IMPROVING THE PHYSICOCHEMICAL PROPERTIES OF MoVNbTe BY USING REFLUX METHOD

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JULY 2009

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by

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7711

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JULY 2009

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CERTIFICATION OF APPROVAL

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Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

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July 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(Mohd Rifae b. Saroji)

ABSTRACT

MoVNbTe catalyst has been found to be a good catalyst for ammoxidation of propane to Acrylonitrile (ACN). MoVNbTe is to be prepared via reflux method. Synthesised catalyst is then characterized by using Fourier Transform Infra Red Spectrometry (FTIR), scanning electron microscopy (SEM), Brunauer, Emmet and Teller (BET) equation and X-ray Diffraction (XRD). The surface area and pore size of these catalysts were measured using physical adsorption of nitrogen following (BET) equation. The textural and morphological of these catalysts was determined using (SEM) and (XRD). Modification will be done primarily for process temperatures especially reflux temperatures ranging from 90°C, 115°C and calcinations temperatures will be vary between 450°C and 600°C. This is to relate the heat treatment with the formation of the catalyst. Duration of the heat treatment also being studied by changing of the reflux time which are 4 hours and 12 hours. Application of alcohol (e.g. ethanol, methanol) as the solvent will also be implemented.

ACKNOWLEDGEMENT

First of all, I want to thank the god for the blessing on me upon doing this project. I also want to give millions of appreciations to my supervisor, AP. Dr. Anita Ramli for her kind guidance and superb knowledge that really helping and supporting me while doing this project. Without her this project will not be successful. Not forget to all my dearest friends who helps, support, encourage and assisting me in this project. Also thanks to FYP laboratory coordinators, Mr. Fadzli and Mr. Jailani whom guide and help me during the progress in the laboratory. They also help me in fetching the equipments and chemicals for my project. Finally thanks to UTP for allowing me to do this project.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

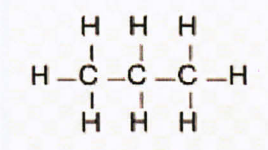
Acrylonitrile is becoming popular upon its usage on the entire world. Many daily materials production is consist of this chemical. Acrylonitrile is used principally as a monomer in the manufacture of synthetic polymers, especially polyacrylonitrile which comprises acrylic fibers, widely used to make clothing and carpeting. Acrylic fibers are, among other uses, is the raw material for well-known carbon-fiber. Acrylonitrile Butadiene Styrene (ABS) also one product of Acrylonitrile polymer, it is a common thermoplastic used to make light, rigid, molded products such as piping, musical instruments, and automotive parts.

Currently, most ACN production in industry is using SOHIO process. The SOHIO process is an ammoxidation of propylene within following equation:

$$2CH_3\text{-}CH{=}CH_2 + 2NH_3 + 3O_2 \rightarrow 2CH_2{=}CH\text{-}C{\equiv}N + 6H_2O$$

Process is founded by scientists and engineers at The Standard Oil Company, or Sohio discovered and developed this reaction in the 1950s. In this process, propylene, oxygen, and ammonia are catalytically converted directly to acrylonitrile using a fluidized-bed reactor operated at temperatures between 400°C and 500°C and gauge pressures between 0.3 and 2 bar. Today, nearly all acrylonitrile is produced by the Sohio process, and catalysts developed at the Warrensville Laboratory are used in acrylonitrile plants around the world. This SOHIO process, using propylene, found to be very efficient in producing more than **80% yield of Acrylonitrile**. Due to the risk of propylene shortage, and increasing demand for ACN, many researches have been carried out in this area.

There was then a research done to **replace propylene with propane**. Propane is far cheaper than propylene, cost only half price of that propylene, primarily because the characteristic of propane which is relatively unreactive. Propylene having double-bond among its carbon atom provide a space for reaction, while propane on the other hand known as a single-bond hydrocarbon, is hardly to gain a chemical reaction.



$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

Above picture show the single-bond propane. In such reaction, the C-H bond activation in propane is nearly 10 times lower than that of propylene (Bowker et. al., 1996), so the conversion of propane is at least ten times smaller than the propylene under similar reaction condition (Sokolovskii et. al, 1995). In order to break the single bond, the process of high temperature is required. This energy demanding reaction has a negative impact on selectivity and proves to be costly. Therefore the propane ammoxidation requires a new catalyst which is more active than those used in SOHIO process.

1.2 Problem Statement

Catalytic research has long been done to develop a suitable catalyst for ammoxidation of propane to acrylonitrile. A catalyst Mo-V-Nb-Te found to be a good catalyst for this purpose. The vanadium ion surface sites are the propane activating sites, while Mo, Nb and Te improve the performance of the system for propane ammoxidation. However the **22% yield of ACN** from propane in presence of MoVNbTe cannot compromise an efficient process for commercial purpose.

Several researches have been done; showing that the way of preparing the catalyst will have an impact on the characteristic of the catalyst itself. Modification will be done on the methodologies of preparing the MoVNbTe catalyst, primarily in regarding with the reflux method. This research is done in attempt to improve the yield of ACN from ammoxidation propane by improving the physicochemical properties of the MoVNbTe catalyst for this reaction.

1.3 Objectives

1) To synthesis MoVNbTe catalyst by using the reflux method.
2) To do the modification on the reflux method by mean of changing the reflux temperature, calcination temperature, and reflux time.
3) To characterized the physicochemical properties of MoVNbTe catalysts using SEM, BET, and XRD.

1.4 Scope of Study

This experiment will be focused on synthesising of MoVNbTe using reflux method only. The main part of the experiment is the modification while preparing the catalyst especially the modification on processes temperatures (e.g. reflux temperatures, Calcinations temperatures) and the duration of the reflux. The physicochemical properties of the produced catalysts will be determined using the X-ray diffraction (XRD), BET Method, and Scanning Electron Microscope (SEM)

CHAPTER 2

LITERATURE REVIEW

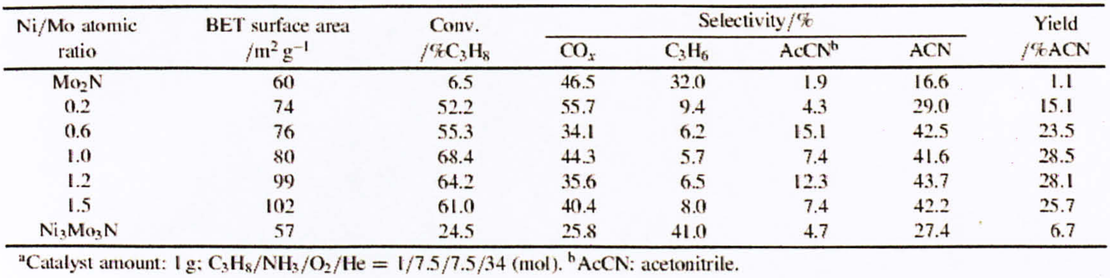
Direct conversion of alkanes to produce high value products,for the chemical industry constitutes an arduous and stimulating scientific and technological challenge. Among the most significant industrial applications in this field is the production of acrylonitrile (ACN) through the propane ammoxidation process. The acrylonitrile, as one kind of the most important chemical intermediates, is used extensively in the manufacture of fibers, polymers, such as styrene–acrylonitrile (SAN) and acrylonitrile–butadiene–styrene (ABS), and other valuable chemicals.

2.1 Research on the Catalyst

Nickel–molybdenum mixed nitride catalysts were first reported for the ammoxidation of propane to acrylonitrile. It was found that the mixed nitrides exhibited high activity and selectivity to acrylonitrile. The mixed nitride catalyst with 1.0 of Ni/Mo atomic ratios showed the best catalytic properties for propane ammoxidation. The highest yield of acrylonitrile was 28.5% at the propane conversion of 68.4% at 773 K (Huimin Zhang et al., 2005).

In the research by Zhang et. al., (2006) for the 'New Class of Catalysts for the Ammoxidation of Propane to Acrylonitrile over Nickel–Molybdenum Mixed Nitrides', they had proven the quality of nitride catalyst for ammoxidation of propane to acrylonitrile. The Ni–Mo mixed nitride, pure Ni_3Mo_3N and pure Mo_2N catalysts were prepared and mixed within specific ratio. Prepared mixtures then are used for the ammoxidation of propane to ACN. The results of propane ammoxidation over the prepared catalysts at 773K are listed in Table 1. The pure Mo_2N or Ni_3Mo_3N catalyst did not show high activity for propane ammoxidation surface area, which suggests that besides the surface area of the catalysts, other factors, such as synergetic effect, also seem to play an important role in the process of propane ammoxidation. The Ni–Mo mixed nitrides show a high activity and selectivity for propane ammoxidation, while the selectivity to acrylonitrile gradually decreases with time on stream

Table 2.1: Catalytic properties of studied catalysts for the ammoxidation of propane at 773Ka. (Zhang et. al., 2006)



Ni/Mo atomic ratio	BET surface area $/m^2\,g^{-1}$	Conv. $/\%C_3H_8$	Selectivity/%				Yield /%ACN
			CO_x	C_3H_6	AcCN[b]	ACN	
Mo_2N	60	6.5	46.5	32.0	1.9	16.6	1.1
0.2	74	52.2	55.7	9.4	4.3	29.0	15.1
0.6	76	55.3	34.1	6.2	15.1	42.5	23.5
1.0	80	68.4	44.3	5.7	7.4	41.6	28.5
1.2	99	64.2	35.6	6.5	12.3	43.7	28.1
1.5	102	61.0	40.4	8.0	7.4	42.2	25.7
Ni_3Mo_3N	57	24.5	25.8	41.0	4.7	27.4	6.7

[a]Catalyst amount: 1 g; $C_3H_8/NH_3/O_2/He = 1/7.5/7.5/34$ (mol). [b]AcCN: acetonitrile.

