MA can be done for various kinds of promoters including Fe, Bi, Zn and Co. The literature on promotion up to 1991 has been reviewed by G. Hutchings, 1991. In this particular journal, it was proposed that the promoters can enable the formation of the required VPO compounds and form solid solutions which can enhance the activity of the catalysts.

Some industrial preparation of VPO catalysts will add in more phosphorus compounds as the catalyst deactivation is related to the phosphorus formed at the surface of the catalyst. However, excess phosphorus will cause the formation of $VO(H_2PO_4)_2$ which showed to have poor selectivity to MA. This was proved by Hutchings *et al*. (1991). Therefore, the promotional effect had to be determined to get the good activity of the catalyst. However, most of the reported studies found out that the promoter will decrease the activity of the catalyst indeed.

Few detailed studies were about the factors which influence the formation and the interrelation between the individual phases by E. Bordes *et al*. (1979). The influence of the calcinations conditions on the phase composition of VPO catalysts is reported. The influence of calcinations conditions on the phase composition of VPO catalysts with P/V ratios in the range of 0.90 to 1.10 is reported. However, the formation of the individual oxides of vanadium or phosphorus might be favoured outside the range. Therefore, the phases might not easily relate to well characterised phases of VPO catalysts with stoichiometric composition.

1.7 Aims and Objectives

The objective of this research is to study the physical and chemical properties of vanadyl pyrophosphate catalysts obtained via different calcination temperatures. The research was done for different calcination temperatures as the parameter to determine the best condition to obtain good catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Vanadyl Pyrophosphate Catalyst $(VO)_2P_2O_7$

Vanadium was first discovered by del Rio in 1801. Vanadium is a bright white metal which is soft and ductile. Vanadium has a good resistance to alkaline, acid and salt water. Vanadium has a good structural strength and a low fission neutron across section. Vanadium Oxide (V_2O_5) is used as a catalyst in manufacturing of sulphuric acid and maleic anhydride (MA). However, the selective oxidation of *n*-butane to maleic anhydride over the vanadium phosphorus oxide (VPO) catalyst is still the only industrial catalytic process for partial oxidation of an alkane. Vanadium pyrophosphate is generally accepted that this crystallographic phase forms a basis for the most active and selective catalyst for maleic anhydride production (Alicja Haras *et al.*, 2003).

Vanadyl pyrophosphate is an important commercial hydrocarbon oxyfunction-alisation process. Vanadyl pyrophosphate catalysts are well known as the active phase and used for the selective oxidation of *n*-butane to MA. Therefore, vanadyl pyrophosphate is the main component in the active catalyst. It is prepared by calcining the vanadium hydrogen phosphate hemihydrates ($VOHPO_4{\cdot}0.5H_2O$). The (100) plane of the vanadyl pyrophosphate is an active plane for the selective oxidation. The crystallographic phase of the vanadyl pyrophosphate forms the active and selective catalyst for MA production. Vanadyl Pyrophosphate activity depends on the surface structure, the nature of the oxygen structure, the nature of the oxygen species and the oxidation state of vanadium (V. V. Guliants *et al*., 1995).

Vanadyl Pyrophosphate catalysts possess unique structural and surface features to allow the activation of alkane. This phase is generated by calcinations of the precursor, $VOHPO_4 \cdot 0.5H_2O$ which is prepared throught the reduction of $VOPO_4 \cdot 2H_2O$ using the isobutanol as reducing agent. The transformation of the precursor to active phase can be influenced by the temperature, time and atmosphere treatment. The surface chemistry and bulk properties of the active VPO catalysts change with the calcinations condition and the calcination duration.

2.2 Preparation of Vanadium Phosphorus Oxide Catalyst

2.2.1 Aqueous medium and organic medium

The morphology of the crystallites of the precursor can be controlled by different preparative routes. For aqueous medium, V_2O_5 will be reduced by a mineral agent in water and phosphoric acid.

For organic medium route, V_2O_5 can be reduced by an organic reagent like methanol, tetrahydrofuran or isobutanol prior to the addition of phosphoric acid. In the research, the preparation of VPO catalyst was done in organic medium route by using the isobutanol to reduce the V_2O_5. In organic medium, a vanadium phosphate (V^{5+}) like $VOPO_4 \cdot 2H_2O$ is reduced by alcohol in alternative way. It had been proved by Ellison *et al*. (1994) that the changing nature of the alcohol will control the morphology of the final precursors. The nature of the final precursors can be changed as well in this route. After the calcinations, the catalyst will have higher specific area compared to the aqueous medium route.

2.2.2 Dihydrate Precursor Route

Vanadyl phosphate dehydrate, $VOPO_4 \cdot 2H_2O$ is one of the precursor to vanadyl pyrophosphate catalyst. VPO catalyst is the sole catalyst used industrially for the partial oxidation of *n*-butane to MA. $VOPO_4 \cdot 2H_2O$ was confirmed by the XRD and were activated in a reaction flow of *n*-butane/air mixture to form vanadyl pyrophosphate catalyst $(VO)_2P_2O_7$.

From Hutchings (1991), the addition cations that act as promoters of different kind were added to improve the catalytic performance of the catalyst. However, the addition of the promoters on the catalyst will form undesirable sites such as aggregated metal oxides which further the combustion of *n*-butane would be proceed. Further modification of the catalyst is needed to improve the performance and activity of the VPO to avoid the undesirable effect of promoters. Therefore, intercalation of VPO catalysts using $VOPO_4 \cdot 2H_2O$ as the host material has been done with organic molecules such as alcohols, carboxylic acid, amines, aldehyde and ketone. However, the metal complex had inserted into the interlayer of $VOPO_4 \cdot 2H_2O$.

2.2.3 Hemihydrate Precursor Route

The catalytic performance of the VPO catalyst depends on the characteristic which can be derived from the preparation of the $VOHPO_4 \cdot 0.5H_2O$ precursors. The $VOHPO_4 \cdot 0.5H_2O$ precursor is the vanadyl hydrogen phosphate hemihydrate which can be prepared in both aqueous and organic medium. The precursor obtained by the aqueous synthesis route is generally more crystalline than the catalysts prepared by the organic route. The organic synthesis route using isobutanol results in a platelet crystalline morphology producing rosette morphology where platelets agglomerate (L. O Mahony *et al.*, 2003).

The transformation of $VOHPO_4 \cdot 0.5H_2O$ to $(VO)_2P_2O_7$ proceeds through a number of complex processes with dehydration, oxidation, and reduction. The activity and selectivity of the resulting catalyst are strongly dependent on a number of the reaction conditions such as the temperature, time and composition of the treatment gas (Naonori Ryumon *et al.*, 2006).

In other cases, only the less reductive isobutanol is employed. The structure of the vanadyl phosphohemihydrate is constituted of pairs of VO_6 octahedra sharing a common face. The couples of octaheadra are connected together through PO_4 tetrahedra to form the (0 0 1) plane of the catalyst. Between the (0 0 1) plane, H_2O molecules are connected through hydrogen bonds. The V=O bonds in one octahedra are in *cis* position.

However, the vanadium pyrophosphate are formed by two octahedra which joined by edges. In this case, the octahedra pairs are connected by PO_4 tetrahedra which will form a layer structure in the (1 0 0) plane. The layers are connected together by pyrophosphate groups. Moreover, the V=O bonds in vanadyl pyrophosphate are in *trans* position which is opposite of the $VOHPO_4 \cdot 0.5H_2O$ precursors. Bordes (1984) indicated that the transformation of $VOHPO_4 \cdot 0.5H_2O$ precursors to vanadium pyrophosphate occurred when a reaction which has been proposed to be topotactic with the elimination of two water molecules.

2.2.4 Sesquihydrate Precursor Route

Vanadyl pyrophosphate catalysts were prepared by sesquihydrate precursor, $VOHPO_4.1.5H_2O$ under the calcinations in a reaction flow of *n*-butane (0.75%) air mixture at 673 K. The $(VO)_2P_2O_7$ catalyst is topotactically transformed from vanadyl hydrogen phosphate hemihydrates precursor, $VOHPO_4.0.5H_2O$.

According to the Hutching (1988), the preparation of vanadium pyrophosphate can be done through three methods:

1. VPA, prepared by using the standard aqueous HCl method followed by a water extraction step
2. VPO, prepared by the reaction of V_2O_5 with H_3PO_4 in isobutanol followed by a water extraction step
3. VPD, prepared by the reaction of $VOPO_4 \cdot 2H_2O$ with isobutanol

From all of these preparations, only vanadyl hydrogen phosphate hemihydrates precursor, $VOHPO_4.0.5H_2O$ is observed.

Another researcher, T. Ishimura *et al*. (2000)T had done the recent research which had found another alternative way in producing vanadyl pyrophosphate by using the $VOHPO_4.0.5H_2O$ precursor. It was done by reducing the sesquihydrate precursor in 1-butanol and activated at 753 K. This will obtain high specific activity in vapour-phase oxidation of *n*-butane. With the 1-butanol, the sesquihydrate will intercalate with the catalysts with high activity to produce MA.

