



UNIVERSITI PUTRA MALAYSIA

***SYNTHESIS OF MoVTenb OXIDE CATALYSTS FOR PROPANE
OXIDATION TO ACRYLIC ACID VIA MICROWAVE IRRADIATION
ASSISTED SLURRY METHOD***

AHMAD AFANDI BIN MUDA

FS 2014 6



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OXIDATION TO ACRYLIC ACID VIA MICROWAVE IRRADIATION-
ASSISTED SLURRY METHOD**

By

AHMAD AFANDI BIN MUDA

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for the degree of Master of Science**

AUGUST 2014

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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AUGUST 2014

Chairman : Assoc. Prof. Irmawati Ramli, PhD

Faculty : Science

MoVTeNb mixed metal oxide catalyst has attracted great attention due to its ability to selectively oxidise propane to acrylic acid. In this work, the physicochemical properties of $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.13}$ oxide catalysts synthesized via slurry method assisted with microwave irradiation were obtained. The catalysts were prepared in different pH of 1.19, 1.80, 2.67 and 3.20. The resulting precursors were calcined in air at 553 K for 1 hour followed by in nitrogen at 873 K for 2 hours. The catalysts were also post-treated through washing with hydrogen peroxide. All of the solids obtained were characterized by X-ray Diffraction (XRD), BET surface area measurement (S_{BET}), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Temperature Programmed Reduction in hydrogen (H_2 -TPR), Transmission Electron Microscope (TEM) and Induced Couple Plasma-Atomic Emission Spectroscopy (ICP-AES). XRD results of the calcined samples displayed the formation of mixed orthorhombic M1 and hexagonal M2 phases. However, when washed with hydrogen peroxide, the hexagonal M₂ phase was eliminated and only orthorhombic M1 phase was found. The removal of hexagonal phase contributes to the improved S_{BET} values up to four times from its original value for each sample. H_2 -TPR profiles revealed higher amount of removable lattice oxygen for after washed with H_2O_2 catalysts. TEM analysis found that the washed MoVTeNbOx catalyst showed rod structure which was in line with the observed morphology in SEM. ICP-AES analysis for washed catalysts revealed that the composition of Te less than that of the theoretical value. Catalytic test showed that the catalysts achieved up to 25 % propane selectivity towards acrylic acid with propane conversion reached up to 38 %.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**PENGHASILAN MANGKIN MoVTenNb OKSIDA UNTUK PENGOKSIDAAN
PROPANA KEPADA ASID AKRILIK MELALUI KAEDAH BUBURAN
DIBANTU OLEH SINARAN GELOMBANG MIKRO**

Oleh

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Campuran oksida logam MoVTenNb telah menarik perhatian kerana kebolehannya untuk mengoksida secara selektif propana kepada asid akrilik. Dalam kajian ini, sifat fisikokimia mangkin oksida $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.13}$ yang dihasilkan dengan kaedah buburan dibantu oleh penyinaran gelombang mikro telah diperolehi. Mangkin berkenaan telah disediakan pada pH berbeza iaitu 1.19, 1.80, 2.67 dan 3.20. Prekursor terhasil telah dikalsin dalam udara pada 553 K selama 1 jam diikuti dengan nitrogen pada 873 K selama 2 jam. Mangkin juga dirawat lanjut dengan membasuh menggunakan hidrogen peroksida, H_2O_2 . Semua pepejal diperolehi telah dianalisis oleh Pembelauan Sinar-X (XRD), Pengukuran Luas Permukaan (S_{BET}), Spektroskopi Inframerah Transformasi Fourier (FTIR), Mikroskop Imbasan Elektron (SEM), Penurunan Terprogram Suhu dengan hidrogen (H_2 -TPR), Mikroskop Electron Transmisi (TEM) dan Plasma Gandingan Teraruh-Spektroskopi Pancaran Atom (ICP-AES). Keputusan XRD ke atas sampel mangkin yang telah dikalsinasi menunjukkan pembentukan fasa campuran iaitu ortorombik M1 dan heksagonal M2. Walau bagaimanapun, apabila dirawat dengan hidrogen peroksida, fasa heksagonal M2 hilang dan hanya fasa ortorombik M1 yang tinggal. Penyingkiran fasa heksagonal menyumbang kepada luas permukaan S_{BET} yang lebih tinggi sehingga empat kali ganda daripada nilai asal bagi setiap sampel. Profil TPR menunjukkan peningkatan jumlah oksigen kekisi tersingkir selepas dibasuh dengan H_2O_2 . Analisis TEM mendapati mangkin MoVTenNbOx yang dibasuh menunjukkan struktur rod yang sejajar dengan morfologi yang diperhatikan dalam analisa SEM. Analisis ICP-AES pula menunjukkan mangkin yang dibasuh mempunyai komposisi Te berkurangan daripada nilai sebenar. Ujian pemangkinan menunjukkan mangkin tersebut adalah aktif dengan pemilihan tindakbalas pengoksidaan propana kepada asid akrilik sebanyak 25 % dengan penukaran propana mencapai sehingga 38 %.