After that, many catalysts have been tested for the ammoxidation of propane to acrylonitrile, and the most effective ones fall into two main classes: they are either VMo*x*M*y* mixed oxides (M is most often Bi or Te) or VSb*x*M*y* mixed oxides (M are elements used as a promoter such as W, Te, Nb, Sn, Bi, Al, and Ti) (R. K. Grasselli et al., 1999). The highest acrylonitrile yields to date (about 60%) (H. Hinago et al., 2000) have already been obtained on laboratory scale from propane using a Mo–V–Nb–Te–O*x* catalyst among VMo*x*M*y* mixed oxides.

In the research by J. Kubo et. al., (2007) in studies of 'Propane ammoxidation with lattice oxygen of Mo–V–O-based complex metal oxide catalysts', they found the function of Mo, V, and Te elements for the catalyst MoVTeNbO in ammoxidation of propane to ACN. These catalysts have the stacked structure that consists of pentagonal, hexagonal and heptagonal units of MO_6 (M=Mo, V) octahedral that were arranged in the high dimension as shown in Fig. 1. Mo and V are located in the octahedral positions and in the pentagonal channels and Te is located in hexagonal rings. The roles of each element in Mo–V–O system revealed that Mo and V in the framework structure caused the oxidative activation of propane to propylene and that Te clearly promotes the transformation from propylene to acrylonitrile.

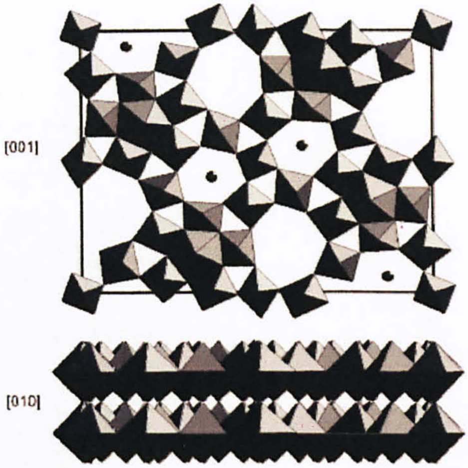


Figure 2.1: Structural model of the orthorhombic phase along [0 0 1] and [0 1 0] directions for MoVTeNbO catalyst. (Kubo et. al., 2007)

In order to clarify the reactivity of lattice oxygen of MoVTeNbO catalyst in the experiment, the conversion of reactant and product distribution was measured using pulse technique. When the mixture of propane and ammonia was pulsed onto the MoVTeNbO catalyst (prepared by hydrothermal method) at 420°C, the conversion of propane and ammonia and the selectivity to various products were greatly changed with the number of pulses as shown in Fig. 2. As we see, in increase of pulse, conversion of reactant is decreased. Considering that only the oxygen of the surface is consumed by the reaction as soon as the catalytic activity is greatly decreased, the results obtained indicates that only the surface can supply active oxygen, that is, the lattice oxygen consumed by the reaction is not quickly supplied from the bulk.

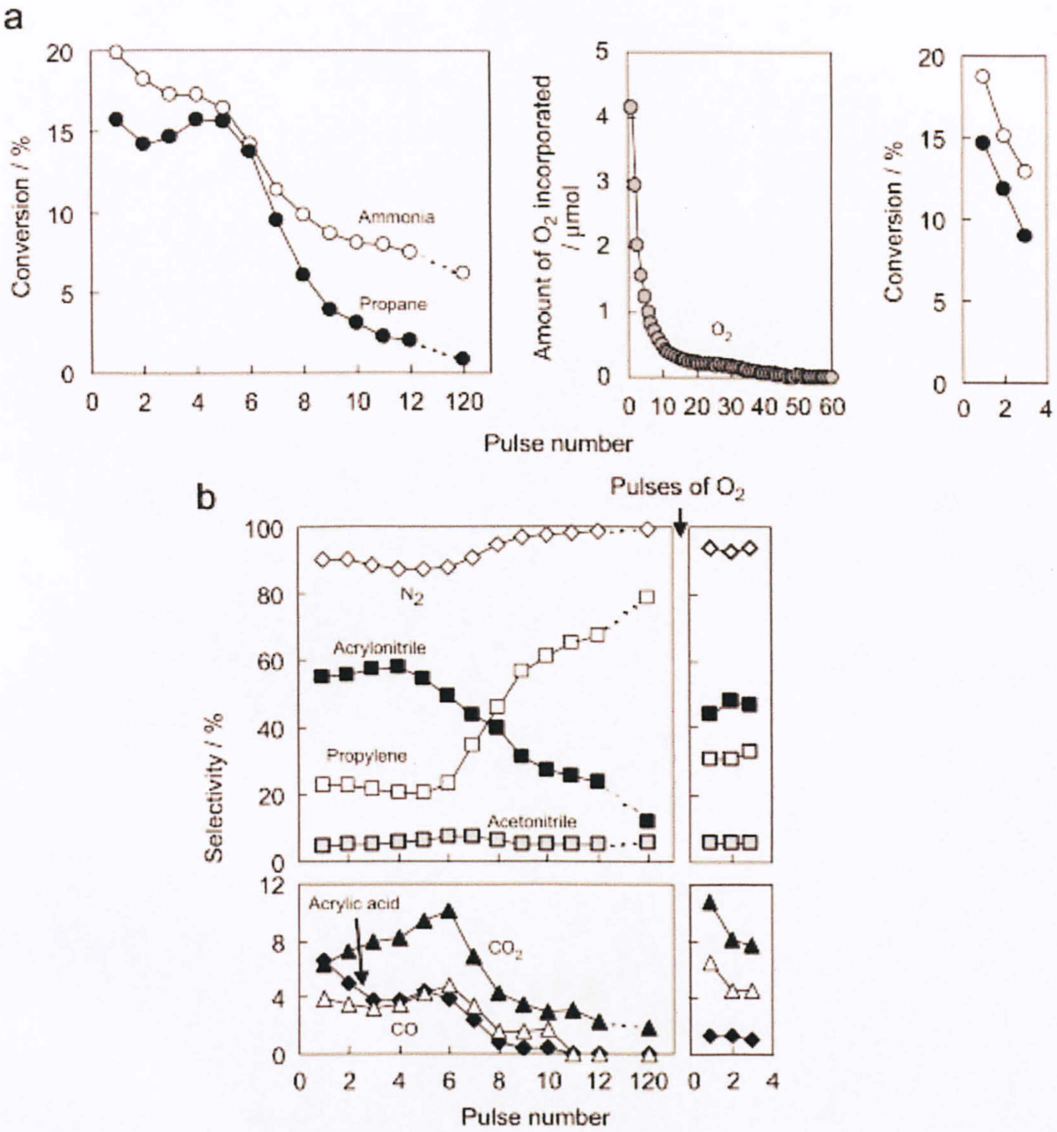


Figure 2.2: The reaction profiles of propane ammoxidation by lattice oxygen of MoVTeNbO catalyst. (Kubo et. al., 2007)

From the selectivity graph, clearly shown that selectivity to ACN is high that reaching up to 60%. This result proves that MoVTeNbO serve potentially as a good catalyst for ammoxidation of propane to acrylonitrile. But because only the lattice oxygen of the surface of the catalyst mainly takes part in the catalytic oxidation, thus greatly reducing reactant conversion, so it might be necessary to design the catalyst from which the lattice oxygen of the catalyst is quickly supplied from the bulk of the catalyst.

Research done on V–Sb mixed oxides also have been reported to yield 34–40% ACN (A. T. Guttmann e. al., 1988). In addition, several other mixed oxides, such as Bi–Mo (J. S. Kim et al., 1994), P–V (G. Centi et al., 1987), and Fe–Sb (M. Bowker et al., 1996), are also active in the conversion of propane to acrylonitrile. However, the yield of ACN does not exceed 20% (T. Ushikubo et al., 1997). With the exception of the above mixed oxides, a few other catalytic materials are used in the propane ammoxidation to acrylonitrile. Recently, the vanadium aluminum oxynitrides have been first reported for the propane ammoxidation process (Florea et al., 2003) and the catalysts yield up to 30% ACN,(M. Florea et al., 2005) which present the opportunity for the mixed metal oxynitrides or nitrides used in the ammoxidation of propane to acrylonitrile. In the end, Mo-V-Nb-Te-O is the best combination to serve as catalyst for propane ammoxidation. This is validated by Johan Holmber et. al., (2004) saying that all four components which are vanadium, molybdenum, niobium, and tellurium are needed to obtain best proposed catalyst.

Grasselli et. al. (2004) said that the Mo-V-Te-Nb-Ox catalyst system is compromised of three crystalline phases: orthorhombic Mo7.8V1.2NbTe0.94O28.9 (M1), pseudo-heaxagonal Mo4.67V1.33Te1.82O19.82 (M2), and a trace of monoclinic TeMo5O16. One of the main differences between the two phases is that the M1 phase contains V^{5+} centers, while the M2 phase does not. This is one of the main reasons why the M1 phase is capable of activating paraffin, while M2 is not.

Another significant difference between the two phases is that M1 contains Nb, while M2 contains very little. Nb plays two vital roles in the M1 structures: (i) spatially separate the active catalytic centers from each other (site isolation) and thereby imparts this structure its high selectivity to produce acrylonitrile from propane under ammmoxidation condition. (ii) stabilizes the overall structure, which is of great importance under catalytic operating conditions. The yield maximum of 61.8% (86 % conversion, 72% selectivity, 420°C) is reached at a composition of approximately 60% of M1, 40% of M2 and a trace of $TeMo_5O_{16}$. This proved that M1 is a great important while M2 phase is not really effective in the activity of the catalyst.