2.3 Parameters of Vanadium Phosphorus Oxide Catalyst

2.3.1 Calcination condition

Maleic anhydride is produced by partial oxidation of *n*-butane over VPO catalyst. The calcination of the VPO precursor is an important step to get the active phase of the catalyst. After the calcinations, vanadium pyrophosphate is obtained. During the calcinations, the water molecule in the precursor will be eliminated to form the active phase (Ali Shekari *et al*.).

During the calcination process, the first step will be the evaporation of the surface water. Then the active phase of the catalyst is formed by elimination of the structural water at high temperature. Therefore, the activity and selectivity of the catalyst produced is depending on the calcinations condition.

The most active phase of VPO catalysts is formed up by a well-crystallined vanadium pyrophosphate which has unique structural and surface features to allow the activation of alkane. The active phase is generated by a long-term calcination of the precursor followed by treatment in a reaction environment. However, the transformation of the precursor will be affected by the calcinations temperature, time and atmosphere.

The investigation of the influence of calcinations agents on the catalytic performance of the VPO catalysts was done by Taufiq-Yap *et al*. (2007). The changes in the physical and chemical properties of the VPO catalysts calcined in two different conditions were observed. The two conditions were calcinations under *n*-butane/air and propane/air. From the research, it showed that the specific area of the catalysts in *n*-butane/air was higher compared to the propane/air condition. Besides, *n*-butane calcined catalyst will show higher conversion compared to the propane/air calcined catalyst. From here, the calcinations conditions definitely will affect the catalytic performance of the catalyst to form the MA.

Another research done by the Waugh *et al*. (2003), had showed the effect of varying the duration of butane/air pretreatment on the morphology and reactivity of vanadium pyrophosphate catalysts. From the research, it was concluded that the increasing of calcinations time will increase the surface are of the catalysts as well as change the bulk morphologies. Therefore, more oxygen can be removed from the lattice by reaction with hydrogen. As a conclusion, it was predicted that the longer duration of calcinations will produce a more active and more selective catalyst (K.C. Waugh *et al*., 2003).

Furthermore, the effect of calcinations temperature of the VPO catalyst was also observed by Arias-Perez *et al*. After the calcinations for 400 °C, 500 °C and 600°C, it showed that the vanadium pyrophosphate is present in the VPO with a P/V = 1.0. A higher crystallinity will be obtained with the calcinations temperature of

600°C. The crystal sizes were confirmed by X-ray diffraction (XRD). The calcinations temperature showed significant effect on the specific area of the VPO catalyst. Therefore, it was confirmed that the specific area of the vanadates of phosphorus was improved. Nevertheless, the increase in the calcinations temperature will have a gradual reduction of the acidity (Arias-Perez *et al.*).

2.3.2 Support System

Vanadyl pyrophosphate is the main component in the active catalyst. However, there is still little is known about the exact nature of the catalytic active sites. Therefore, many efforts have been devoted to develop the supported VPO systems as the supported VPO express the characteristics to the bulk VPO catalysts. Despite of that, supported VPO usually consisted of V^{5+} species mostly in α–$VOPO_4$ and γ- $VOPO_4$ form. This will exhibited low MA selectivity and low butane conversion according to Burfield *et al.* (1978).

One example showed in the research by Ostroushko *et al.* (1971) is the titania-supported VPO. It showed that the catalyst was already active at moderate temperatures. This is caused by the strong interaction between the VPO species and the reducible support titania. Titania as a support system will make the VPO species to be more reducible and the catalytic activity will be increased. Therefore, the MA selectivity will be lower. By using silica as a support material, it will improve the MA selectivity and the butane conversion.

The supporting VPO on various oxides has several potential advantages over unsupported one. Therefore, supported VPO catalysts on different support materials have been tried. The different support material in VPO catalyst will have different affect to the catalytic performance and selectivity. This will definitely influence the production of MA and the conversion of the butane (Z. Q. Zhou *et al.*, 2004).

2.3.3 Doped System

The precursor is converted to the vanadium pyrophosphate during the activation. However, several $VOPO_4$ phases are in low proportion. Therefore, a variety of cations have been added to vanadium phosphorus catalysts to improve the activity and selectivity. Besides, the catalytic properties and the mechanical resistance are improved. The promoters are added to improve the activity and selectivity of the catalyst though the roles of promoters are still unresolved (L.Cornaglia *et al.*, 2003).

From the research by Hutchings *et al.* (1991), the effect of cobalt used as a promoter is observed. Y.Takita *et al.* (1993) sustained that the additives were incorporated into the crystal lattice of vanadyl pyrophosphate. On the other hand, Hutchings *et al.* (1996) studied that the presence of cobalt enhanced the surface phosphorus enrichment and modified the surface acidity. In spite of this, Zazhigalov *et al.* (1993) proposed that the cobalt stabilize the catalyst performance. The formation of the cobalt phosphate will improve the catalytic properties. The smallest amount of the dopant produced the most beneficial effect (V. A. Zazhigalov *et al.*, 1993).

The beneficial effects of cobalt upon the performance of the VPO formulations were proved (L.Cornaglia *et al.*, 2003). The concentration of Lewis acid sites increased. But the limit as the excessive abundance of the surface sites will decrease the selectivity of the system. Nevertheless, the formations of the cobalt phosphate will stablilize the excess phosphorus in the formulations. Cobalt was found to stabilize phosphorus in the lattice of the catalyst and reduce the sublimation of phosphorous under the high operating temperatures.

2.3.4 P/V Atomic Ratio

For the journal by M. R. Tousi *et al*. (2010), it had been found that the P/V atomic ratio plays important role in the reaction of VPO catalyst. However, the structure of the catalyst and the conversion was lack of discussion.

For present study, VPO catalyst was prepared with the different P/V ratio in organic medium. The crystallinity of the catalyst will increase by increasing the P./V ratio. The pattern of XRD was done to observe the main phase of the $VOHPO_4 \cdot 0.5H_2O$. Furthermore, the SEM micrographs of the catalysts showed that the morphology of the catalyst changed by varying the P/V ratio. Besides, the conversion increased by increasing the P/V ratio as well. The maximum selectivity will be obtained and the yield of the MA will shift to higher temperature.

The effect of P/V ratio is related to the acidity of the VPO catalyst. This will affect the production of MA. From the research, it had been studied that the VPO catalysts will have higher selectivity and activity by increasing the P/V ratio. This is due to the increasing of the surface area and crystallity of VPO catalyst. In addition, the enhancement of the acidity of Bronsted (P-OH) and Lewis acid sites are increased as well (M. R. Tousi *et al*., 2010).

2.4 Maleic Anhydride

Maleic anhydride is an important intermediate for chemical industry. It is used in the synthesis of fumaric and tartaric acid. It is also used for the production of unsaturated polyester resins, argricultural chemicals, lubricating oil additives and pharmaceuticals. MA is produced based on the VPO catalyst from partial oxidation of *n*-butane (Michel Abon *et al*, 1997).

Selective oxidation of *n*-butane to maleic anhydride is commercialized process for light paraffin conversion. The efficient catalysts primarily consist of unsupported vanadyl pyrophosphate. The research about the conversion of *n*-butane to maleic anhydride has been subjected (Z. Q. Zhou *et al.,* 2004). Several investigations have been reported with the catalytic chemistry of *n*-butane conversion to maleic anhydride using VPO catalysts. The identification and evaluation of the catalytically active VPO phases are investigated. The synthesis and characterization of the phases are observed.

The selective oxidation of *n*-butane to MA over VPO catalyst is attractive in view of the availability of *n*-butane and the carbon efficiency of the reaction. The *n*-butane content in the gas flow will contain oxygen. It is dangerous to let the oxygen pass over the catalyst due to the explosion danger.

Selective catalytic oxidation over the VPO catalyst proceeds through a Mars-Van-Krevelen mechanism. During the process, there is a circulation of the gas flow in which the catalyst is exposed exclusively to *n*-butane. The gaseous oxygen which is viable will ore-oxidized the catalyst. As a result, the recovery of the concentrated MA from the gas flow can be performed more easily. Moreover, the risk of explosion will be lower. As mentioned by Gleaves et al., the passing of oxygen in the flow of *n*-butane will leads to a rapid non-selective oxidation of the catalyst. Therefore, the selective catalytic oxidation with the absence of gaseous oxygen will achieve a higher selectivity of the catalyst (Daxiang Wang *et al.*, 2003).