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I certify that a Thesis Examination Committee has met on 20 August 2014 to conduct the final examination of Ahmad Afandi bin Muda on his thesis entitled "Synthesis of MoVTeNb Oxide Catalysts for Propane Oxidation to Acrylic Acid via Microwave Irradiation-Assisted Slurry Method" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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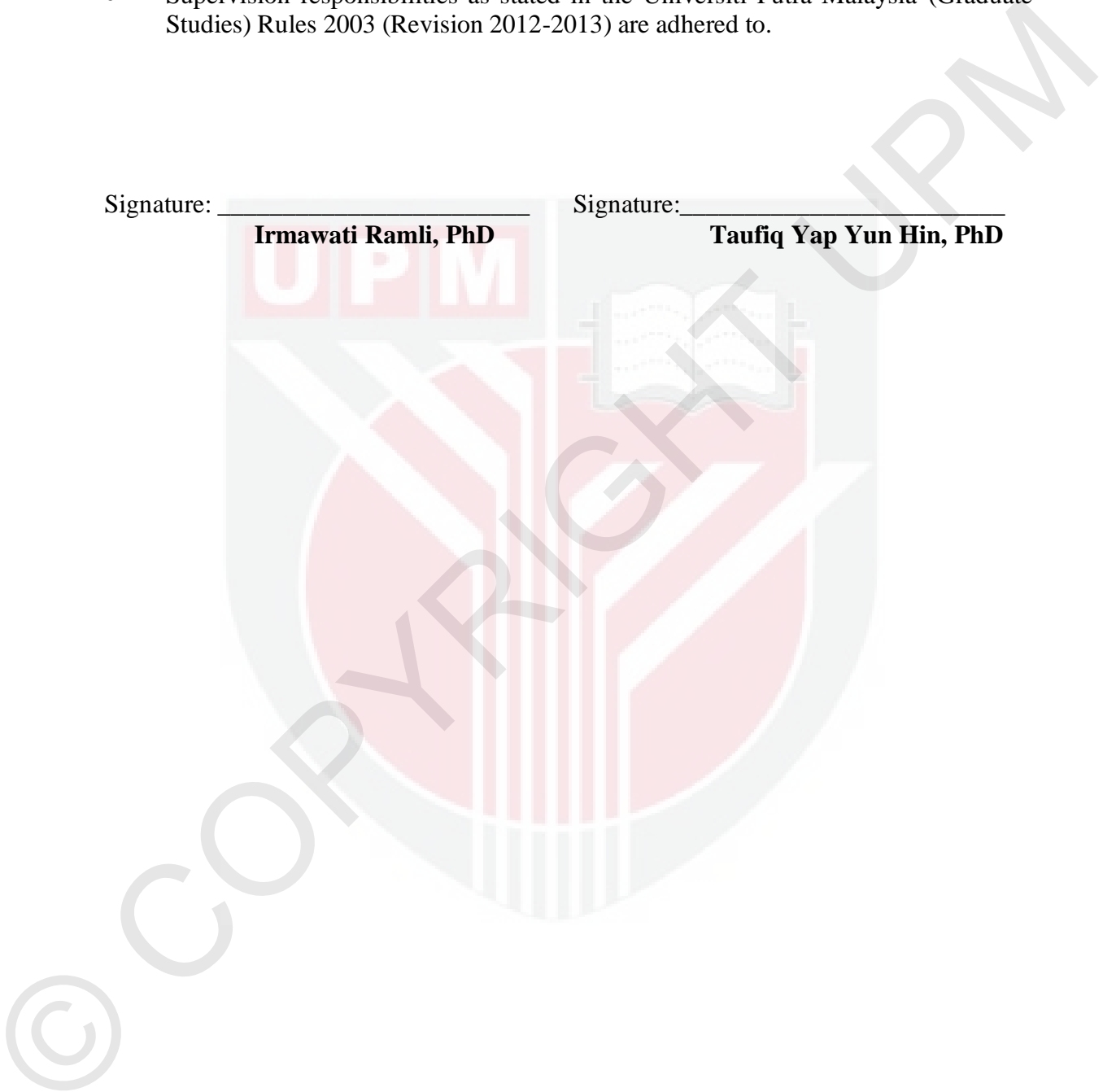