Adding the support to MoVNbTe catalyst can also improve the structure, pore size and surface area of the catalyst. This characteristic also can be manipulated in researching a better catalyst for propane ammoxidation to ACN. Research done by Anita Ramli et. al., (2007), introducing MgO, SiO_2, and Al_2O_3 as supports to the MoVNbTe catalyst along with unsupported MoVNbTe oxide as control. The surface area and pore size of these catalysts were measured Brunauer, Emmet and Teller (BET) equation and shown in table 2.

Table 2.2: BET Surface area (m^2g^{-1}) of the samples with different supported (Anita Ramli et. al., 2008)

Catalyst	Surface Area (m^2g^{-1})	Pore Size (nm)
$MoVNbTeO_x$	1.55	-
MoVNbTe/MgO	25.42	-
MoVNbTe/SiO_2	13.13	-
MoVNbTe/Al_2O_3	76.61	5.19
MgO	39.21	-
SiO_2	213.70	-
Al_2O_3	176.60	4.15

The textural and morphological of these catalysts on the other hand, were determined using scanning electron microscopy (SEM) and X-ray Diffraction (XRD), clearly shown the difference in the structure of different catalysts. Figure below shows the difference between three supported MoVNbTe catalysts along with unsupported one.

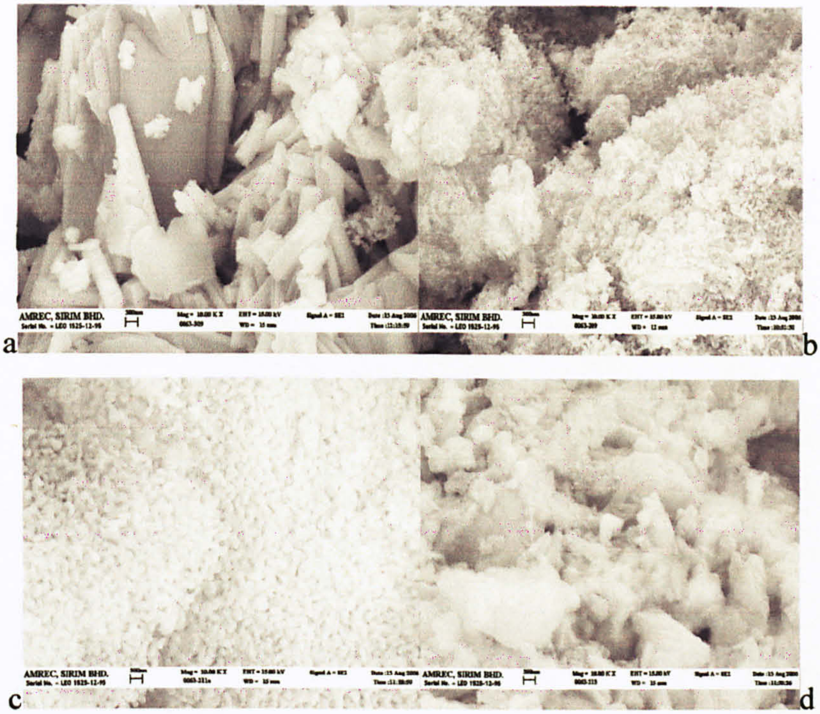


Figure 2.3: SEM micrograph for a) MoVNbTe, b) MoVNbTe/MgO, c) MoVNbTe/SiO2, d) MoVNbTe/Al2O3 (Ramli et. al., 2008)

Anita Ramli concludes in her article that supporting the MoVNbTe catalyst with Al2O3, MgO and SiO2 improves the surface area of the catalyst, thus increases the propane conversion. However, the introduction of these supports hindered the formation of crystalline phases required for the amoxidation to ACN. Insufficient existence of these crystalline phases reduces the selectivity to ACN

MoVNbTe prove to be the best catalyst for ammoxidation of propane to acrylonitrile. But Haber et al., (1995) said that methods of catalyst preparation are very diverse and each catalyst may be produced via different routes. Preparation usually involves several successive steps. Many supported metal and oxide catalysts are prepared by the succession of impregnation, drying, calcinations, activation; zeolite catalysts are prepared by precipitation of gel, crystallization, washing, ion exchange, and drying. The properties of heterogeneous catalysts depend on all their previous history.

An experiment is carried out by Othman et al., (2008) promising five methods on preparing MoVNbTe catalyst which are Slurry method (control), Calcinations temperature, Hydrothermal, Reflux, and Alcohol as the solvent. Each method produces MoVNbTe catalyst with different physicochemical properties. All five samples of MoVNbTe are prepared with the same composition 5.19g of Ammonium molybdate, 4.59g of Ammonium metavanadate, 0.47g of Ammonium niobium oxalate, and 0.18g of Telluric acid. Catalyst characterization is done by X-ray diffraction method, BET method, and Fourier Transform Infra Red Spectrometry (FTIR).

In his experiment, he concluded hydrothermal method as the best method for preparation of MoVNbTe catalyst. Result below shows the X-ray diffraction for all the methods, showing that hydrothermal method did give more intense peaks of V2MoO8 thus producing better crystal.

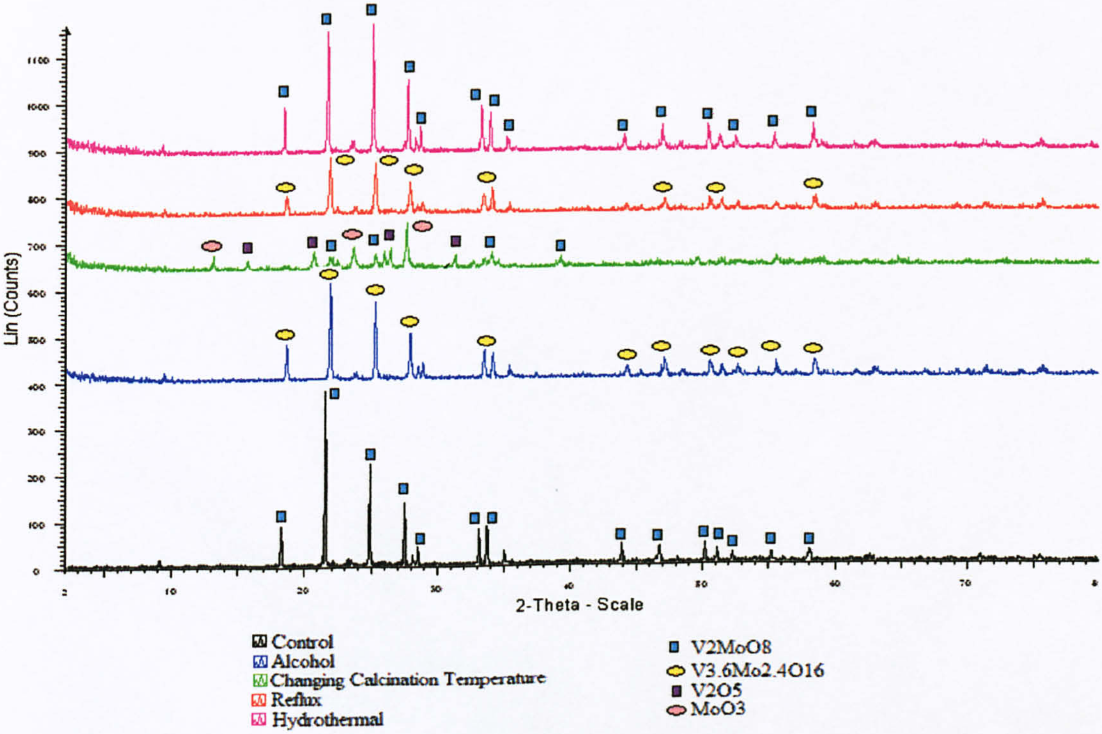


Figure 2.4: X-ray diffraction patterns for the catalyst with different preparation method and activation process (Control, Alcohol, Changing calcinations temperature, reflux and hydrothermal). (Othman et. al., 2008)

Although hydrothermal method proved to be the best method of MoVNbTe preparation, reflux method should be studied more because introducing reflux to the experiment should improve the formation of the crystal since the catalyst was given a heat treatment (Othman et. al., 2008).

Liu in his article 'CeO2 Nanocrystalline-Supported Palladium Chloride: An Effective Catalyst for Selective Oxidation of Alcohols by Oxygen', find that refluxing the precursor of the catalyst and varying the heat treatment time from 4 hours, 12 hours, and 16 hours resulting in different structure of the catalyst. This eventually will differentiate the surface area of produced catalyst. Figure 5 show the structure of his catalyst in different reflux time. Lopez-Sanchez et. al., (2003) in his research stated that refluxing the precursors in water prior to activation was crucial in obtaining high surface area materials, and ^{31}P spin echo mapping NMR together with electron microscopy data indicate that the water reflux step influences the relative amounts of V4+ and V5+ phases present in the catalyst, as well as reducing the size of the crystallites. Thus the reduced crystal size causes the increased surface area of the catalyst, increasing its activity, complying with Ramli et. al., (2008) statement. Therefore, research on Mo-V-Nb-Te preparation by reflux method should be carried on.

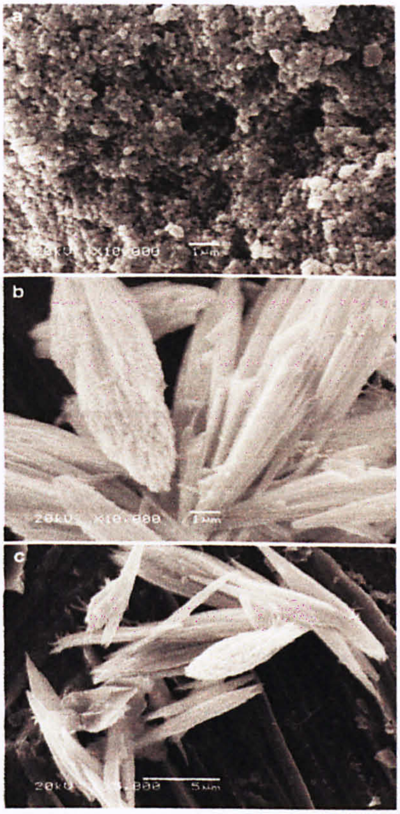


Figure 2.5: SEM images of CeO2 nanoparticles after heating under reflux for 4 h (a), 12 h (b) and 16 h (c). (Liu et. al., 2009)

2.2 Catalyst Characterization

X-ray diffraction (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Samples are analyzed as powders with grains in random orientations to insure that all crystallographic directions are "sampled" by the beam. When the Bragg conditions for constructive interference are obtained, a "reflection" is produced, and the relative peak height is generally proportional to the number of grains in a preferred orientation. Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained. A host of application techniques for various material classes is available, each revealing its own specific details of the sample studied. Figure 6 shows the example of X-Ray diffraction pattern of catalyst characterization.