CHAPTER 3

METHODOLOGY

3.1 Materials and Gases used

The chemicals used in research:

1. Vanadium (V) pentoxide, V_2O_5 (Merck)
2. *ortho*-Phosphoric acid, *o*-H_3PO_4 (85%) (Merck)
3. 1-butanol, $Ch_3(CH_2)_3OH$ (R&M Chemicals)
4. Nitric acid, HNO_3 (Fisher Scientific)
5. Sulphuric acid, H_2SO_4 (95-98%) (Systerm)
6. Potassium permanganate, $KMnO_4$ (Fisher Scientific)
7. Ammonium iron (II) sulphate, $(NH_4)_2Fe(SO_4)_2$ (R&M Chemicals)
8. Diphenylamine, Ph_2NH (ACROS)
9. Ammonium Dihydrogen Phosphate, $NH_4H_2PO_4$ (Merck)
10. Ammonium metavanadate, NH_4VO_3 (Merck)

The gases used in research:

1. 1 % oxygen in nitrogen (Malaysia Oxygen Berhad (MOX))
2. Liquefied Nitrogen Gas (Malaysia Oxygen Berhad (MOX))
3. 99.99 % Purified Argon (Malaysia Oxygen Berhad (MOX))
4. 99.99 % Purified Nitrogen (Malaysia Oxygen Berhad (MOX))
5. 99.99 % Purified Helium (Malaysia Oxygen Berhad (MOX))
6. Compressed Air

3.2 Methodology

The preparation of the bulk vanadyl pyrophosphate catalyst can take place via different routes:

1. **Sesquihydrate precursor route (VPOs)**
2. Organic route (VPOo)
3. Reduction of vanadyl phosphate dehydrate, $VOPO_4 \cdot 2H_2O$ phase (VPOd)

The preparation of the doped vanadyl pyrophosphate catalysts can take place via organic route and the reduction of $VOPO_4 \cdot 2H_2O$ phase. In this research, the preparation of the vanadyl phosphorus oxide catalyst takes place via the sesquihydrate precursor $VOHPO_4 \cdot 1.5H_2O$.

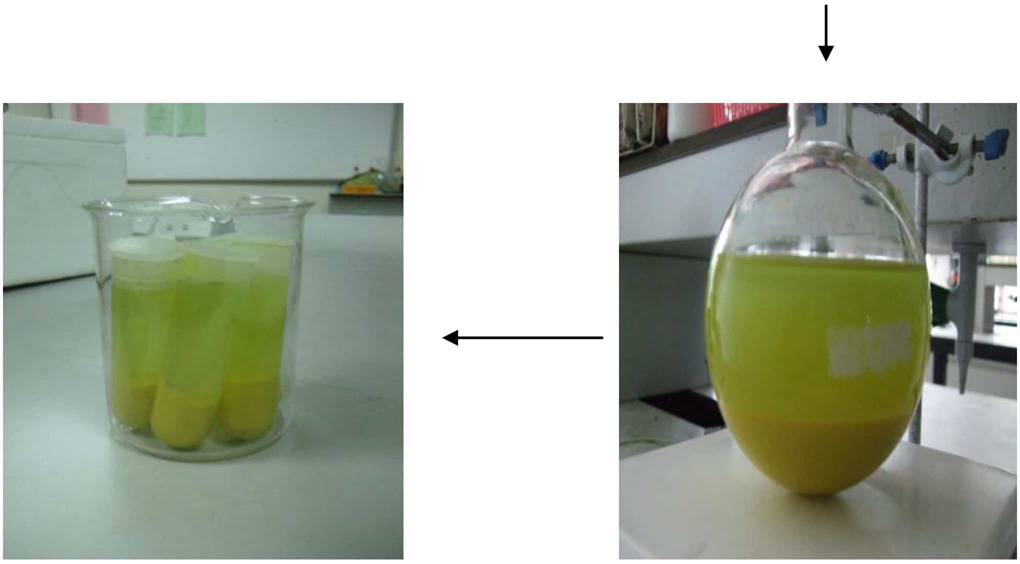
3.2.1 Preparation of the Vanadyl Phosphate Dihydrate ($VOPO_4 \cdot 2H_2O$)

The producing of vanadyl pyrophosphate catalyst has been developed via vanadyl hydrogen phosphate sesquihydrate precursor, $VOHPO_4 \cdot 1.5H_2O$ (Matsuura, 1995). The synthesis of sesquihydrate precursor has been divided into two-step procedure. This will involve vanadyl phosphate dehydrate, $VOPO_4 \cdot 2H_2O$ as an intermediate before obtaining the precursor.

Firstly, 15 g of vanadium pentoxide, V_2O_5 was weighted. It was then added with 90 ml of *ortho*-phosphoric acid, *o*-H_3PO_4 (85%) and 360 ml of distilled water. The mixture was then refluxed for 24 hours at 120 ^{o}C. A yellow intermediate will be formed. The mixture was cooled to room temperature and was centrifuged. Yellow solids recovered by centrifuge technique were washed sparingly with acetone and were oven dried (80 ^{o}C) for 24 hours. The yellow solids obtained are vanadyl phosphate dehydrate ($VOPO_4 \cdot 2H_2O$).

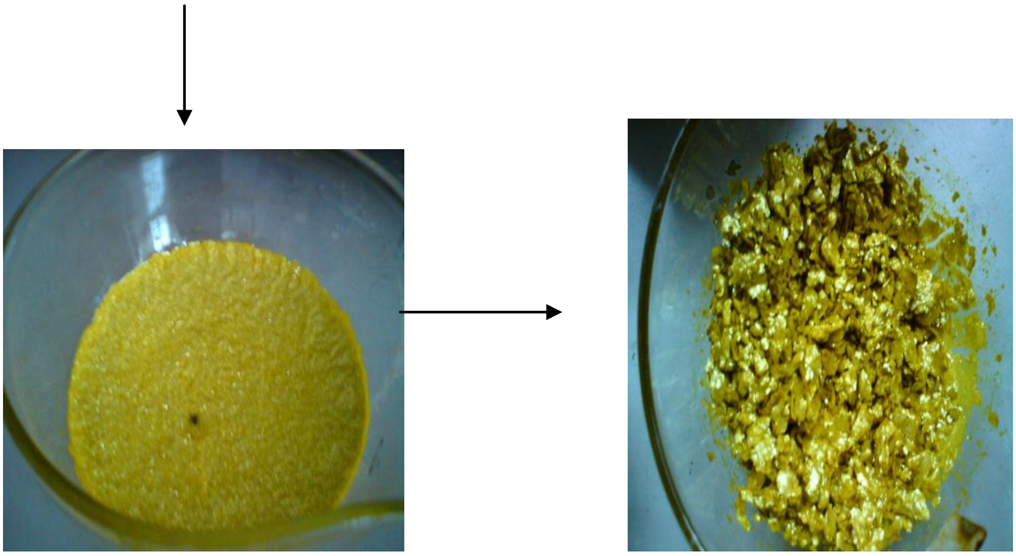
Before Reflux

Reflux



Centrifuge

After Reflux



Yellow Solid ($VOPO_4 \cdot 2H_2O$)

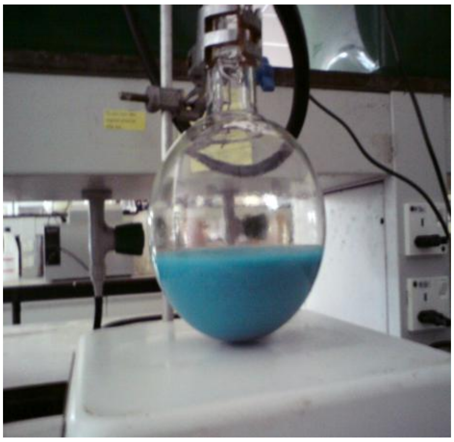
Figure 3.1: Preparation steps of the $VOPO_4 \cdot 2H_2O$

3.2.2 Preparation of the Vanadium Phosphorus Oxide Catalysts

10 g of $VOPO_4 \cdot 2H_2O$ precursors were added with 150 ml 1-butnanol. The mixture was then under reflux for 24 hour. After being cooled to room temperature, the resultant precipitate which is whitish-blue powder is referred to vanadyl hydrogen phosphate sesquihydrate precursor. Whitish-blue powder was recovered by centrifuge technique, washed sparingly with acetone and oven dried at 80 °C for 24 hours.

The resulting powder was then undergone calcinations in a reaction flow of 1% oxygen in nitrogen mixture for 18 hours for the following temperatures; 380 °C, 420 °C, 460 °C, 500 °C.

Before reflux



After reflux

After centrifuge and grinding

Before calcinations

After calcinations

Figure 3.2: Diagrams shows the preparation steps of VPO catalysts

3.3 Characterisation Techniques and Instrumentations

In this research, there are a few instruments involved to examine the physical and chemical properties of the catalysts produced. They are used to analyse the catalyst formed, which is vanadyl pyrophosphate catalyst.

