EFFECTS OF pH ON THE PHYSICOCHEMICAL PROPERTIES OF MoVTeNbOx CATALYSTS FOR OXIDATION OF PROPANE

SYAZWANI BINTI MOHD NOOR

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

June 2015

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

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Chairman : **Assoc. Prof. Irmawati Ramli, PhD**
Faculty : **Science**

$Mo_{0.1}V_{0.3}Te_{0.23}Nb_{0.12}$ mixed metal oxide catalysts were prepared via slurry method followed by microwave irradiation. The effect of pH was studied by varying the pH of the resultant solution at pH = 1.0, 3.0. 5.0 and 7.0 (± 0.01). The catalysts precursor obtained were calcined for 1 h in air at 553 K and 2 h in N_2 stream at 873 K. The catalysts were post treated by washing with 30% H_2O_2. An Anderson-type heteropolyanion was formed in samples prepared at pH 3.0–7.0 (±0.01). After calcination, X-ray Diffraction Analysis (XRD) explained that the active orthorhombic M1 phase was obtained for samples prepared at lower pH (pH 1.0 and pH 3.0 (±0.01)). From Fourier Transform-Infrared (FT-IR) spectra, no significant difference in the formation of functional group of different synthesised pH of the MoVTeNbOx catalysts. Thermo Gravimetry-Differential Thermal Gravimetric Analysis (TG-DTG) for all samples show a similar thermal behaviour with four decomposition signals. Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) revealed that a remarkable loss of tellurium was observed after calcination. The catalysts borne rod-shaped morphology under Field Emission-Scanning Electron Microscopy (FE-SEM). XRD analysis after post treatment suggested the elimination of hexagonal M2 phase and modification of orthorhombic M1 crystal surfaces. Washing with hydrogen peroxide also gave better reducibility of the catalysts in Temperature Programmed Reduction in Hydrogen (H_2-TPR) by shifting the peak maximum to lower temperature compared to the unwashed catalysts. Brunauer-Emmett-Teller surface area analysis (S_{BET}) exposed that the catalysts prepared at lower pH value has a higher surface area than catalysts prepared at higher pH value. Overall, the catalytic study of MoVTeNbOx catalysts revealed that catalyst prepared at pH 1.0 (±0.01) has high selectivity towards acrylic acid in anaerobic oxidation of propane. Thus, the different synthesis pH has a strong effect on the final phase composition and distinct activities of MoVTeNbOx catalysts.