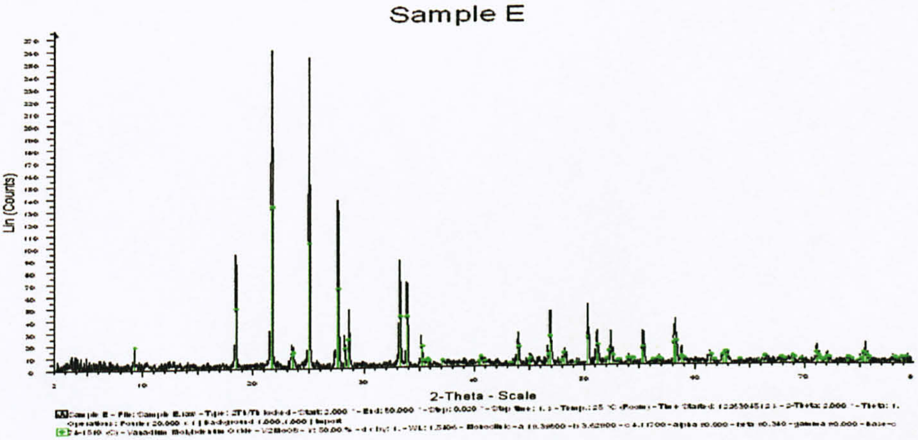


Figure 2.6: XRD pattern for Mo-V-Nb-Te by hydrothermal (Othman et. al., 2008)

The advantages of X-ray Powder Diffraction are:

- Rapid identification of materials
- Ease of sample preparation
- Computer-aided material identification
- Large library of known crystalline structures
- Multi-sample stage

Brunauer, Emmet and Teller Method (BET)

BET method to provide information about the total surface area of a catalyst, the surface area of the phase carrying the active sites, or possibly even the type and number of active sites. Physical adsorption is used in the BET method to determine total surface areas. The interaction between the adsorbate and the physical adsorbent (physyiorption) in nature and ideally should be a surface-specific interaction. A total surface area S_{total} and a specific surface area S are evaluated by the following equations:

$$S_{BET,total} = \frac{(v_m N s)}{V}$$

$$S_{BET} = \frac{S_{total}}{a}$$

N: Avogadro's number

s: adsorption cross section

V: molar volume of adsorbent gas

a: molar weight of adsorbed species

It is necessary to be aware, however, that in some cases the interaction between the adsorbate and the adsorbent can lead to a chemical reaction in which more than just the surface layer of the adsorbent is involved. For example, when using oxidizing compounds as adsorbates (0_2 or N_2O) with metals such as copper or nickel or sulfides, sub-surface oxidation may occur.

Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

SEMs are patterned after reflecting light Microscopes and yield similar information:

1. **Topography**

   The surface features of an object or "how it looks", its texture; detectable features limited to a few manometers

2. **Morphology**

   The shape, size and arrangement of the particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching; detectable features limited to a few manometers

3. **Composition**

   The elements and compounds the sample is composed of and their relative ratios, in areas around 1 micrometer in diameter

4. **Crystallographic Information**

   The arrangement of atoms in the specimen and their degree of order; only useful on single-crystal particles >20 micrometers

Fourier Transform Infra Red Spectrometry (FTIR)

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. FTIR also can determine the functional group for the sample of analysis. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. FTIR is used before the catalysts are calcinated and once again after the calcinations process in the preparation method.

(Resource from Haber et. al., 1995)

The characterization of the catalyst is done using XRD, BET, FTIR and SEM method. The activity of the catalyst will be studied using a fixed-bed micro reactor with online GC at 420°C. The feed gas molar ratio are 5.8% propane, 7.0% ammonia, 17.4% oxygen and 69.8% helium with the Helium as carrier to give a total flow rate of 120 ml min-1 as stated in the published journal by Ramli *et al* (2007).

CHAPTER 3

METHODOLOGY AND PROJECT WORK

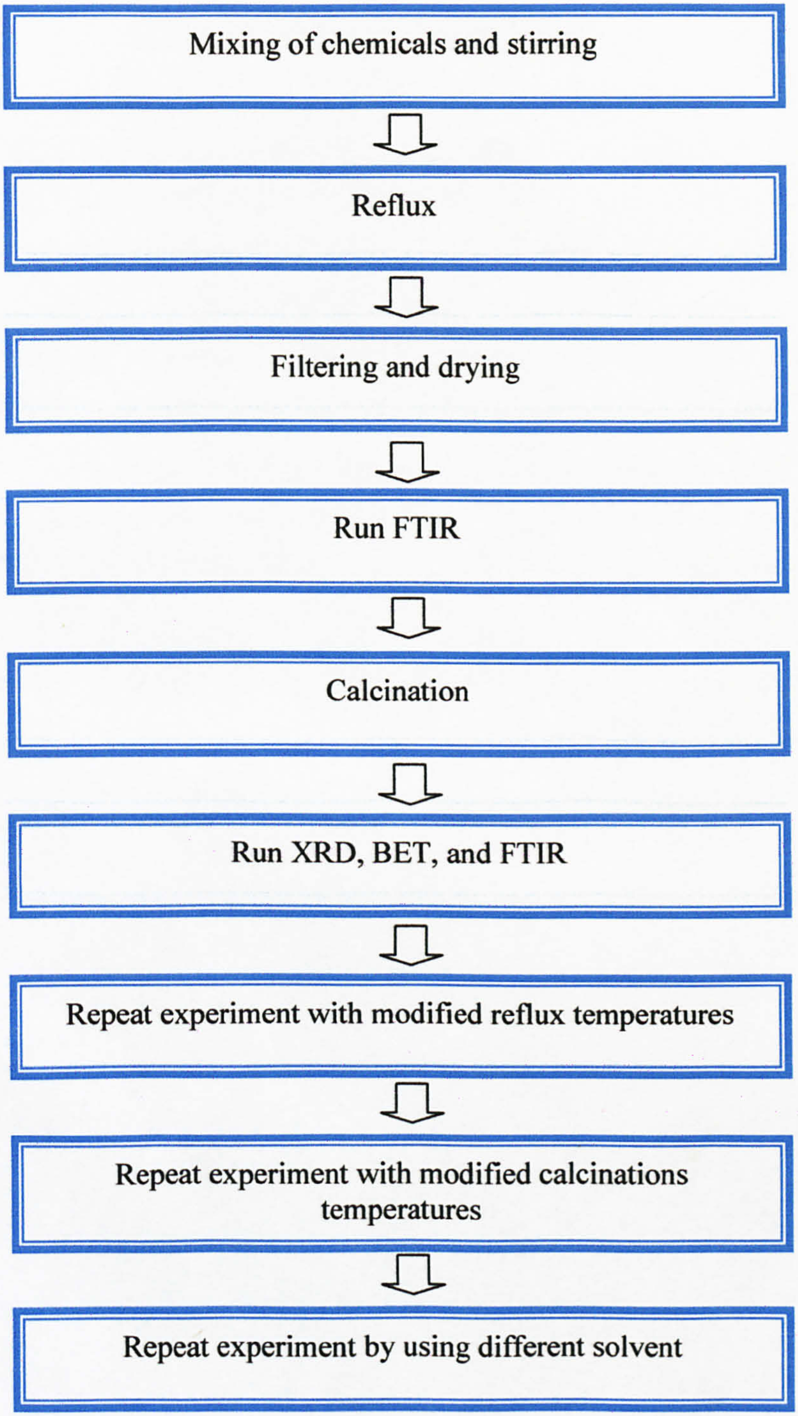
3.1 Gantt Chart of the Project

No	Detail/ Week	1	2	3	4	5	6	7	8	9		10	11	12	13	14
1	Project Work Continues (lab preparation)	🟦	🟦	🟦												
2	Submission of Progress Report 1				*											
3	Project Work Continues (synthesis catalyst)				🟦	🟦	🟦	🟦	🟦	🟦						
4	Submission of Progress Report 2								*							
5	Seminar								*							
6	Project Work Continues (catalyst characterization)											🟦	🟦	🟦	🟦	
7	Poster Exhibition											*				
8	Submission of Dissertation (Final Draft)															*
9	Oral Presentation															*
10	Submission of Dissertation (Hard Bound)															*

*	Suggested milestone
🟦	Process

Figure 3.1: Project Milestone chart

3.2 Project Flow Sheet



3.3 Details on Methodology

3.3.1 Solution Preparation Method

After proposing the required chemicals and equipment for synthesizing the catalyst Mo-V-Nb-Te, lab is set up for the experiment. First part of the experiment is conducted which is the solution preparation. Below are the chemicals required for 1 sample of Mo-V-Nb-Te catalyst:-

- Ammonium molybdate, (NH4)6Mo7O24.4H2O - 5.19g
- Ammonium metavanadate, H4NO3V - 4.59g
- Ammonium niobium oxalate, C10H8N2O33Nb2 - 0.47g
- Telluric acid, H6O6Te - 0.18g

Procedures:-

1. Weight and dissolve ammonium molybdate into 100mL of distilled water.
2. Stir for awhile at 80°C.
3. Weight ammonium metavanadate and mix it into the ammonium molybdate solution. Add distilled water little by little.
4. Weight and dissolve ammonium niobium oxalate into 20mL distilled water.
5. Then weight telluric acid and mix it into the ammonium niobium oxalate solution. Distilled water can be added if telluric acid not dissolved.
6. Mix the two solutions. Heat the mixed solution at 80°C and stir for 4 hours.