The characterisation techniques used are:

1. X-ray Diffractometer (XRD)
2. BET surface area measurements
3. Redox titration
4. Scanning Electron Microscope (SEM) – EDX
5. Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES)

3.3.1 XRD Analysis

X-ray diffraction method is used for the structure analysis of crystals. The phase composition of catalysts is determined at ambient temperature and under normal atmospheric conditions. XRD technique is used for qualitative and quantitative analysis for crystalline structure compounds. The sample is irradiated with monochromatic X-ray light and the radiation is recorded. The sample must be plane-parallel and smooth. However, the amorphous fractions are not analysed. For this technique, simple texture measurements of layers on substrates can be rapidly carried out using position-sensitive detectors (I. Chorkendorff, J. W. Niemantsverdriet, 2003).

XRD analysis uses the property of crystal lattices to diffract monochromatic X- ray light. The diffraction occurs as waves interact with a regular structure which repeat distance is same as the wavelength. X-rays have wavelengths which is the same as typical interatomic distances in crystalline solids. This shows that X-rays can be diffracted from minerals which are crystalline and have repeating atomic structures. This will caused the waves scattered at the successive planes. Bragg’s law explained the interference pattern of X-rays scattered by crystals. The diffraction has been developed to study the structure of all states of matter with beam. This will be explained by the Bragg’s equation:

$$n\lambda = 2d\sin\theta$$

where,

λ = wavelength
d = lattice plane distance
θ = diffraction angle

Source: (Geochemical Instrumentation and Analysis)

In 1912, W. L. Bragg recognized a predicatable relationship among several factors:

1. The distance between similar atomic planes in a mineral which is called as the d-spacing and measure in angstroms.
2. The angle of diffraction which is called the theta angle is measured in degrees.
3. The wavelength of the incident X-radiation is symbolized by the Greek letter lambda.

The application of the XRD technique is widely used for the identification of unknown crystalline materials. The determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. Other applications include:

1. Characterization of crystalline materials
2. Identification of fine-grained minerals such as clays and mixed layer clays
3. Determination of unit cell dimensions
4. Measurement of sample purity

Source: (Geochemical Instrumentation and Analysis)

With this specialized technique, XRD can be used to determine crystal structures using Rietveld refinement and the modal amounts of minerals. Moreover, the thin films samples can be characterized by determine the lattice mismatch between film and substrate. The dislocation density and quality of the film can be determined by rocking curve measurements. Besides, the superlattices in multilayered epitaxial structures can be measured (Geochemical Instrumentation and Analysis).

XRD technique is powerful and rapid technique for identification of an unknown mineral. It provides an unambiguous mineral determination and minimal sample preparation is required. However, this technique shows some limitations. The XRD technique must have access to a standard reference file of inorganic compounds.

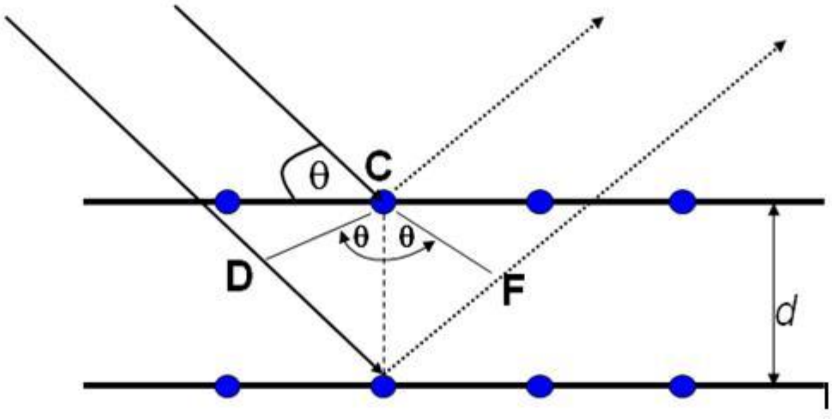


Figure 3.3: Bragg's Law Diagram

In this study, XRD patterned were obtained using Shimadzu diffractometer model XRD-6000 which employing CuKα radiation generated by a Philips glass diffraction X-ray tube broad focus 2.7 kW type on the catalysts at ambient temperature. The basal spacing was determined via powder technique. The samples were scanned at the range 2θ = 2 ° - 60 ° with a scanning rate of 1.2000 ° min^{-1}. The diffractograms obtained were matched against the Joint Committee on Power Diffraction Standards (JCPDS) PDF1 database version 2.6 to confirm the catalysts phases (Shimadzu).

Figure 3.4: Shimadzu XRD 6000

A gram of the catalyst powder was placed onto a sample holder and measured uniformly to create a flat upper surface. This is necessary to achieve a random distribution of lattice orientations. Then, a powder XRD scan was recorded as a plot of scattering intensity versus the scattering angle. The d spacing can be calculated by using Bragg's law. The identification of the VPO phases was obtained by comparing to the literature values reported by Bordes *et al.* (Masilo, 2009).

3.3.2 BET Multi-Point Surface Area Measurement

BET method is based on adsorption of gas on a surface. The BET surface area used the nitrogen adsorption at liquid temperature during the analysis. The amount of gas adsorbed will determine the surface area of the VPO catalyst.

BET method is a cheap, fast and reliable method to find the surface area of the catalyst. The BET extended the lattice gas model to the case of multi-layer films. This allows the particles to occupy a 3D array of sites above the surface. Moreover, BET plot provide a fairly reliable estimate of the monolayer capacity for nitrogen adsorption.

There are few assumptions for this BET techniques:

1. Homogeneous surface
2. No lateral interactions between molecules
3. Uppermost layer is in equilibrium with vapour phase
4. First layer: Heat of adsorption
5. Higher layer: Heat of condensation
6. At saturation pressure, the number of layers becomes infinite

Source: (http://zumbuhllab.unibas.ch/pdf/talks/080425_Tobias_BET.pdf)

The Sorptomatic 1990 is a complete computerized instrument based on a static volumetric principle to characterize solid samples by the technique of gas adsorption. It can be used to determine the specific surface area and the mesopore size distribution in porous materials by using inert gases such as nitrogen, argon, and carbon dioxide in the mode of physisorption measurements. However, the turbomolecular vacuum pump is used to assure the correct vacuum degree in the sample holder during the pre-treatment and before analysis start in the mode microporous materials. Other than that, an additional pressure transducer to measure very low equilibrium pressures with a suitable precision allows to properly characterize micropore size and volume (Sorptomatic 1990 (ThermoFinnigan)).

Figure 3.5: BET multipoint surface area measurement (ThermoFInnigan Sorptomatic 1990)

3.3.3 Redox Titration

This method was developed by Miki Niwa and Yuichi Murakami in 1982. They had investigated the reaction mechanism of the ammoxidation of toluene on V_2O_5/Al_2O_3 catalyst. The bifunctional activity of this catalyst which consists of the oxidation activity of V_2O_5 and the dehydration property of Al_2O_3 is stressed. However, some problems about the active sites of vanadium oxide and alumina and how they actually contribute to the ammoxidation of toluene remain a question (M. Niwa and Y. Mukakami, 1982).

In this research, redox titration was carried out to determine the average vanadium valence (AV) of the VPO catalysts and to obtain the average oxidation state of vanadium. First, a known amount of the sample is dissolved in 100 ml sulphuric acid (2 M). It is then cooled to room temperature before being titrated with potassium permanganate solution (0.01 N). This titrant is used to oxidise V^{3+} and V^{4+} in the solution to V^{5+}. The end point is reached when the change of colour from the original greenish blue to pink was observed. The volume of potassium permanganate used was recorded as V_1. Then the oxidised solution was treated with ammonium iron (II) sulphate solution (0.01 N). This is to reduce V^{5+} and V^{4+} in the solution. Diphenylamine is used as an indicator. The end point is reached when the purple colour of the solution disappeared and became colourless. The volume of ammonium iron (II) sulphate used was recorded as V_2 (M. Niwa and Y. Mukakami, 1982).

Another fresh 25 ml of the original solution was then titrated with 0.01 N ammonium iron (II) sulphate solution. Diphenylamine is also used as indicator. This stage of titration is to determine the V^{5+} in the original solution. The end point is reached when the solution changes from the purple to greenish blue. The volume of ammonium iron (II) sulphate solution used was recorded as V_3.

The average oxidation state of vanadium (AV) can be determined by solving the equation below:

$$AV = \frac{5V^{5+} + 4V^{4+} + 3V^{3+}}{(V^{5+} + V^{4+} + V^{3+})}$$

Where V^{3+}, V^{4+} and V^{5+} are concentrations of vanadium at different oxidation states. In order to obtain the values for V^{3+}, V^{4+} and V^{5+} values respectively. The following equations are used:

$$V^{3+} = 20(0.01)V_1 - 20(0.01)V_2 + 20(0.01)V_3$$
$$V^{4+} = 40(0.01)V_2 - 40(0.01)V_3 - 20(0.01)V_1$$
$$V^{5+} = 20(0.01)V_3$$

Where V_1= the volume of potassium permanganate used and V_2 = the volume of ammonium iron (II) sulphate used.