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

KESAN-KESAN pH TERHADAP SIFAT FIZIKOKIMIA MANGKIN MoVTeNbOx UNTUK PENGOKSIDAAN PROPANA

Oleh

SYAZWANI BINTI MOHD NOOR

Jun 2015

Pengerusi : Prof. Madya Irmawati Ramli, PhD
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Mangkin $Mo_{0.1}V_{0.3}Te_{0.23}Nb_{0.12}$ campuran logam oksida telah disediakan dengan kaedah buburan diikuti oleh penyinaran gelombang mikro. Kesan pH telah dikaji dengan mengubah pH larutan yang dihasilkan kepada pH = 1.0, 3.0. 5.0 dan 7.0 (±0.01). Mangkin prekursor yang diperoleh telah dikalsin selama 1 jam di dalam udara pada 553 K dan 2 jam di dalam aliran N_2 pada 873 K. Mangkin melalui pasca rawatan dengan pembasuhan menggunakan 30% H_2O_2. Heteropolianion jenis Anderson telah terbentuk dalam sampel yang disediakan pada pH 3.0-7.0 (±0.01). Selepas dikalsinasi, analisis Pembelauan Sinar-X (XRD) menjelaskan bahawa fasa aktif ortorombik M1 diperoleh daripada sampel yang disediakan pada pH yang rendah (pH 1.0 dan 3.0 (±0.01)). Daripada spektrum Fourier Transformasi-Inframerah (FT-IR), tidak ada perbezaan yang signifikan terhadap pembentukan kumpulan berfungsi bagi mangkin MoVTeNbOx yang disintesis pada pH yang berbeza. Analisis Termogravimetri-Terbitan Termogravimetri (TG-DTG) bagi semua sampel menunjukkan sifat terma yang serupa dengan empat signal penguraian. Plasma Gandingan Teraruh-Spektroskopi Pancaran Atom (ICP-AES) menunjukkan bahawa pengurangan elemen telurium yang ketara diperhatikan selepas dikalsinasi. Mangkin menunjukkan morfologi berbentuk rod di bawah Mikroskopi Imbasan Elektron-Pancaran Medan (FE-SEM). Analisis XRD selepas pasca rawatan mencadangkan penghapusan fasa heksagonal M2 dan pengubahsuaian permukaan hablur fasa ortorombik M1. Pembasuhan dengan hidrogen peroksida juga memberikan mangkin kebolehturunan yang lebih baik dalam Penurunan Berprogramkan Suhu dalam Hidrogen (H_2-TPR) dengan menganjakkan puncak maksimum kepada suhu yang lebih rendah berbanding dengan mangkin yang tidak dibasuh. Analisis luas permukaan Brunauer-Emmett-Teller (S_{BET}) mendedahkan mangkin yang disediakan pada nilai pH yang lebih rendah mempunyai luas permukaan yang lebih tinggi berbanding mangkin yang disediakan pada nilai pH yang lebih tinggi. Secara keseluruhan, kajian pemangkin MoVTeNbOx mendedahkan bahawa mangkin yang disediakan pada pH 1.0 (±0.01) lebih selektif terhadap asid akrilik di dalam pengoksidaaan anaerobik propana. Oleh itu, pH sintesis yang berbeza mempunyai pengaruh yang kuat terhadap komposisi fasa terakhir dan perbezaan aktiviti bagi mangkin MoVTeNbOx.

ACKNOWLEDGEMENTS

In the name of Allah, The Benevolent and Merciful.

I am using this opportunity to express my gratitude to everyone who supported me throughout the completion of this study. I am thankful for their aspiring guidance, invaluably constructive criticism and friendly advice during the research work. I am sincerely grateful to them for sharing their truthful and illuminating views on a number of issues related to the study.

I express my warm thanks, gratitude to my project supervisor, Associate Prof Dr. Irmawati binti Ramli for her extra supervision, guidance, suggestion, constructive supports and continuous supports throughout this study. I really appreciate her commitments towards this study and without supervision from her this study may become impossible.

I would also like to thank my Co-Supervisor, Prof Taufiq Yap Yun Hin for his constructive comments and suggestion to make this research became better. I also would like to thank to all the staff of Chemistry Department especially their kind assistance in order to get my project done in terms of technical guidance and material preparations which has contributed towards the success of this research.

In addition, my grateful thanks to all my friends in PutraCAT Laboratory for their help during my laboratory work. Your invaluable help make this study possible. We go through the up and down together and encourage each other for the future.

Last but not least, lots of love for my parents and family for their support and understanding through this journey.

Finally, I would like to express my deepest appreciation to all those who provided me the possibility to complete this research study.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