3.3.2 Catalyst Synthesis by Reflux Method (control)

The experiment is run under below condition (control):

1) *Solvent: Water*
2) *Reflux temperature: 115°C*
3) *Calcination temperature: 450°C*
4) *Reflux time: 4 hours*

Details of the methodologies are as follow:

- Ammonium metavanadate is dissolved in 100mL of distilled water.
- The dissolved ammonium metavanadate is added to a solution containing ammonium molybdate, ammonium niobium oxalate and telluric acid.
- The mixture is heated and stirred for 4 hours.
- Set up the equipment as in Figure 8. Put the mixture inside the round flask. Set the heating mantle to 115°C. Reflux the mixture for 4 hours.

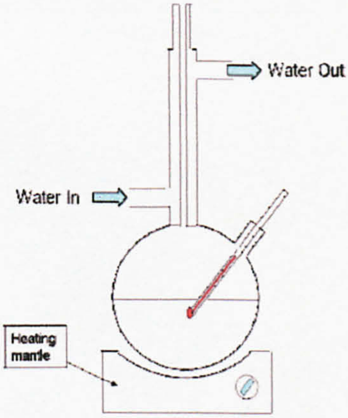


Figure 3.2: Set up for reflux

- The mixture is filtered using filter paper.
- The resulting mixture in the filter paper is dried for 17 hours at 120°C.
- Run FTIR on the mixture.
- The mixture is calcinated in air at temperature between 450°C for 10 hours.
- Run XRD, BET, SEM, and FTIR again on the resulting mixture.

3.3.3 Changing the Reflux Temperature

The experiment is run under below condition:

1) *Solvent: Water*
2) *Reflux temperature:* ***90°C***
3) *Calcination temperature 450°C*
4) *Reflux time: 4 hours*

Details of the methodologies are as follow:

- Ammonium metavanadate is dissolved in 100mL of distilled water.
- The dissolved ammonium metavanadate is added to a solution containing ammonium molybdate, ammonium niobium oxalate and telluric acid.
- The mixture is heated and stirred for 4 hours.
- Set up the equipment as in Figure 8. Put the mixture inside the round flask. Set the heating mantle to **90°C**. Reflux the mixture for 4 hours.
- The mixture is filtered using filter paper.
- The resulting mixture in the filter paper is dried for 17 hours at 120°C.
- Run FTIR on the mixture.
- The mixture is calcinated in air at temperature between 450°C for 10 hours.
- Run XRD, BET, SEM, and FTIR again on the resulting mixture.

3.3.4 Changing the Calcination Temperature

The experiment is run under below condition:

1) *Solvent: Water*
2) *Reflux temperature: 115°C*
3) *Calcination temperature:* ***550°C***
4) *Reflux time: 4 hours*

Details of the methodologies are as follow:

- Ammonium metavanadate is dissolved in 100mL of distilled water.
- The dissolved ammonium metavanadate is added to a solution containing ammonium molybdate, ammonium niobium oxalate and telluric acid.

- The mixture is heated and stirred for 4 hours.
- Set up the equipment as in Figure 8. Put the mixture inside the round flask. Set the heating mantle to 115°C. Reflux the mixture for 4 hours.
- The mixture is filtered using filter paper.
- The resulting mixture in the filter paper is dried for 17 hours at 120°C.
- Run FTIR on the mixture.
- The mixture is calcinated in air at temperature between **550°C** for 10 hours.
- Run XRD, BET, SEM, and FTIR again on the resulting mixture.

3.3.5 Changing the Reflux Duration

The experiment is run under below condition:

1) *Solvent: Water*
2) *Reflux temperature: 90°C*
3) *Calcination temperature 450°C*
4) *Reflux time: **12 hours***

Details of the methodologies are as follow:

- Ammonium metavanadate is dissolved in 100mL of distilled water.
- The dissolved ammonium metavanadate is added to a solution containing ammonium molybdate, ammonium niobium oxalate and telluric acid.
- The mixture is heated and stirred for 4 hours.
- Set up the equipment as in Figure 7. Put the mixture inside the round flask. Set the heating mantle to 90°C. Reflux the mixture for **12 hours.**
- The mixture is filtered using filter paper.
- The resulting mixture in the filter paper is dried for 17 hours at 120°C.
- Run FTIR on the mixture.
- The mixture is calcinated in air at temperature between 450°C for 10 hours.
- Run XRD, BET, SEM, and FTIR again on the resulting mixture.

3.4 Project works

3.4.1 Solution Preparation

By referring to the step by step procedure on methodology, solution of MoVNbTe is prepared. During sample solution preparation, I observed that:-

1. The 1st solution (ammonium molybdate + ammonium metavanadate) is in white orange colour.
2. The 2nd solution (ammonium niobium oxalate + telluric acid) is in white colour.
3. When both solutions are mixed, 2nd solution is sedimented at the bottom.
4. After heating and stirring started, then the both solutions are mixed and formed a white orange solution. This means, by stirring and heating, then the chemicals will be mixed in a solution.

Figure 3.3: Heating and stirring

3.4.2 Refluxing

After a minimum of 4 hours heating and stirring, the solution becomes concentrated. Then the concentrated solution is being refluxed. The variations of reflux are temperature ranging from 90°C and 115°C, while the reflux time is from 4 hours to 10 hours. From the reflux, it is observed that:

1. Solution colour did not change.
2. Solution becomes more concentrated.

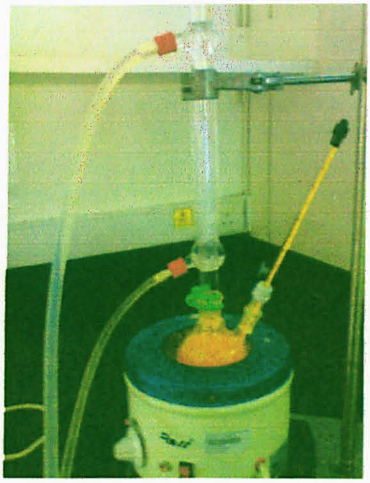


Figure 3.4: Refluxing the solution

3.4.3 Filtering and Drying

After reflux, the concentrated solution is then filtered, to get the solid product. Then the solid product is put into oven for one day to dry it. By this point, **MoVNbTe** is obtained. From these steps, I observed that:

1. The solid product is coloured white yellow.
2. After drying in oven, the solid become greenish yellow.

Figure 3.5: Filtering

Figure 3.6: Drying in oven

3.4.4 Calcination

The dried greenish-yellow solid product of MoVNbTe is then put into the furnace to obtain the **MoVNbTe oxide**. The variations on these steps are the calcinations temperature which ranging from 450°C and 600°C. From what I observed:

1. The greenish-yellow solid MoVNbTe turn into black greenish or black particles.
2. Quantity of solid decreased after being calcined in the furnace.

Figure 3.7: Furnace

Figure 3.8: Sample MoVNbTe oxide

CHAPTER 4

RESULT AND DISCUSSION

4.1 Scanning Electron Microscope (SEM)

In order to characterize the synthesized MoVNbTe catalyst, SEM is used to study the nanoparticle structure of the catalysts. Such structure is categorized as nanoparticle if it has the diameter within the range of 1nm to 100nm. Catalyst has many different kind of structure such as rotten shape, granular shape, and slab shape. Rotten and slab shape can also be categorized as the crystal shape, but notice that those two are definitely the different structure with each carry a different properties explanation.

With knowledge and experience on the study of catalyst structure, picture from SEM can give the overview of properties of the produced catalyst and if specified knowledge to a certain catalyst is posses, the understanding would be deeper. For example, having knowledge on the MoVNbTe catalyst would be a best assist to know which structure is best for the catalyst, or which structure gives the highest effective surface area as well as providing the best activation site to act as catalyst for its reaction (function of MoVNbTe to ammoxidation of Propane reaction). Thus SEM is run and the obtained pictures of nanoparticle structures are studied. Note that all information and knowledge is referred by an experienced chemist who studied the MoVNbTe catalyst. Magnifications used for the SEM are 500 times, 2000 times, and 5000 times.