3.3.4 SEM – EDX

SEM-EDX is called as the energy dispersive X-ray spectroscopy analysis which is conducted by SEM. It determines the chemical composition of the specimen as well as the morphology and structure of the specimen.

An SEM is essentially a high magnification microscope which uses a focussed scanned electron beam to produce images of the sample. The primary electron beam interacts with the sample in few ways. The primary electrons generate low energy secondary electrons which tend to emphasize the topographic nature of the specimen. Then primary electrons can be backscattered which produces images with a high degree of atomic number contrast. Besides, the ionized atoms can relax by electron shell to shell transitions which lead to X-ray emission or Auger electron ejection. The X-rays emitted are characteristic of the elements (Handbook of analytical methods for materials).

SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of the solid specimens. The beam is produced by heating of a metallic filament. The beam makes its way through the electromagnetic lenses which focus and direct to the samples. After that, other electrons are ejected from the sample. The backscattered electrons are collected by the detectors. The detectors convert the electrons to a signal and the signal is sent to a viewing screen to produce an image (Handbook of analytical methods for materials).

The characteristic of SEM includes morphology, chemical composition, topography (texture), and crystallographic information. The morphology will show the shape and size of the catalysts. SEM analysis is non-destructive. The x-ray generated by electron interactions will not cause volume loss of the sample. Therefore, it is possible to reuse the sample to do the analysis repeatly. SEM is used to generate high-resolution images of shapes of objects to show the chemical composition. The phases can be identified by SEM based on the crystalline structure of the catalyst (Handbook of analytical methods for materials).

Figure 3.6: Hitachi S-3400N SEM and EDAX

The Hitachi S-3400N determined the catalyst's structure and the elemental composition. A small amount of the catalyst was used in the analysis. For the EDS characterization, the atoms on the surface of the catalyst powders are excited by the electron beam from the SEM. Then a specific wavelength which shows characteristic of the structure of the elements will be emitted. Before the analysis, the coating of the catalysts must be done. The catalyst surface will be coated with a thin layer of gold metal for conductive purposes during the analysis (Masilo, 2009).

SEM analysis involves focusing a finely collimated beam of electrons into a small probe which scans across the surface of the specimen. The interaction between the beam and the sample result in the emission of the electrons and photons, as the electron penetrates the surface of the sample. Lastly, the emitted particles are collected and set to the detector to provide information regarding the surface morphology (Masilo, 2009).

3.3.5 Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma Spectroscopy techniques are the sampling methods which are introduced in liquid form for analysis.

Inductively coupled plasma – optical emission spectrometry is used to determine the concentration of a wide range of elements in a solution. The instrument is typically directed to determinations of the light elements in the periodic table such as the alkali metals, alkaline earth metals, transition metals, metalloids and non-metals (Green).

In OES, a sample solution is introduced into the core of ICP which generates temperature of approximately 8000 ^{o}C. At this temperature, all elements become thermally excited and emit light at their characteristic wavelengths. This light is collected by the spectrometer and passes through a diffraction grating that serves to resolve the light into a spectrum of its constituent wavelengths. Within the spectrometer, this diffracted light is then collected by wavelength and amplified to yield an intensity measurement that can be converted to an elemental concentration by comparison with calibration standards (LLC, 2011).

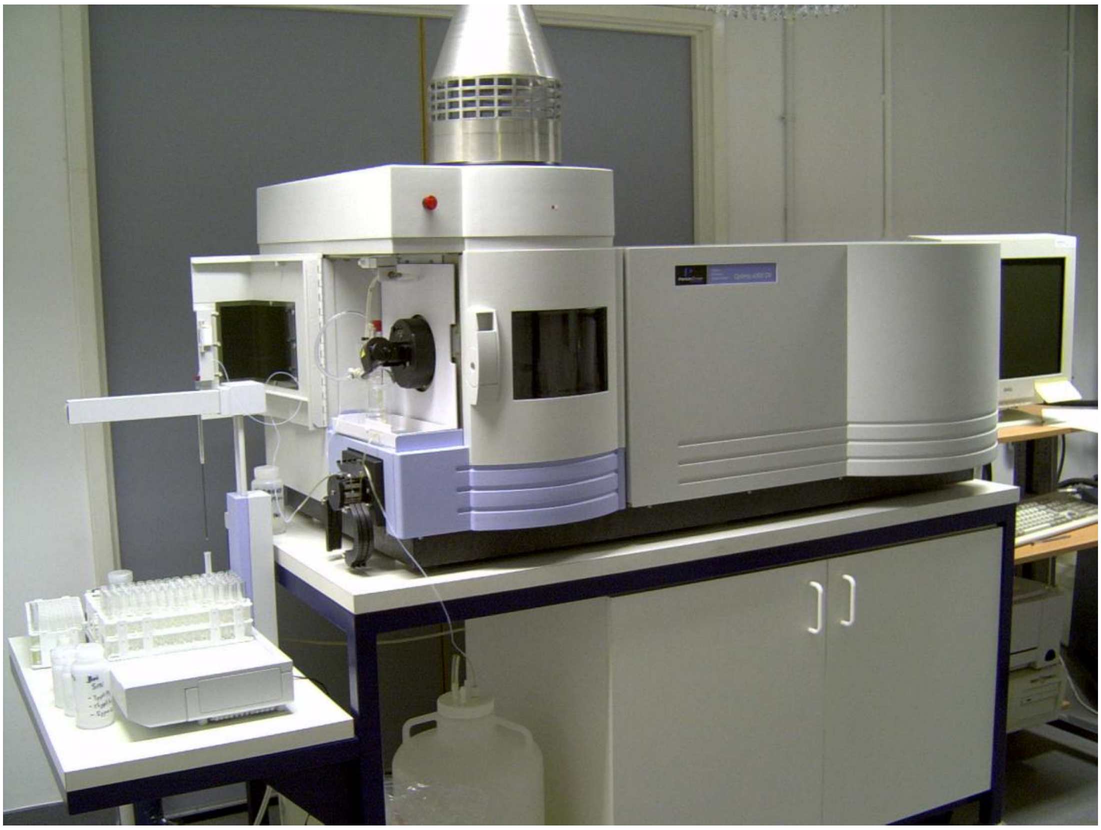


Figure 3.7: Perkin-Elmer Emission Spectrometer Model Plasma 1000

For this technique, the sample is aspirated into an inductively coupled plasma discharge. The analyte is converted into the gas-phase atoms in their excited states. Besides, the emitted light produced by the excited atoms is measured relative to the concentration range of the standards to give the sample concentration (Masilo, 2009).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 X-ray diffraction (XRD)

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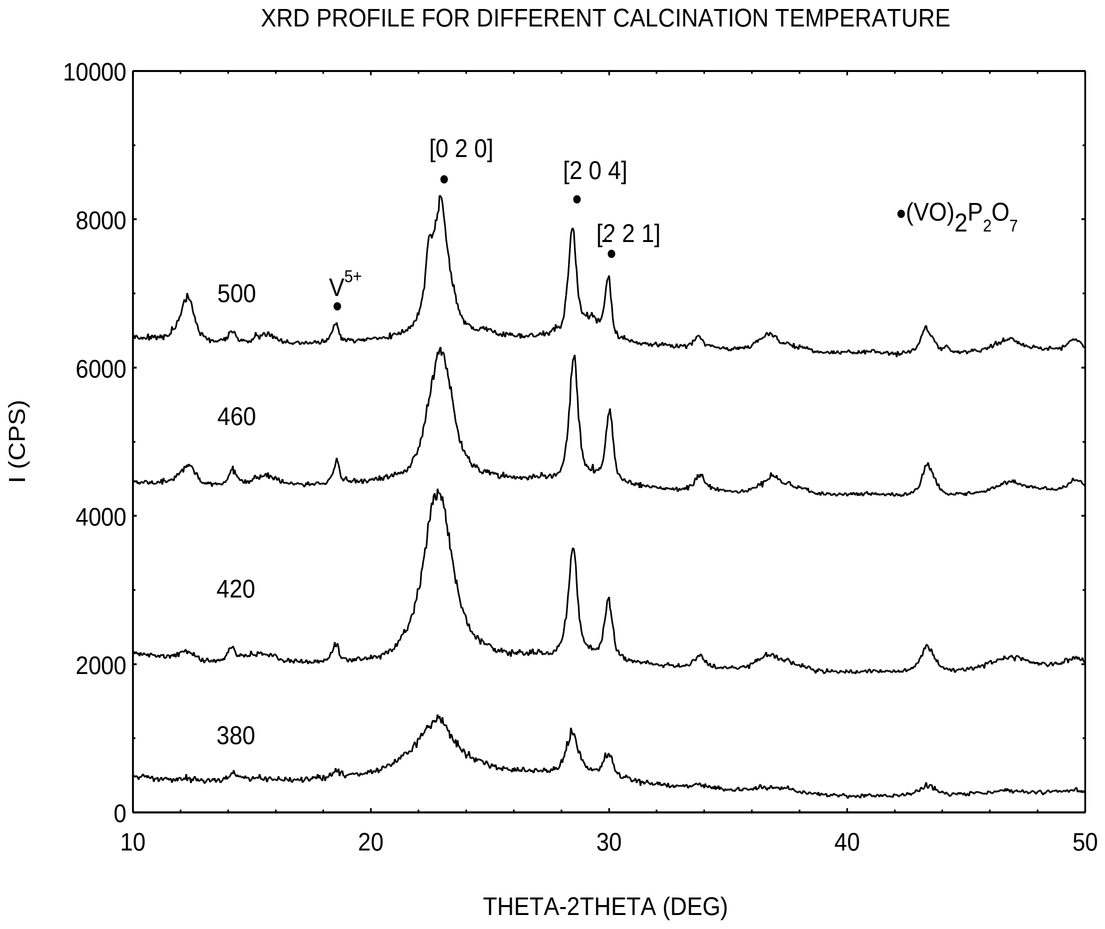