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LIST OF ABBREVIATIONS

| | |
|-----------------------|--|
| CO _x | Carbon oxides |
| MoV | Molybdenum-Vanadium |
| MoVTeNbO _x | Molybdenum-vanadium-tellurium-niobium oxide |
| M1 | Orthorhombic M1 phase |
| M2 | Hexagonal M2 phase |
| XRD | X-ray Diffraction Analysis |
| BET | Brunauer, Emmett, and Teller method for surface area measurement |
| FTIR | Fourier Transform Infra-Red Spectroscopy |
| SEM | Scanning Electron Microscopy |
| TPR | Temperature Programmed Reduction |

CHAPTER ONE

INTRODUCTION

1.1 General introduction

At the end of 20th century, petrochemical industrialist recognizes the increasing availability of cheap C1 (methane), C2 (ethane), C3 (propane) and C4 (butane) alkanes and their potential as feedstock for fuels and chemicals (Lange, 2005). Since then, it has attracted the attention of scientists, engineers and researchers to investigate further on the applicability of these alkanes especially on replacing related olefins. The discovery of catalysts that shows some promising activity for the always inactive saturated hydrocarbons contributed to this interest.

In petrochemical industry upgrading of a cheaper feedstock to higher valuable products is a continuous effort. One of the reaction used is a selective reaction of propane, substituting propene which is more expensive to produce a highly demanded oxygenated compounds (Bettahar *et al.*, 1996). The reactions utilize catalysts, which made of 25 % of catalyst market in petrochemical industry. Table 1 shows the fractions of the global petrochemical market of petrochemical (Mulla *et al.*, 2002). It is shown that the oxidation process becomes the second important contribution for the chemical catalyst world market in 2001.

Table 1: The 2001 global market of petrochemicals (Mulla *et al.*, 2002)

| Area | Billion US\$ |
|----------------------|--------------|
| Ammonia and methanol | 698 |
| Oxidation | 537 |
| Hydrogenation | 350 |
| Organic synthesis | 292 |
| Aromatics | 206 |
| Dehydrogenation | 202 |

1.2 Catalysis

Catalysis is defined as an acceleration process of chemical reaction due to the involvement of any catalyst substances. Thus, catalysis is believed as an essential part of manufacturing processes due to the efficiency of production. Catalysis occurs when there is a chemical interaction between catalyst and the reactant-product system without changing the chemical nature of the catalyst except at the surface. This means that there is a surface interaction and does not penetrate into the interior of the catalyst (Widegren *et al.*, 2003).

The explanation of a catalyst has been discussed many times (Lin, 2001). For instance, a catalyst is a substance that transforms reactants into products, through an uninterrupted and repeated cycle of elementary steps in which the catalyst participates while being regenerated to its original form at the end of each cycle during its lifetime. A catalyst changes the kinetics of the reaction, but does not change the thermodynamics (Grasselli, 1999).

Catalyst works by lowering the activation energy of a reaction. This allows less energy to be used, thus speeding up the reaction. Therefore, more molecular collisions have the minimal amount of energy needed to reach the transition state. At the same time, catalyst may increase reaction rate or selectivity, or enable the reaction at lower temperatures (Hagen, 2006).

Although catalysts can greatly affect the rate of a reaction, the equilibrium composition of reactants and products is still determined solely by thermodynamics. This effect can be illustrated with a Boltzmann distribution and energy profile (Figure 1).