4.1.1 Sample 1 (control)

Sample 1 is the control sample which is run under following condition:

1) *Solvent: Water*
2) *Reflux temperature: 115°C*
3) *Calcination temperature: 450°C*
4) *Reflux time: 4 hours*

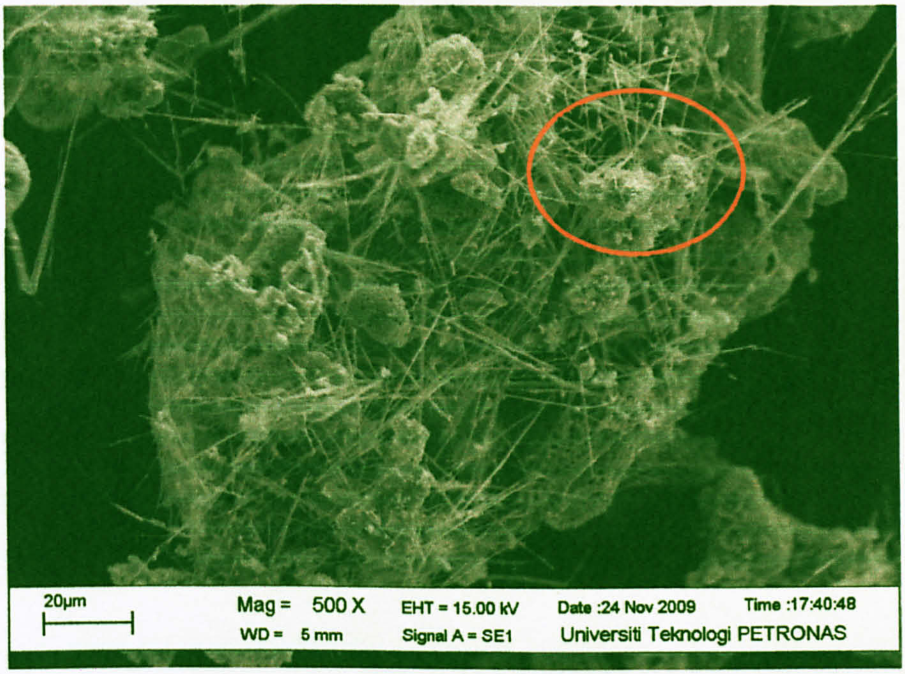


Figure 4.1: SEM for sample 1 (mag X500)

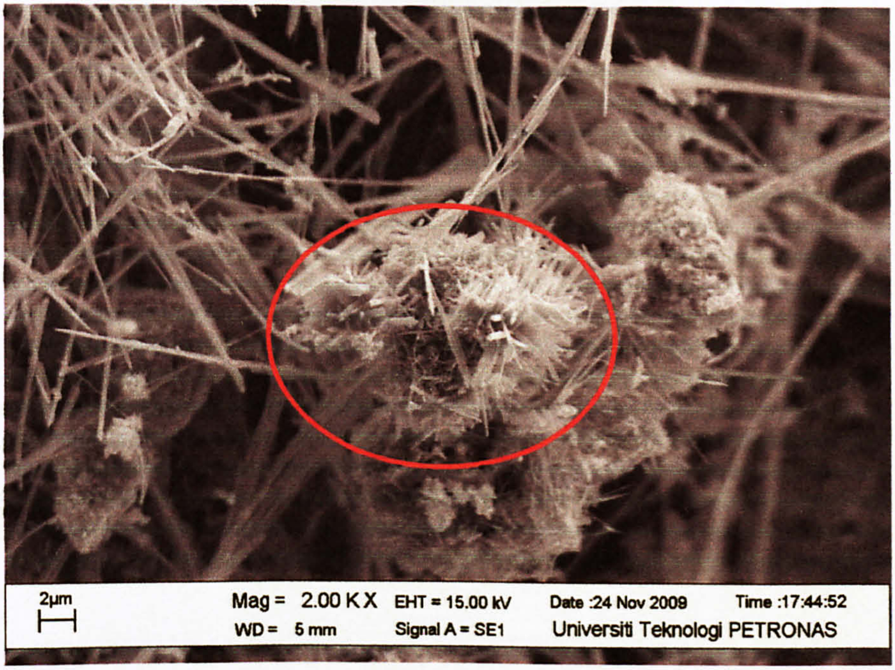


Figure 4.2: SEM for sample 1 (mag X2000)

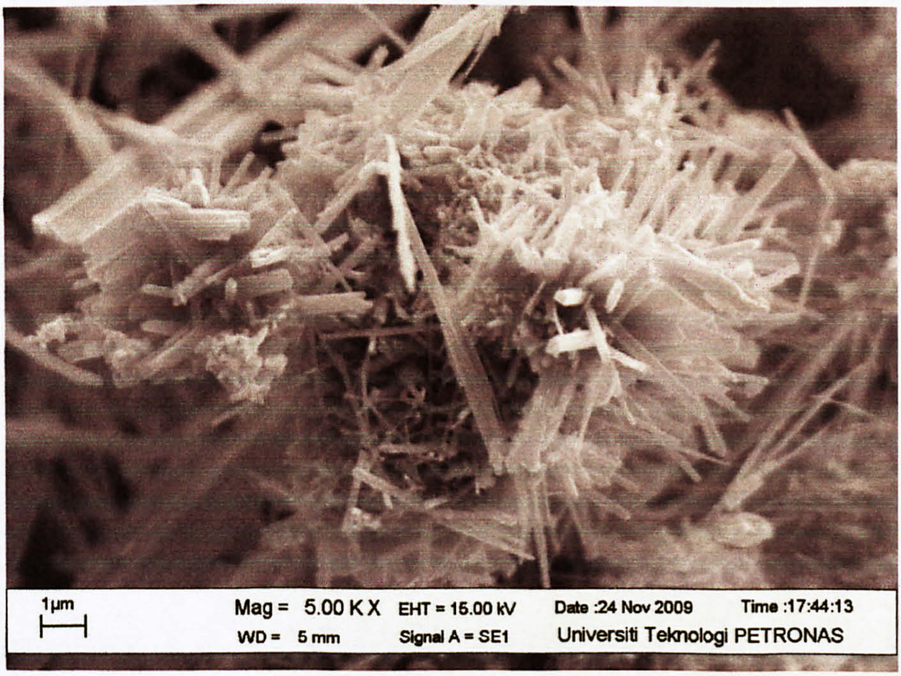


Figure 4.3: SEM for sample 1 (mag X5000)

From above SEM pictures, sample 1 is categorized as the **rotten shape** structure. It has the long crystal rod on its surface and dominantly all its particles are with the same shape. So it is categorized as rotten shape. Rotten shape has a high surface area but it cannot compromise as the best structure for the MoVNbTe because this type of structure did not promote to a complete activation in the ammoxidation reaction. For example, propane activation site (V) is far from the hydrogen abstraction site (Te). If propane is to undergo ammoxidation to ACN with presence of this catalyst, it will take time for propane to be converted to ACN or parts of propane are not properly converted. This is due to the rotten rod that cause the activation site of MoVNbTe is not placed side by side. Thus the propane might not completely activated or converted into ACN.

By changing the reflux temperature and duration as well as calcinations temperature, it is assumed that the long crystal rods structure will break donwn to form a better shape.

4.1.2 Sample 2 (change the calcinations temperature)

Sample 2 is made to study the effect of calcinations temperature variation to the structure of catalyst which is run under following condition:

1) *Solvent: Water*
2) *Reflux temperature:* $115^{o}C$
3) *Calcination temperature:* $550^{o}C$
4) *Reflux time: 4 hours*

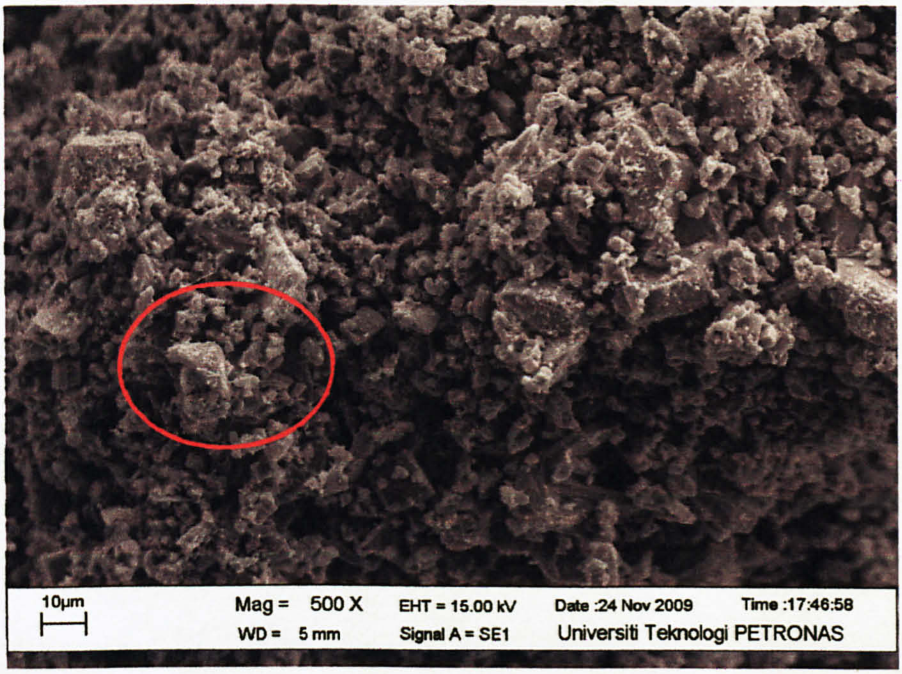


Figure 4.4: SEM for sample 2 (mag X500)

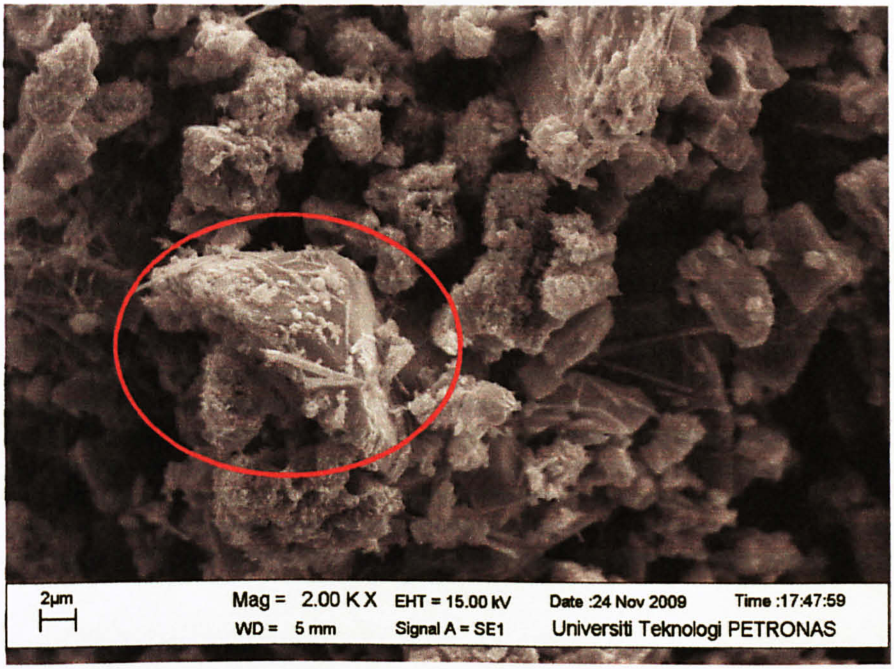


Figure 4.5: SEM for sample 2 (mag X2000)