Figure 4.1: XRD patterns for VPO of different calcinations temperatures

The XRD pattern of the four catalysts in Figure 4.1 shows the characteristic reflection of vanadium pyrophosphate, $(VO)_2P_2O_7$. The four catalysts were calcined under different temperature of 380, 420, 460, 500 degree Celcius in the flow of 1% oxygen in nitrogen. This well-crystallized $(VO)_2P_2O_7$ phase shows three main characteristic peaks appeared at $2\theta = 22.8^{o}$, 28.4^{o} and 29.8^{o} which corresponding to [0 2 0], [2 0 4], and [2 2 1] planes respectively. Moreover, XRD reveals the presence of the V^{5+} phases.

The development of the crystalline structure transformation of the surface morphology is affected by duration of calcinations as well as the calcinations atmosphere. As compared to the calcination under the flow of *n*-butane, the catalyst calcined by 1% of oxygen in nitrogen has higher crystallinity.

From XRD data, the crystalline size of the catalyst can be calculated. The sample calculation will be attached in appendix. The table below will show the crystalline size of four catalysts. It shows that the crystalline size of the catalysts increase with higher calcinations temperature.

Table 4.1: Crystalline size for four catalysts under different calcination temperature

Catalysts	Crystalline size, T (Ǻ)		
	[0 2 0]	[2 0 4]	[2 2 1]
VPO-380	37.5914	90.6358	84.4816
VPO-420	55.0037	114.4000	115.0634
VPO-460	63.7685	125.5868	127.13995
VPO-500	70.3325	112.3988	100.8134

4.2 Brunauer-Emmet-Teller (BET)

BET analysis is to get the surface area of the catalysts. From the table 4.2, it shows that the surface area of catalysts decrease with the increasing of the calcinations temperature of catalysts. As in the XRD diffraction patterns, the increasing of crystalline size will have decreasing surface area of catalysts. This is due to the sintering effect during the high temperature of calcinations. The surface recrystallization of the catalysts will cause the activity of the catalyst surface area reduced. The surface areas of the catalysts are shown below:

Table 4.2: BET surface area for the catalysts of different calcinations temperature

Catalysts	Surface area (m^2/g)
VPO-380	15.5942
VPO-420	12.2660
VPO-460	11.5825
VPO-500	6.9233

When looking at the variation of the BET surface area as a function of the VPO amount, the surface of the samples will be affected by the contribution of the VPO phase to the surface area. This indicated that the porosity of the catalyst will affect the surface area of the catalyst (Z. Q. Zhou *et al.*, 2004). Besides, the amount of the platelets present in the VPO crystalline structure and the degree of isolation for the platelets should be considered as well.

4.3 Redox Titration

Redox titration was performed in the analysis to determine the average oxidation state of vanadium in the catalysts. Active and selective VPO catalysts present a mean oxidation state of vanadium slightly higher than 4.0 usually associated with a P/V ratio slightly higher than 1.0. They are the characteristic of the $(VO)_2P_2O_7$ phase. The redox role of V^{5+} and V^{4+} sites during the catalytic process has been proposed. Further works have considered that the active phase is constituted by the main $(VO)_2P_2O_7$ phase (V^{4+}) with some $VOPO_4$ (V^{5+}) (Michel Abon *et al*, 1997).

From the table 4.3, it shows that the average oxidation state of vanadium all above 4. This shows that the oxidized phase such as $VOPO_4$ exist in the catalyst. However, this is not shown in the XRD profile. The results of the redox titration are shown below:

Table 4.3: V_{av} for catalysts under different calcinations temperature

Catalysts	V_{av}	V^{4+} (%)	V^{5+} (%)
VPO-380	4.34	66	34
VPO-420	4.277	72.3	27.7
VPO-460	4.2318	76.82	23.18
VPO-500	4.3204	67.96	32.04

The different calcination temperatures of catalysts show that V_{5+} decrease with the increasing of temperature. However, it shows higher percentage of V^{5+} at the highest temperature of 500°C. This result reflects that the selectivity of the catalyst will decrease with the increase of temperature until the highest temperature of 500 °C. On the other hand, the percentages of V^{4+} in catalysts increase with the temperature but decrease at the highest temperature of 500 °C. This indicates that the activity of the catalysts increase with the temperature but decrease at the highest temperature due to the sintering effect upon the catalyst.