MoVTeNbOx	Molybdenum, Vanadium, Tellurium, Niobium oxide catalyst
$MVTN_{1p}$	MoVTeNbOx catalyst precursor sample prepared at pH 1.0 (±0.01)
$MVTN_{3p}$	MoVTeNbOx catalyst precursor sample prepared at pH 3.0 (±0.01)
$MVTN_{5p}$	MoVTeNbOx catalyst precursor sample prepared at pH 5.0 (±0.01)
$MVTN_{7p}$	MoVTeNbOx catalyst precursor sample prepared at pH 7.0 (±0.01)
$MVTN_{1c}$	MoVTeNbOx catalyst calcined sample prepared at pH 1.0 (±0.01)
$MVTN_{3c}$	MoVTeNbOx catalyst calcined sample prepared at pH 3.0 (±0.01)
$MVTN_{5c}$	MoVTeNbOx catalyst calcined sample prepared at pH 5.0 (±0.01)
$MVTN_{7c}$	MoVTeNbOx catalyst calcined sample prepared at pH 7.0 (±0.01)
$MVTN_{1w}$	MoVTeNbOx catalyst washed sample prepared at pH 1.0 (±0.01)
$MVTN_{3w}$	MoVTeNbOx catalyst washed sample prepared at pH 3.0 (±0.01)
$MVTN_{5w}$	MoVTeNbOx catalyst washed sample prepared at pH 5.0 (±0.01)
$MVTN_{7w}$	MoVTeNbOx catalyst washed sample prepared at pH 7.0 (±0.01)
XRD	X-ray Diffraction Analysis
FT-IR	Fourier Transform - Infrared Spectroscopy
TG-DTG	Thermo Gravimetry - Differential Thermal Gravimetric Analysis
ICP-AES	Inductive Coupled Plasma - Atomic Emission Spectroscopy
FE-SEM	Field Emission - Scanning Electron Microscopy
H_2-TPR	Temperature Programmed Reduction in Hydrogen
S_{BET}	Brunauer-Emmett-Teller Surface Area Measurement
TPRn	Anaerobic Temperature Programmed Reaction

CHAPTER I

INTRODUCTION

1.1 Background of study

Lower alkanes (C1-C4) are global affluent revenue from the natural gas and petroleum refinery off-gases. In the recent time, much effort has been attempted to convert these alkanes into more beneficial petrochemicals or feedstocks in the development of novel selective oxidation catalysts. This great interest is due to their possible application as a feedstock of low-cost raw materials especially for replacing corresponding olefins.

Among selective oxidations of alkane, the conversion of propane to acrylic acid has gained focus of comprehensive research worldwide since the early of 1990s (Lin, 2001). Upon this, the most promising mixed metal oxide catalyst to accomplish this conversion is the bulk mixed Mo-V-Te-Nb-O system (Yu *et al.*, 2009; Beato *et al.*, 2006; Lin, 2001). This catalyst was studied in this research as it has been revealed as highly active and selective catalyst for the propane oxidation to acrylic acid.

The method applied for the synthesis of MoVTeNbOx catalyst is the microwave-assisted slurry method. The presence of microwaves has been reported in greatly improves the rate of many chemical reactions, with a strong reduction of the reaction time, without altering the final yield (Fini and Breccia, 1999).

1.1.1 Catalyst

The origin of word catalyst is from the Greek word. The word “kata” means down and “lyein” means loosen or split. These two words are combined to develop the word of catalyst. A catalyst is a substance that speeds up the chemical reaction by lowering the activation energy of a particular reaction. A catalyst is not being consumed in the reaction and can be recovered chemically unchanged at the end of the reaction it has catalysed.

Thermodynamically, during the operation of catalysis, the reactants and the catalyst are combined and undergo a rearrangement of chemical bonds which head to the formation of transition states. Energy that is required to form the transition state is called the activation energy, E_a. Reactants with lower energy than E_a cannot go through the transition state to react will become products.

The energy profile for the reaction as a function of a reaction pathway, moving from reactants to products is schematically illustrated in Figure 1.1. Clearly, in order to transform the reactants into products, molecules must overcome the energy barrier represent by the activation energy.

The role of the catalyst is therefore to modify this energy profile, provide an alternative reaction pathway, featuring lower activation energy compared to non-catalysed system (Farnetti *et al.*, 2009). From the Figure 1.1, a clear difference can be observed in term of activation energy between catalysed and uncatalysed reaction. In the existence of catalyst, the activation energy is lowered and speed up the rate of reaction.