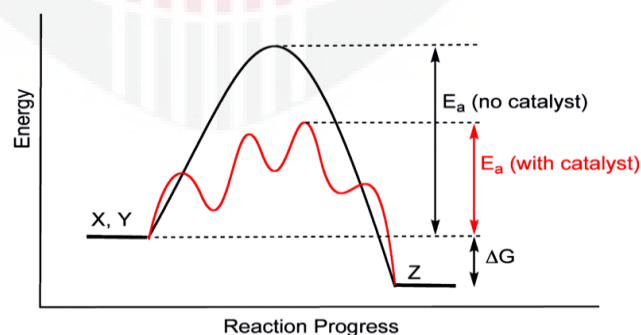


Figure 1: Activation energy, E_a profile for reaction with (black) and without (red) present of the catalyst

Potential energy diagram showing the effect of a catalyst in a hypothetical exothermic chemical reaction $X+Y$ to give Z . The presence of the catalyst shows a different reaction pathway (shown in red) with lower activation energy. The final results and the overall thermodynamic are the same. It has no effect on the chemical equilibrium of a reaction although the rate of both forward and reverse reaction was affected and consequently affects the rate of reaction. If a catalyst does change the equilibrium, then it must be consumed as the reaction proceeds, and thus it is also a reactant.

1.3 Heterogeneous catalyst

Catalysts can be divided into two main types which are heterogeneous and homogeneous. The difference between these two types of catalyst is the phase present in the reaction. Homogeneous catalysts are catalysts which have a same phase as the reactants or substrates and there is no phase boundary existing between both of them. Typically the homogeneous catalysts are dissolved in a solvent with substrates (Widegren *et al.*, 2003). Heterogeneous catalyst on the other hand present in solid state in a liquid or gaseous reaction system. The advantage of using heterogeneous catalyst is that, being a solid, it is easy to separate from the gas and/or liquid reactants and products of the overall catalytic reaction. Furthermore, heterogeneous catalysts are typically more tolerant of extreme operating conditions than their homogeneous counterpart. The heart of a heterogeneous catalyst is the active sites (or active centers) is at the surface of the solid. The catalyst is typically a high surface area material from 10 up to 1000 m^2g^{-1} , and it is usually desirable to maximize the number of active sites per reactor volume. Identifying the reaction intermediates and hence the mechanism for a heterogeneous catalytic reaction is often difficult, because many of these intermediates are difficult to detect using conventional methods (e.g., gas chromatography or mass spectrometry) because they do not desorb at significant rates from the surface of the catalyst (especially for gas-phase reactions) (Grasselli *et al.*, 2004).

Heterogeneous catalysts normally contain different types of surface sites, because crystalline solids exhibit different crystallographic orientation or crystalline anisotropy. Equilibrated single crystals expose different face with different atomic structure so as to minimize total surface energy. The different crystallographic planes exposing sites with different coordination conditions possessed identical properties for chemisorptions and catalytic reactions. Moreover, most solids catalysts are polycrystalline. Furthermore, in order to achieve high surface area of the catalyst, most of the catalysts contain nanometres size of particles. If the catalyst contains more than one component, the surface composition might be different from the bulk and differently with each exposed crystallographic plane (Grasselli *et al.*, 2004).

Generally, the key factors that contribute to the good performance of heterogeneous catalyst are:

- 1) The catalysts must have excellent selectivity to the desired products and at the same time lowest the selectivity to undesired product.
- 2) The catalyst should achieve adequate rates of reaction at desired reaction conditions of the of the process; need to mentioned that basically achieving high selectivity towards desired products is more important than achieving high catalytic activity (conversion).
- 3) The catalysts must have highly stability of catalytic performance at optimum conditions for longer duration time of the reactions.
- 4) The active sites on the catalysts must have better accessibility of reactants and products so that high rates can be achieved per reactor volume.

The first three key factors that contributed to the better catalysts are affected by the interaction between the surface of the catalysts with the reactants, products as well as intermediates of the catalysts reaction scheme. The above key factors are based on the principle of Sabatier (Cavani *et al.*, 1998 and Levy *et al.*, 1974).