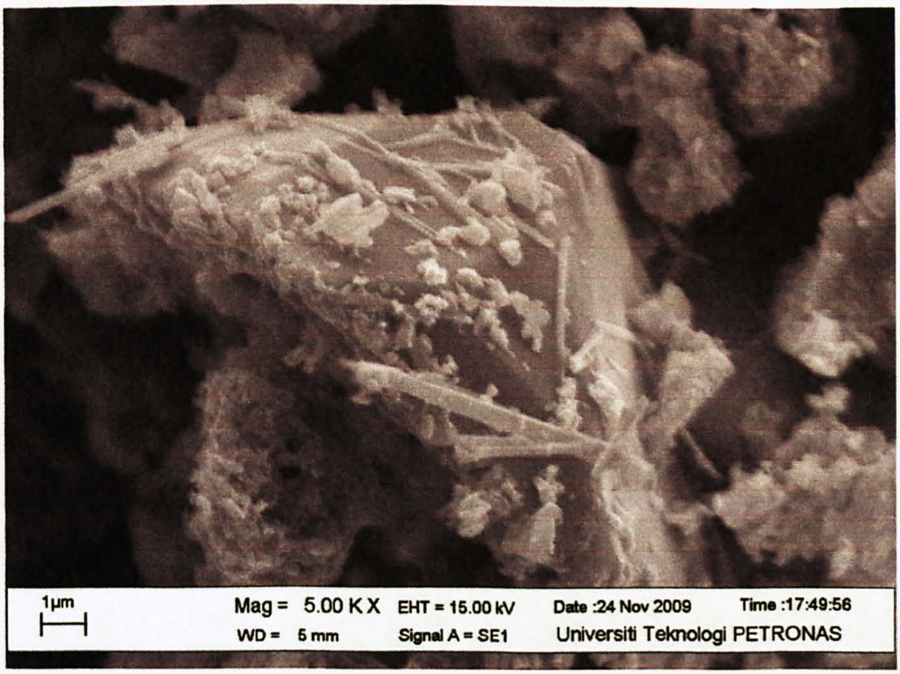


Figure 4.6: SEM for sample 2 (mag X5000)

Referring to the above pictures, magnification 500 times shows roughly that the structure of sample 2 is granular shape. From magnification 2000 times, we can see some crystal rod on the granular shape and if zoomed to 5000 times magnification, we can see that it actually have the granular as well as crystal rod shape on the surface.

It is assumed that the long crystal rods particles of the catalyst are broken down to granular-shaped particles due to increase in calcination temperature. Although the granular shape also has a high surface area, it cannot be chosen in this MoVNbTe catalyst because the crystalline phase is needed for the activation of the catalyst in the ammoxidation of propane reaction.

4.1.3 Sample 3 (change the reflux temperature)

Sample 2 is made to study the effect of reflux temperature variation to the structure of catalyst which is run under following condition:

1) *Solvent: Water*
2) *Reflux temperature: 90°C*
3) *Calcination temperature: 450°C*
4) *Reflux time: 4 hours*

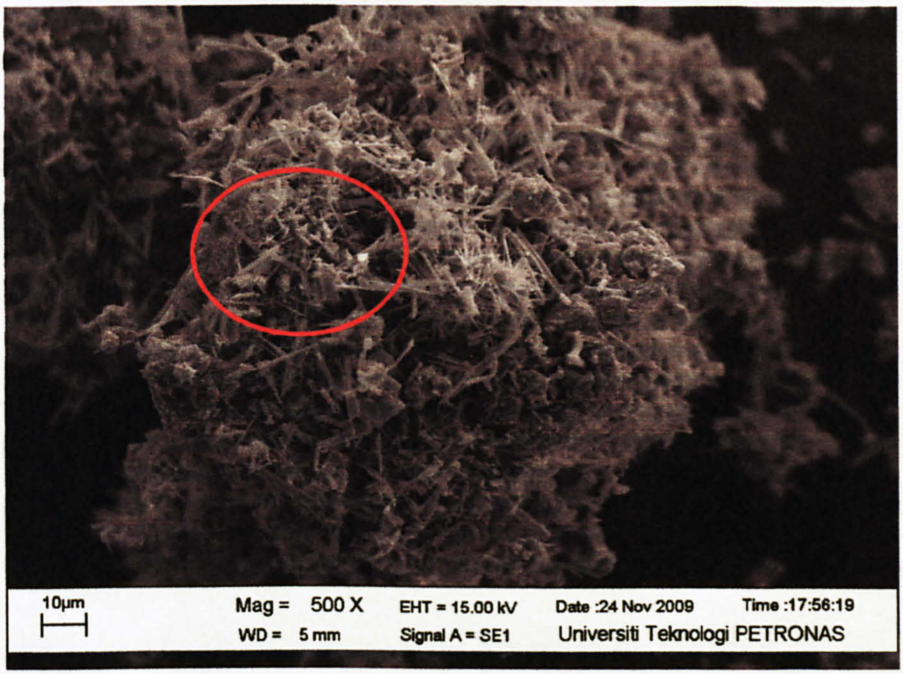


Figure 4.7: SEM for sample 3 (mag X500)

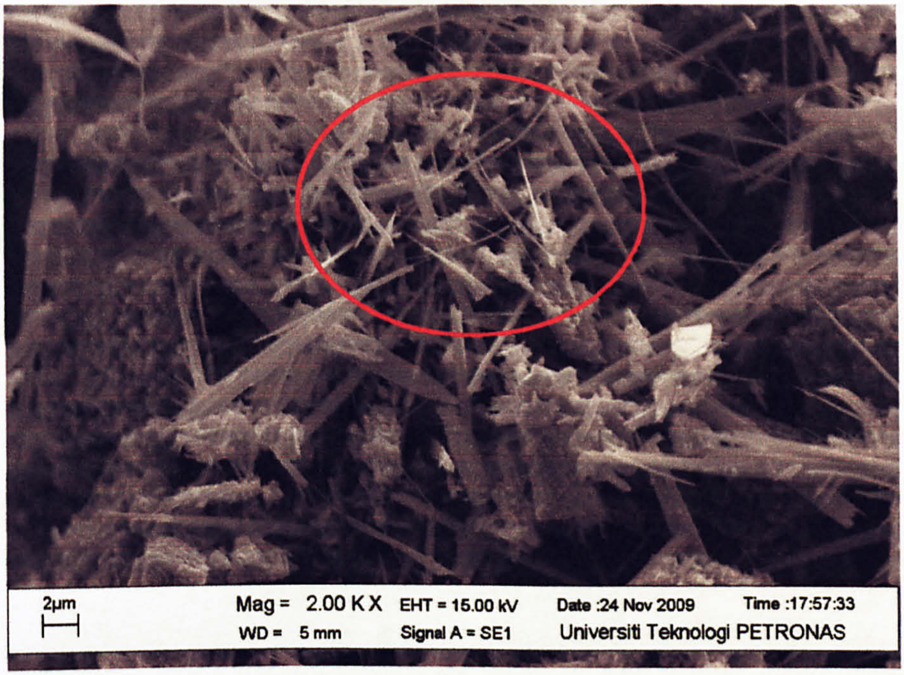


Figure 4.8: SEM for sample 3 (mag X2000)

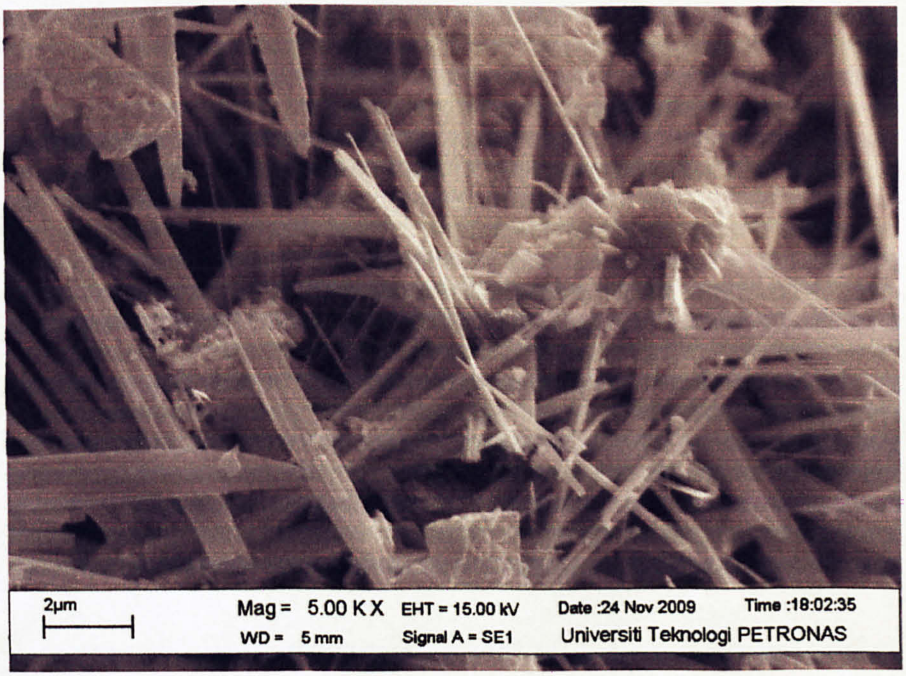


Figure 4.9: SEM for sample 3 (mag X5000)

By looking at the SEM of sample 3, magnification 500 times shows a rough structure of the catalyst. From this magnification, it is observed that the structure majorly crystal shape with some parts of granular-like shape. By zooming into 2000 times magnification, we can see that the crystal rods began to melt down into other shape which can be granular or slab structure. Then it is clearly shown by magnification 500 times that the crystal rods actually start to melt down or break down into slabs.