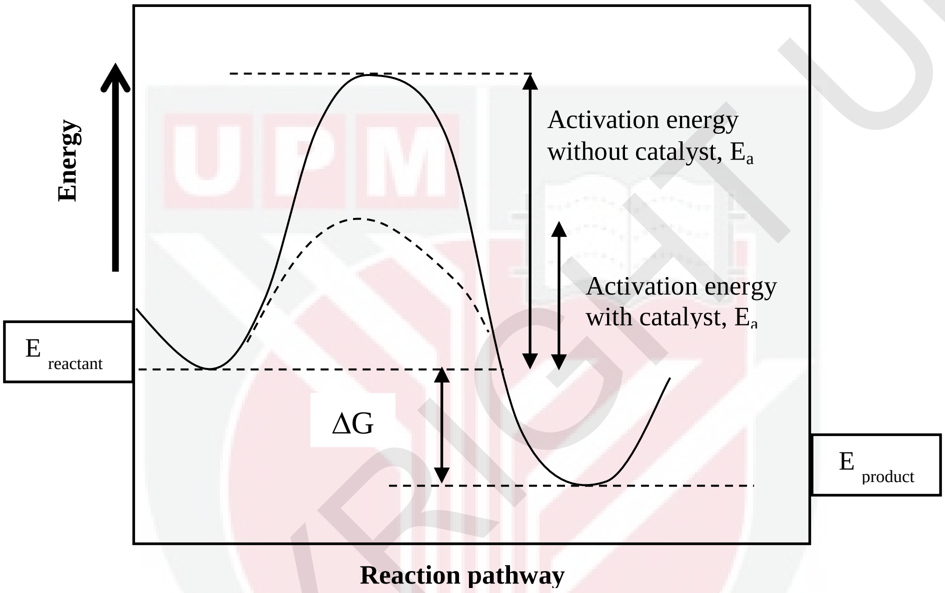

Figure 1.1: Comparison of activation energy between reaction with and without catalyst

Catalysts can be categorised into homogeneous catalysts and heterogeneous catalysts. Heterogeneous catalysts can be distinguished over homogeneous catalysts by the different phases present during the reaction. Most of the processes using homogeneous catalysts occur when catalyst and reactants present in the same phase, usually liquid. Meanwhile, in heterogeneous catalysts, the catalyst and reactants usually present in a different phase, which is the catalyst is usually in a solid form and the reaction occurs either in the liquid or gaseous phase. The conversion of propane in a gas phase over a solid MoVTeNbOx catalyst to acrylic acid is one of the examples of heterogeneous catalyst.

1.1.2 Heterogeneous Catalysis

Selective heterogeneous oxidation catalysis is indispensable to the society, since it recovers about 25% of the most essential chemical industry and intermediates were used in the manufacture of industrial products and consumer goods (Grasselli, 2002). The products include intermediates such as acrolein, acrylic acid, acrylonitrile, ethylene, maleic anhydride, methacrylic acid and propylene oxide.

A heterogeneous catalytic reaction involves both adsorption of reactant and desorption of product on various sites of the catalyst. Since the heterogeneous catalysis involves the complex mechanism, it is important to study the principles of heterogeneous catalysis in order to develop an efficient reaction system. Grasselli, (2002) has highlighted the seven principles of selective heterogeneous oxidation catalysis towards a better understanding of catalyst behaviour. The seven principles of selective heterogeneous oxidation catalysis are described as follows;

1) The first principle is the lattice oxygen. It has been postulated that the lattice oxygen of a reducible metal oxide might serve as a selective oxidising agent in the oxidation process.

2) The second principle is the metal–oxygen bond strength. The metal–oxygen bond of active oxygen atoms must be in intermediate strength under the reaction conditions (Callahan and Grasselli, 1963). If the metal-oxygen bond is too strong, no reaction will occur, if it is too weak, over-oxidation will occur, leading to undesired waste products.

3) The third principle is the host structure. An appropriate host structure is required to contain the desired lattice oxygen(s) and metal–oxygen bonds. The chosen host structure must be able to accommodate anion vacancies without being collapsed in structure.