4.4 Scanning Electron Microscope (SEM)

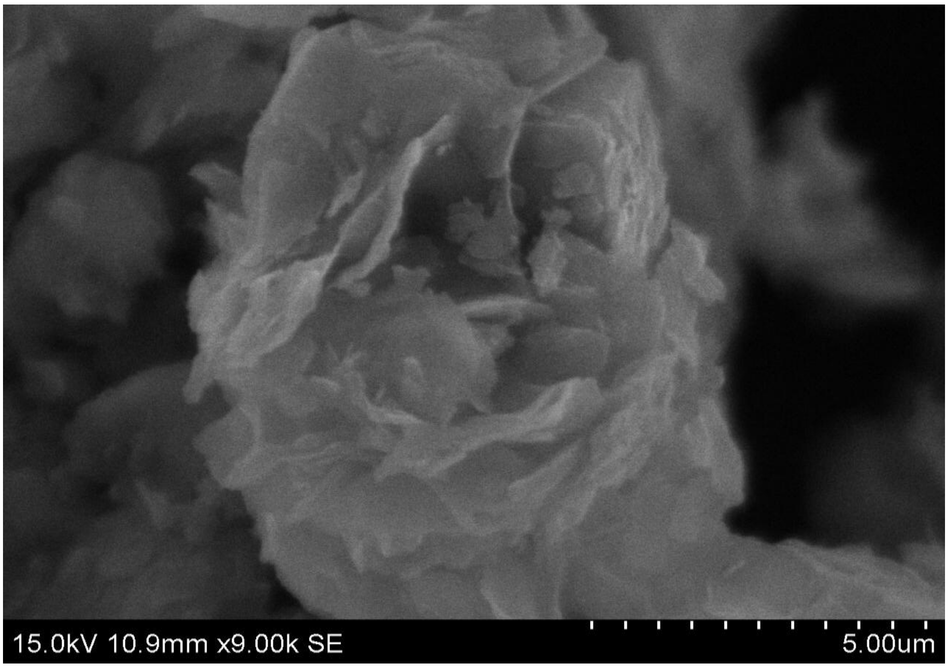

Figure 4.2: SEM image for VPO-380

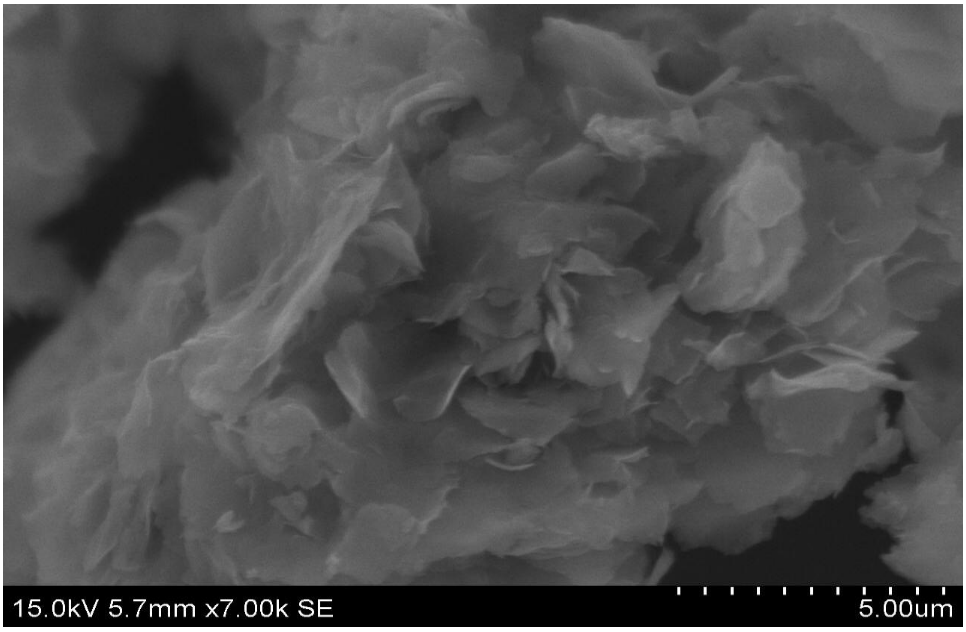

Figure 4.3: SEM image for VPO-420

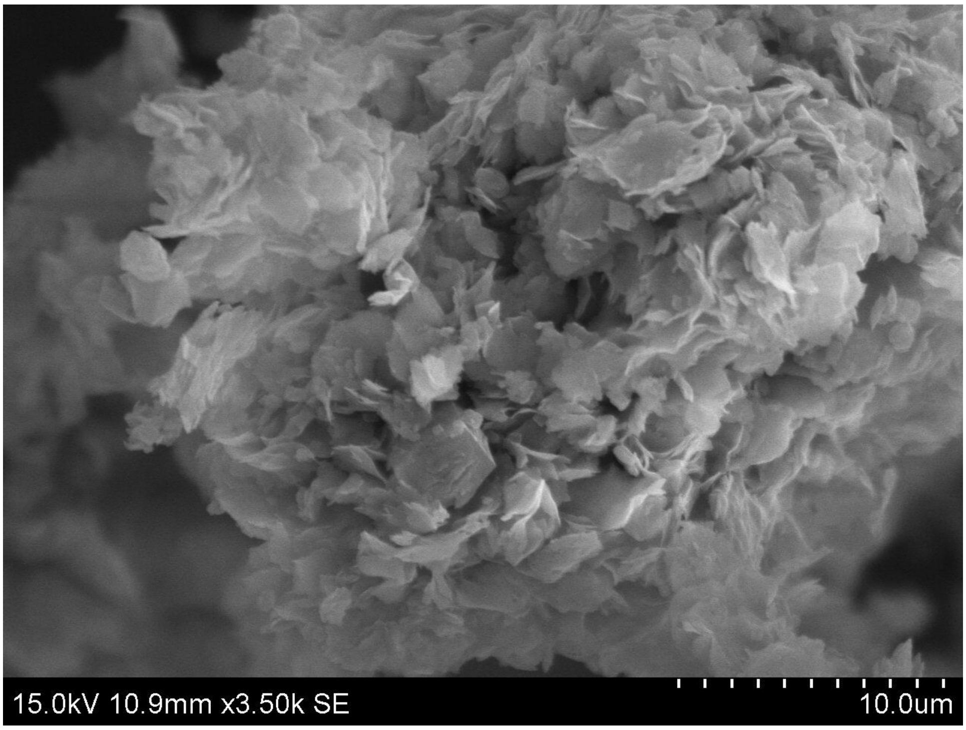

Figure 4.4: SEM image for VPO-460

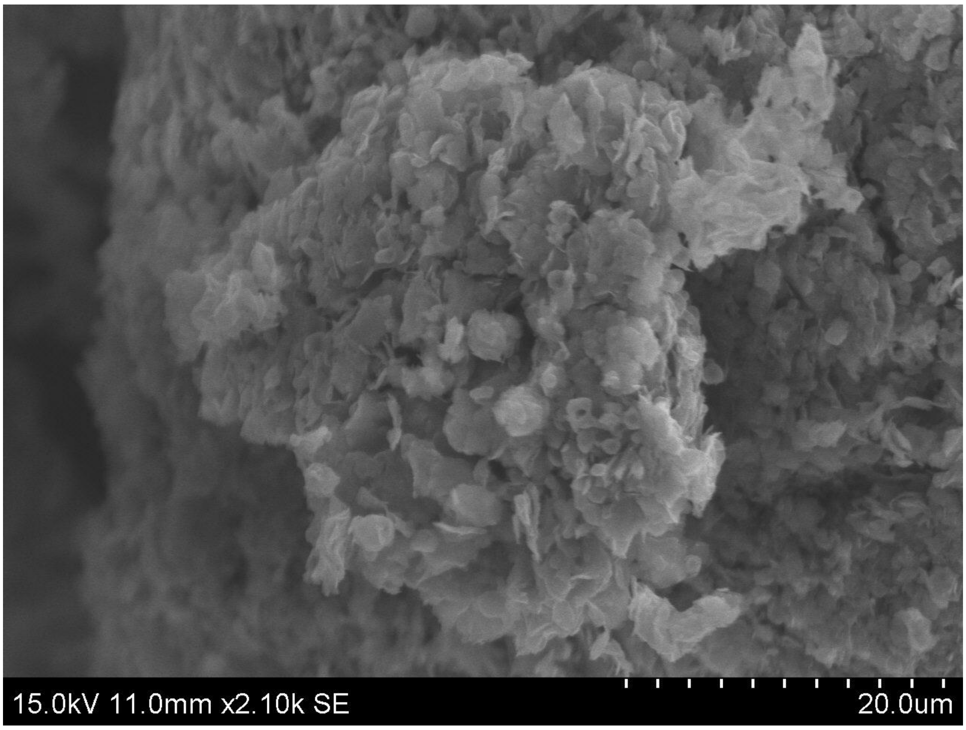

Figure 4.5: SEM image for VPO-500

The result of scanning electron microscopy shows the surface morphologies of the catalysts obtained with different calcination temperatures. The basic structure of the VPO catalyst is rosette-platelet like crystal. The difference among these four catalysts is the amount of the platelet in the characteristic rosebud shape agglomerates. These rosebud shapes agglomerates are made up of vanadium pyrophosphate platelets which expose the [0 2 0] crystal plane (K.C. Waugh *et al.*, 2003).

The figures above show the SEM images for different calcination temperature from 380, 420, 460 to 500 degree Celcius. A lower surface area obtained from the synthesized catalyst may due to the bulk morphologies of the catalyst after sintering effect. This can be proved by BET analysis. Figure 4.5 shows the bulky catalyst which has the lowest specific surface area in BET analysis. However, Figure 4.2 shows the platelet crystals and has the highest surface area among all catalysts.

4.5 Scanning Electron Microscope (SEM-EDX)

SEM-EDX refers to the electron dispersive x-ray spectroscopy. By using SEM-EDX, the P/V ratio can be calculated. However, the P/V ratio obtained from SEM-EDX is not as precise as ICP-OES. As compare the P/V ratio of EDX and ICP, EDX will get lower P/V ratio than ICP as EDX calculate the P/V ratio based on surface technique which penetrating a few microns of the catalyst surface. This is due to little of phosphorus is at the surface of the catalysts than the vanadium. Therefore, the P/V ratio will be lower. However, the catalysts are dissolved in nitric acid with different concentration to calculate the concentration of the component in the sample for ICP analysis. Therefore, the P/V ratio obtained from ICP will be more precise.

The table below will show the P/V ratio for catalysts under different calcinations temperature.

Table 4.4: SEM-EDX which show P/V ratio

Catalysts	Phosphorus,P (At%)	Vanadium, V (At%)	P/V ratio
VPO-380	24.18	23.36	1.04
VPO-420	23.58	20.29	1.16
VPO-460	23.24	19.18	1.21
VPO-500	23.92	22.17	1.08

4.6 Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

ICP-OES is used to determine the bulk chemical composition in the samples. The concentration of phosphorus and vanadium is obtained in the inductively coupled plasma-optical spectroscopy. The P/V ratio is calculated and stated at the table below:

Table 4.5: P/V ratio from ICP-OES

Catalysts	Concentration of phosphorus, P (mg/L)	Concentration of Vanadium, V (mg/L)	P/V ratio
VPO-380	22.9	33.73	1.1166
VPO-420	19.77	27.70	1.1739
VPO-460	21.79	26.67	1.3438
VPO-500	22.60	30.00	1.2390

From this chemical analysis, it shows that the content of phosphorus is getting higher with increasing calcinations temperature. The P/V ratios of catalysts are between 1.11 to 1.34 which were in the range of optimal P/V ratio to produce the vanadium pyrophosphate phase. However, the phosphorus component for VPO-500 drops slightly compared to VPO-460. The slightly excessive of phosphorus helps to stabilize the V^{4+} oxidation state and limits the over oxidation of $(VO)_2P_2O_7$ to $VOPO_4$ in the reactant's atmosphere and in air (Y.H.Taufiq-Yap *et al.*, 2007).

From table 4.3, it shows the V^{4+} and V^{5+} increasing with the calcinations temperature. This indicates that the catalyst with higher temperature have high activity but low selectivity. The catalysts with high phosphate concentration will have low activity catalysts.