By referring to an experienced chemist on MoVNbTe catalyst, it is known that the common shape for MoVNbTe catalyst's structure is the slab shape. So the aim is to get the slab structure for the catalyst. Although the reflux temperature is lowered from 115°C to 90°C, the structure of the catalyst is forming into a better result. One way of explaining this situation is that during the MoVNbTe preparation, its reflux phase might not require high temperature condition as the high-temperature itself did not contribute to the better formation of catalyst. So it is better to keep the reflux in low temperature (e.g. 90°C) rather than increasing it because high-temperature reflux did not assure for a better structure (sample 1) while low-temperature reflux (sample 3) shows improved structure formation.

4.1.3 Sample 4 (change the reflux duration)

Sample 2 is made to study the effect of reflux temperature variation to the structure of catalyst which is run under following condition:

1) *Solvent: Water*
2) *Reflux temperature: 90°C*
3) *Calcination temperature: 550°C*
4) *Reflux time: 8 hours*

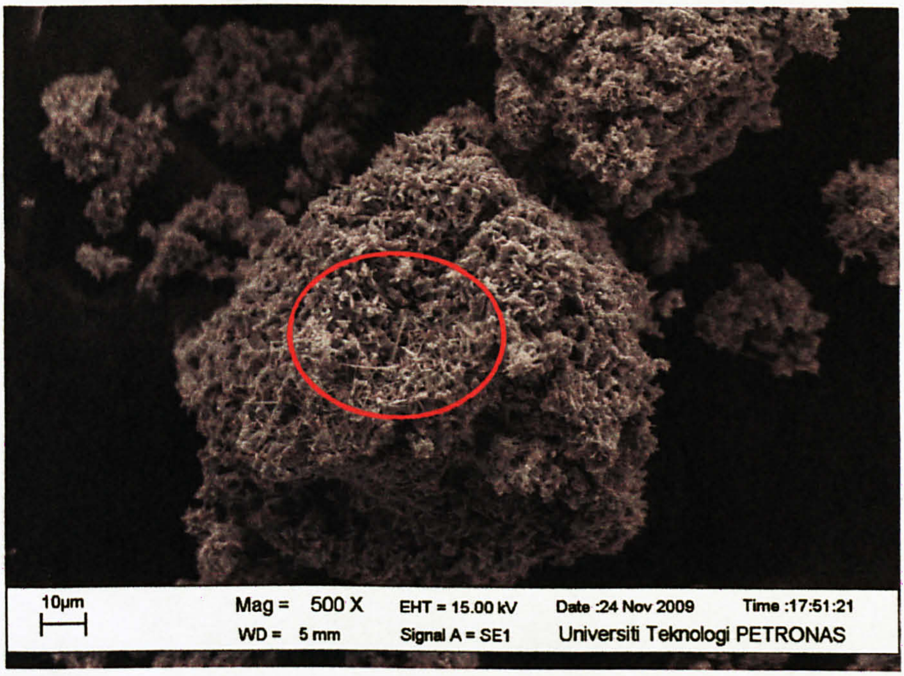


Figure 4.10: SEM for sample 4 (mag X500)

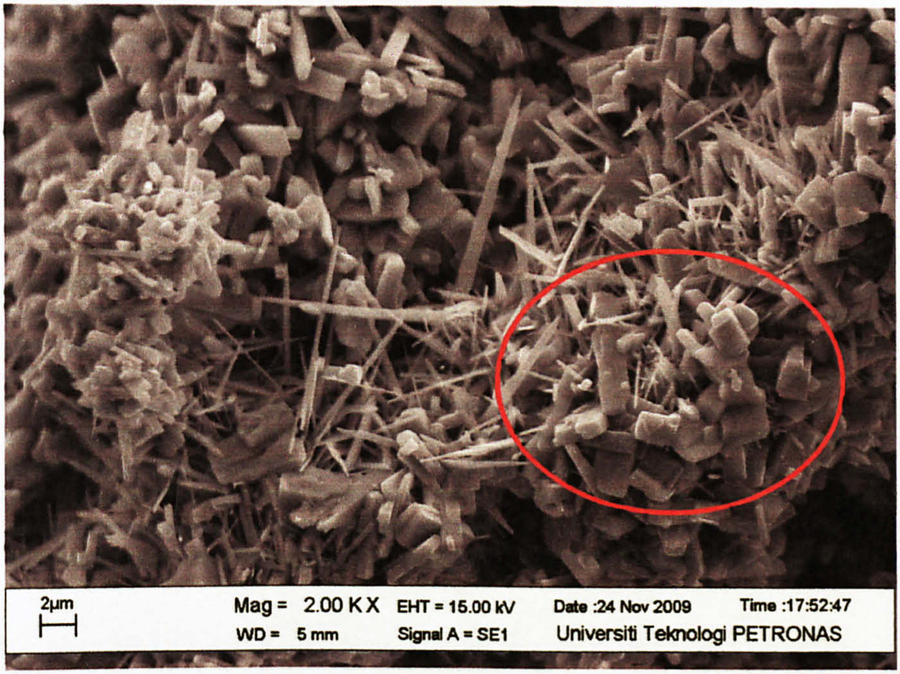


Figure 4.11: SEM for sample 4 (mag X2000)

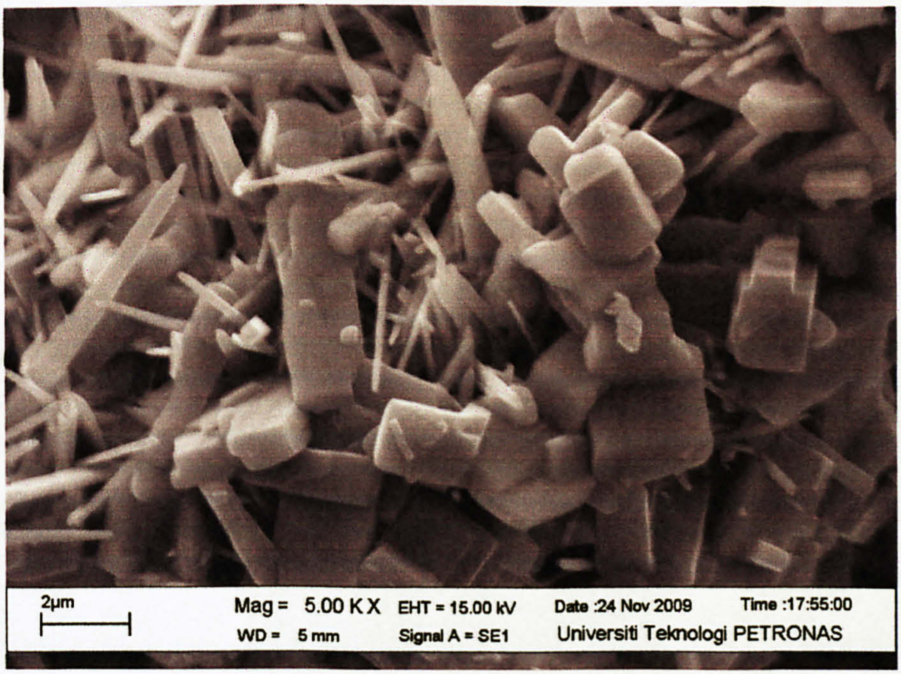


Figure 4.12: SEM for sample 4 (mag X5000)

From above SEM figures of sample 4, magnification 500 times shows a granular-like structure of the catalyst but by looking closely to magnification 2000 times, it is observed that actually the structure of sample 4 is slab shape with some crystal rods. Magnification 5000 times gives a better view on the slab structure of the catalyst.

As mentioned before, slab shape is the most common structure for MoVNbTe catalyst. This slab shape also being determined as the most appropriate structure for the catalyst because having a high surface area, this structure also provide all the activation site side-by-side within the crystalline structure. Slab shape is also categorized as crystal structure but better than crystal rod shape. Because sample 3 (low reflux temperature) shows a better structure than sample 1 (high reflux temperature), 90°C reflux temperature is selected. This sample proved that longer duration of reflux lead into better structure formation of catalyst, thus increasing its performance. With longer duration, crystal rods particles are slowly broken down into slab particles. So sample 4 can be assumed as the best sample for this project.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Conclusion

Although the XRD and BET for sample characterization cannot be completed, almost all objectives are fulfilled and this project could be and up with some conclusions. From study on the nanoparticle structure of the MoVNbTe catalyst, it is observed that by decreasing the reflux temperature, better structure formation of catalyst is obtained but should be limited to a certain temperature range, else too lower temperature could not give the effect of reflux. On the other hand, longer reflux duration provide the time for the formation of better structured catalyst. Calcinations also have an impact on the catalyst's structure formation. Higher temperature of calcinations can helps with catalyst structure formation, but too high calcinations temperature can cause the sample to melt down and waste it. Better catalyst structure lead to a better performance of the catalyst, thus slow heating in a long duration with the mean of reflux can contribute to a better MoVNbTe catalyst formation.

Recommendations

Some recommendation is made up in order to improve this project. These recommendations is important to enables the completion, smoothness, and might end up with successful result not just for this project, but also for the best of future project also. Those recommendations are:

1. All the equipments and chemicals should be properly prepared for student usage and it is suggested that the chemicals ordering should be done earlier.
2. If possible, it is required to have more of those sample characterization equipments such as X-RD, SEM, and BET. It is known that the quantities of these equipments are limited plus their usages are shared among all students from various departments as well as Master students and the lecturers. If this problem can be solved, catalyst characterization can be done. Future projects which required these equipments also can come into ease procedure.

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