4) The fourth principle is the redox. Metal oxides must also exhibit redox properties, in order to become useful either in a cyclic oxidant process or a catalytic oxidation process.

5) The fifth principle is the multifunctionality of active sites. The active sites of selective metal oxide catalysts are generally multifunctional and multimetallic or usually at least bifunctional and bimetallic to perform various functions in the catalytic cycle.

6) The sixth principle is the site isolation. The site isolation hypothesis that reactive surface lattice oxygens must be isolated from each other on a catalyst surface, so that the selectivity can be obtained and overoxidation can be avoided.

7) The seventh principle is the phase cooperation. Two or more phases that contain the necessary functions for catalytic reaction should be in close contact so that they can disclose to each other and thereby cooperate between the phases.

The main advantage of using a heterogeneous catalysis is the ease of separation of the catalyst from the product leading to the continuous chemical processes. Additionally, compared to homogenous catalysts, heterogeneous catalysts are normally more tolerant in extreme operating conditions.

1.1.3 Acrylic Acid

Acrylic acid (IUPAC: 2-propenoic acid) is the unsaturated carboxylic acid with the chemical structure shown in Figure 1.2. It is consisting of a vinyl group and the carboxylic acid functional group, with the vinyl group attached directly to the carboxylic acid terminal. This polar molecule is miscible in water, alcohols, ethers and chloroform.

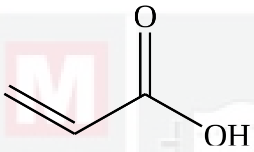

Figure 1.2: Chemical structure of acrylic acid

Acrylic acid has two reactions points for polymerisation process which are carbon-carbon double bond and carboxyl group. These two points made the acrylic acid can be manipulated for a broad range of usage in chemical reactions. Acrylic acid and its esters go through double bond reaction and easily combine with themselves or other monomer to form homopolymers and co-polymers which are indispensable for the formation of various products in the chemical industry.

The Dow Chemical Company has summarised that there are mainly two uses for acrylic acid (Product Safety Assessment: DOW™ Acrylic Acid, 2014). Firstly, it has served as a chemical intermediate to produce acrylic acid esters (such as ethyl acrylate). These esters are used to make ingredients in adhesives, paints, coatings, textiles, plastics, and many other applications. Secondly, it acts as a building block to produce polyacrylic acid, or crosslinked polyacrylic acid compounds. These products are the key element in the hygienic products such as diapers, detergents and chemicals for wastewater treatment.

Based on the Chemical Economics Handbook *Superabsorbent Polymers* Report (2014), growth in demand for crude acrylic acid is forecast at almost 4.5% annually during 2015–2018, govern by growth in acrylate esters at 4.3% and superabsorbent polymers at 4.8%. For global glacial acrylic acid (purified crude acrylic acid), the consumption was estimated for about 45% of total crude acrylic acid consumption in 2014 and were forecast to grow at 5.4% annually during 2015–2018. Thus, there will be a huge challenge for the industries to cope with the world demand of acrylic acid. The pie chart in Figure 1.3 summarises the world consumption of acrylic acid in 2013.

Hence, acrylic acid is an important intermediate in the chemical industry for the manufacture of acrylates and polyacrylic acid. In industries, acrylic acid is the fastest growing commodity chemicals with current worldwide demand approximately 3-4 million tons per year (Trunschke, 2011).