It was also reported that P/V ratio is one of the key factors in catalysts preparation to avoid the oxidation of $(VO)_2P_2O_7$ to a V^v phosphate. The preparation route of the VPO catalysts appears to be more important in determining the P/V ratio of the catalysts.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The VPO catalyst under temperature 460 °C showed the optimum temperature to get optimum activity. This is shown in table 4.3 that the V^{4+} percentage of VPO-460 is the highest among other catalysts. However, the selectivity of VPO-460 decreased compared to others. This can be proved by BET analysis which shows that the specific surface area of the catalysts decreased with the increasing calcination temperature.

For the physical characteristic of the catalysts, the changes of the catalysts morphology were shown through the SEM analysis. The catalysts will form agglomerated rosette platelet from stacked platelet and then become bulky at highest temperature of 500 °C. This is due to the sintering effect. This statements can be proven by the x-ray diffractograms which indicates the crystallize size of the catalysts. The highest crystallize size will show the lowest surface area in BET analysis and therefore will get the bulky catalysts at highest temperature.

The redox titration of the catalysts indicated the average oxidation state close to 4 which proved that the presence of $(VO)_2P_2O_7$ in catalysts as the major phase. Overall, the catalysts show a trend to improve the maleic anhydride selectivity by changing the calcinations environment. This will influence the morphology and the reducibility of the catalysts

5.2 Recommendations

The catalytic performance should be done to obtain the conversion of maleic anhydride, as well as the selectivity and the activity of the catalysts. This can support the chemical and physical performance of the catalysts of this final year project.

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APPENDICES

APPENDIX A:

Volume of Isobutanol Used

Molecular formula of vanadyl phosphate dihydrate = $VOPO_4\ _2H_2O$

Molecular weight of Vanadium = 50.9414 g/mol

Molecular weight of Phosphate = 30.97376 g/mol

Molecular weight of Oxygen = 15.9994 g/mol

Molecular weight of Hydrogen = 1.0079 g/mol

Molecular weight of $VOPO_4\ _2H_2O$ = 50.9414 g/mol + (7×15.9994 g/mol) + 30.97376 g/mol + (4×1.0079 g/mol)

= 197.94256 g/mol

No. of mol of $VOPO_4\ _2H_2O$ $= \frac{mass}{molecular\ weight}$

$= \frac{10\ g}{197.94256\ g/mol}$

= 0.05052 mol

(50 mol alcohol/ mol $VOPO_4\ _2H_2O$)

For 1 mol of $VOPO_4\ _2H_2O$, 50 mol of alcohol (iso-butanol) is needed.

From the calculation as shown above, 0.05052 mol of $VOPO_4\ _2H_2O$ is used.

$$\frac{0.05052\ mol\ \mathrm{VOPO4 \cdot 2H2O}}{1\ mol\ \mathrm{VOPO4 \cdot 2H2O}} \times 50\ mol\ alcohol = 2.5260\ mol\ alcohol$$

Thus, 2.5260 mol of alcohol (iso-butanol) is needed for 0.05052 mol of $VOPO_4\ _2H_2O$.

Molecular formula of iso-butanol = $C_4H_{10}O$

Molecular weight of Carbon = 12.011 g/mol

Molecular weight of Oxygen = 15.9994 g/mol

Molecular weight of Hydrogen = 1.0079 g/mol

Molecular weight of $C_4H_{10}O$ = $(4\times12.011\text{ g/mol}) + (10\times1.0079\text{ g/mol}) + 15.9994\text{ g/mol}$

= 74.1224 g/mol

Density of $C_4H_{10}O$ = 0.802 g/cm^3 at 20 ℃

Mass of $C_4H_{10}O$ = $74.1224\text{ g/mol} \times 2.5260\text{ mol}$

= 187.2332 g

Density $= \frac{mass}{volume}$

Volume of iso-butanol $= \frac{mass}{density}$

$$= \frac{187.2332\ g}{0.802\ g/cm^3}$$

$= 233.4578\text{ cm}^3$

Therefore, total volume of iso-butanol added is 233.4578 cm^3.

APPENDIX B:

Volume of Distilled Water Used

(24 ml H_2O/ g solid)

15 g of V_2O_5 is used as a starting material.

Thus, the volume of distilled water needed = 15 g × (24 ml H_2O/ g solid)

= 360 ml

APPENDIX C:

Crystallite Size Measurements by using Powder XRD Technique

Crystallite size, T given by Debye-Scherrer equation: $T(\text{Å}) = \frac{0.89\lambda}{FWHM \times cos\theta}$

Given $\lambda_{\text{Cu K}\alpha} = 1.54\text{Å}$

$$\text{FWHM (rad)} = \text{FWHM} (^\circ) \times \frac{\pi}{180^\circ}$$

APPENDIX D:

Preparation of Diphenylamine, Ph_2NH Indicator (Redox Titration)

1 g of diphenylamine was weighed and dissolved in a few ml of concentrated sulphuric acid, H_2SO_4. Then the solution was transferred to a 100 ml volumetric flask and further top up with concentrated H_2SO_4.

Preparation of 2 M sulphuric acid, H_2SO_4 solution

Concentrated H_2SO_4 (95-98 %)

1 L = 1.84 kg = 1840 g/ 1000 cm^3 = 1.84 g/ cm^3

Molecular weight of H_2SO_4 = 2 (1.00 g/mol) + 32.07 g/mol + 4 (16.00 g/mol)

= 98.07 g/mol

Concentration of 95-98 % H_2SO_4 = $\frac{1.84\ g/cm^3}{98.07\ g/mol} \times \frac{95}{100} \times 1000$ = 17.82 M

$M_1V_1 = M_2V_2$ where M_1 = concentration of 95-98 % H_2SO_4

M_2 = concentration of diluted H_2SO_4 (2M)

V_1 = volume of 95-98 % H_2SO_4

V_2 = volume of diluted H_2SO_4 (2M)

$(17.82\ M)(V_1) = (2\ M)(1000\ cm^3)$

$V_1 = 112.23\ cm^3$

Preparation of 0.1 M sulphuric acid, H_2SO_4 solution

$M_1V_1 = M_2V_2$ where M_1 = concentration of 95-98 % H_2SO_4
M_2 = concentration of diluted H_2SO_4 (0.1)
V_1 = volume of 95-98 % H_2SO_4
V_2 = volume of diluted H_2SO_4 (0.1)

$(17.82\ M)(V_1) = (0.1M)(1000\ cm^3)$
$V_1 = 5.61\ cm^3$

Preparation of 0.01 N Potassium Permanganate, $KMnO_4$ (Redox Titration)

Normality, N (eq/L) = M (mol/L) x *n* (eq/mol)

$MnO^{4-} + 8\ H^+ + 5\ e^- \leftrightarrow Mn^{2+} + 4\ H_2O$

$$\text{Molarity, M (mol/L)} = \frac{N(eq/L)}{n(eq/mol)} = \frac{0.01}{5} = 0.002\ M$$

Molecular weight for $KMnO_4$ = 39.10 g/mol + 54.94 g/mol + 4 (16.00 g/mol)
= 158.04 g/mol

Weight for $KMnO_4$ in 1000 cm^3 diluted (0.1 M) H_2SO_4 = 0.002 x 158.04
= 0.3161 g

Preparation of 0.01 N ammonium iron(II) sulphate, $(NH_4)_2Fe(SO_4)_2\ 6H_2O$ (Redox Titration)

Normality, N (eq/L) = M (mol/L) x *n* (eq/mol)

$Fe^{2+} + e^{-} \leftrightarrow Fe^{3+}$

$$\text{Molarity, M (mol/L)} = \frac{N(eq/L)}{n(eq/mol)}$$

$$= \frac{0.01}{1}$$

$$= 0.01 \text{ M}$$

Molecular weight for $(NH_4)_2Fe(SO_4)_2\ 6H_2O$ = 2 (14.00 g/mol) + 20 (1.00 g/mol) + 55.85 g/mol + 2 (32.07 g/mol) + 14 (16.00 g/mol)

= 391.99 g/mol

Weight for $(NH_4)_2Fe(SO_4)_2\ 6H_2O$ in 1000 cm^3 diluted (0.1 M) H_2SO_4

= 0.01 x 392.14

= 3.9214 g

APPENDIX E:

Oxidation State of Vanadium (Redox Titration)

According to Niwa and Murakami (1982),

For stage 1 titration:

The amount of $KMnO_4$ used in titration = V_1

The amount of Ammonium Iron (II) Sulphate used = V_2

For state 2 titration:

The amount of Ammonium Iron (II) Sulphate used = V_3

$V^{4+} = 40(0.01)\,V_2 - 40(0.01)\,V_3 - 20(0.01)\,V_1$

$V^{5+} = 20(0.01)\,V_3$

The average vanadium valence is calculated as:

$$V_{AV} = \frac{4V^{4+} + 5V^{5+}}{V^{4+} + V^{5+}}$$

If $V_{AV} = 4.3333$,

V^{5+} (%) = 33.3%

V^{4+} (%) = 100-33.3 = 66.7%