The principle of Sabatier states that good heterogeneous catalysts are the substance exhibits an intermediate strength of the interaction between surface of the catalysts with reactants, intermediates and products of the catalytic reaction. As a result, the contact time between the active sites of the catalysts with reactant becomes longer. Thus, the production of unwanted products was higher. Meanwhile, when the interactions are too strong between the surfaces of the catalysts with the absorbed species of the catalytic reaction are causes the excessive blocking of the surface of the catalysts leading to low catalytic activity. As well as, when interactions between the surfaces of the catalysts with these species of the catalytic reaction are too weak lead to highly activation energies for the surface of the catalysts, thus low catalytic activity. This condition cause the contact time between reactant and the active sites of the catalyst become too short. Thus, part of the reactant leaves the surface of the catalyst without reacting. This resulting in decreasing conversion of reactant and increasing selectivity to unwanted products.

1.4 Propane

Fossil fuels are fuels formed by natural processes such as anaerobic decomposition of buried dead organisms. The age of the organisms and their resulting fossil fuels is typically millions of years. It contains high percentages of carbon and includes coal, petroleum, and natural gas (Liang *et al.*, 2012). The main composition of natural gas is saturated aliphatic hydrocarbon such as methane (C1), ethane (C2), propane (C3) and butane (C4). Propane (C3) is a gas formed from natural gas and petroleum. It is found

mixed with petroleum and natural gas deposits. Propane is one of the fossil fuels included in the liquefied petroleum gas (LPG). At atmospheric temperature and pressure, propane form in a gaseous state, colorless and odorless.

Propane produced from petrochemical mixtures via refinement of crude oil and separation from the natural gas. Natural gas and petroleum refinery off-gases are big industries and represents abundant resources of lower alkanes like liquefied petroleum gas (LPG) which contains mainly propane and butanes. The conversions of propane and butanes to valuable chemicals have received much attention. Therefore, more efforts have been undertaken to convert the alkanes into more valuable petrochemicals product by selective oxidation catalysts.

However, due to the low polarity of the C-H bonds in saturated hydrocarbons, their effective activation is a challenging task. Furthermore, increased reactivity of intermediates like olefins involves the risk of consecutive reactions including C-C bond cleavage or deep oxidation leading to unwanted oxygenates and, finally, to CO_x (CO and CO₂). Thus, the reaction conditions needed to obtain the acrylic acid must be mild; therefore, the catalysts for propane oxidation have to be able to activate propane in an efficient manner.

1.5 Acrylic acid

Acrylic acid is the common name for prop-2-enoic acid is the simplest unsaturated carboxylic acid with carboxylic acid terminus and vinyl group attached at the α -carbon position. In its pure physical characteristic form, acrylic acid is a clear and colorless liquid. Besides that it is miscible with alcohols, water, chloroform and ethers. Mostly, acrylic acid is produced from propene, a gaseous product of oil refineries. It was used as an essential monomer for variety of polymers that have gives advantages such as plastics, coating and textile industries. Figure 2 shows the chemical structure of acrylic acid. It consists of two functional group, namely as carbon-carbon double bond and carboxyl group.

These functional groups made the acrylic acid very versatile since it is widely used in a variety of chemical reactions and its modification to outfit the variety of usages. Figure 3 shows uses of acrylic acid. In industry, acrylic acid and its esters are important monomers for the manufacture of homo- and co-polymers such as paints, adhesives, textile finishing, leather processing, and superabsorbent (Lin, 2003).

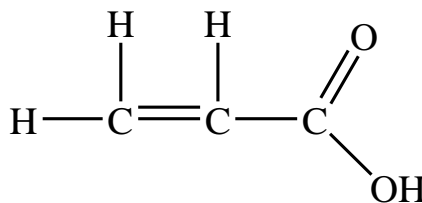


Figure 2: Chemical structure of acrylic acid

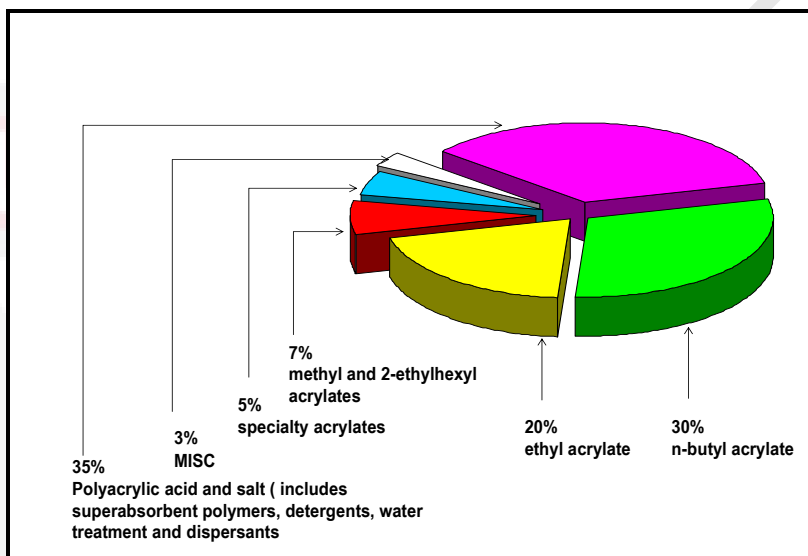


Figure 3: Uses of Acrylic acid (Grasselli, 1997)

1.6 Problem statements

Recently, due to the rising costs of chemicals from natural gas and awareness of environmental problems, researchers have been looking for alternatives for the production of processed chemicals that are cheaper and also less pollution impact. One of the processes is by the use of propane as an alternative to propene in the production of acrylic acid. However, commercially 87% of acrylic acid is produced from propene oxidation (Cavani *et al.*, 1997) compared to 50% acrylic acid is produced in lab scale by using propane (Lin, 2001), yet still awaiting its commercial breakthrough. This is due to the high amount of by-products such as CO and CO₂. Thus, the best catalysts so far that can decrease the production of the byproducts is MoVTenbO_x, a quaternary mixed metal oxide.

Usually, the common synthesis had been used in the synthesis of MoVTenbO_x catalyst are slurry and lab-scale hydrothermal method. In lab-scale hydrothermal, the structure of catalysts MoVTenbO_x obtained is better in terms of compositionally and structurally due to the better control over crystalline growth condition. However, there are some problems in the use of this synthesis method. Among them are the requirement of high

pressure and high synthesis temperature (normally 448 K) to synthesize the active catalyst. Therefore, the preparation requires a special tool called autoclave, where the cost of it is expensive. Usually it has an inside volume 150 – 200 mL which translated that the yield of the catalyst formed is low, roughly in the range of 10 g. Therefore it requires high production cost if the process to be upgraded to pilot scale. In the slurry method, the aqueous slurry was formed from mixtures of ammonium heptamolybdate, ammonium metavanadate, ammonium niobium oxalate and telluric acid. The slurry was calcined in inert condition. One of the problems is the MoVTeNbO_x catalysts obtained via this method is under poor control of the catalyst structures and compositions since the different metal salts are in aqueous slurry form. As the result, this will lead to inhomogeneity of the mixture and consequently resulted in a mixed phases of the catalyst structure.

Recently, Ramli *et al.*, (2011) was successfully attempted the orthorhombic structure via reflux method. In this work, however, the longer period needed to obtain the desired phase which is 3 – 4 days. This leaves the opportunity to improve synthesis technique by reducing the period of synthesis.

Therefore a conventional and controlled synthesis technique is interesting to be embarked in preparing the MoVTeNbO_x catalysts. This can achieve by using the slurry method assisted with microwave irradiation followed by washing with H₂O₂.

Thus, the ability to obtain the suitable crystallinity structure and its composition of the MoVTeNbO_x catalyst is very important for the study of molecular structure and reactivity relationships in propane oxidation to acrylic acid as well as improving designing of the catalyst itself. Hence, to acquire the ideal crystallinity structure of the catalyst MoVTeNbO_x is important for fundamental research to study the active site that responsible for basic research for selective oxidation of propane. Therefore, it is a critical need to develop efficient methods for catalytic synthesis MoVTeNbO_x with desirable catalytic properties.

1.7 Objectives of the study

The objectives of this study are:

- i) To synthesize single phase orthorhombic M1 of MoVTeNb oxide catalysts via slurry method assisted with microwave irradiation.
- ii) To characterize the physicochemical properties of the synthesized catalysts.
- iii) To analyze the catalytic performance of the synthesized catalysts for partial oxidation of propane to acrylic acid.

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