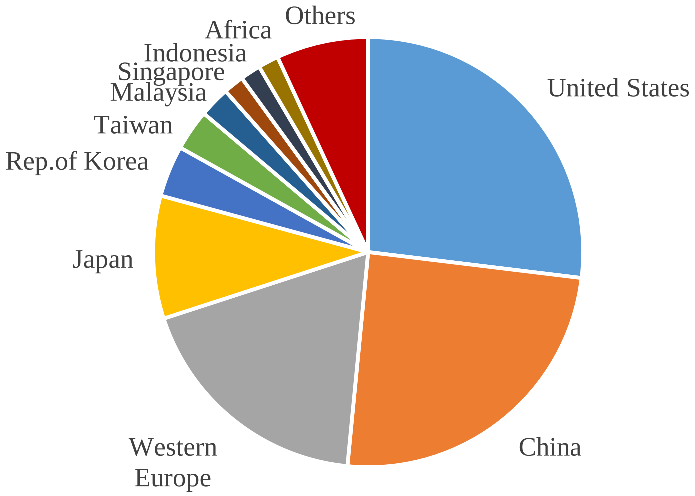

Figure 1.3: World consumption of acrylic acid in 2013 (CEH *Superabsorbent Polymers* Report 2014)

1.1.4 Acrylic Acid Production

Acrylic acid is known to be produced by using unsaturated hydrocarbon, propylene. There is also other chemical pathway to produce acrylic acid, for example, using acetylene as a starting material.

Since the last decades, the use of acetylene has been important for chemical industries as a starting material. Before the modern plant was developed, acrylic acid was manufactured mainly by carbon-carbon coupling reactions (Eq 1.1) until the mid-1990s. In this process, acetylene was converted in the presence of carbon monoxide and water over catalysts containing carbonyl-forming metals, such as $NiBr_2/CuI$ in the BASF process (Beller *et al.*, 1995).

$$HC{\equiv}CH\,(g) + CO\,(g) + H_2O\,(l) \xrightarrow{NiBr_2/CuI} H_2C{=}CH{-}COOH\,(g) \qquad \text{(Eq 1.1)}$$

Currently, the major industrial acrylic acid production is via the catalytic partial oxidation of propylene (Eq 1.2 and Eq 1.3). This industrial process required acrylic acid production via a two-step process by converting propylene to acrolein and then followed by oxidation of acrolein to acrylic acid (Voge and Adam, 1967).

Step 1:

$$H_2C{=}CH{-}CH_3\,(g) + O_2\,(g) \longrightarrow H_2C{=}CH{-}CHO\,(g) + H_2O\,(l) \qquad \text{(Eq 1.2)}$$

Step 2:

$$H_2C{=}CH{-}CHO\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2C{=}CH{-}COOH\,(g) \qquad \text{(Eq 1.3)}$$

However, oxidation of reactants and products resulting the in the occurrence of several side reactions. Therefore, this two step process required two separate reactors with acrolein as an intermediate. The first reactor is usually performed at a higher temperature than the second reactor. These two steps of the reaction usually run over a different catalyst and at a different operating environment to maximise the acrylic acid production. Table 1.1 shows the list of catalysts used for industrial production of acrylic acid and the catalyst component used in this process.

Table 1.1: Catalysts used for industrial production of acrylic acid (Lin, 2001)

Company	Catalyst component	Reaction	Temperature (K)	Product yield (%)
Nippon Shokubai	Mo-Bi-Fe-W-Co-K-Si-O	Propylene → acrolein	593	90.2
Ube Industries	Mo-Bi-Fe-Co-V-K-O	Propylene → acrolein	603	90.3
Nippon Kayaku	Mo-V-Cu-Fe-Mn-Mg-P-O	Acrolein → acrylic acid	483	97.5
Nippon Shokubai	Mo-V-W-Cu-Sr-Al-O	Acrolein → acrylic acid	528	97.5

1.1.5 Propane as an Alternative Feedstock

Propane is a saturated hydrocarbon which naturally exists in a gas phase. This lower alkanes are remarkable raw materials in the manufacture of olefins and oxygen containing products by partial oxidation reaction due to its abundances and less expensive than corresponding olefins. To date, only the partial oxidation of *n*-butane to maleic anhydride over VPO catalysts has achieved commercial operation (Ballarini *et al.*, 2006).

Propane can be alternatively used as a feedstock through one-step oxidation in the gas phase with molecular oxygen over a MoVTeNbOx catalyst to produce acrylic acid (Eq 1.4).

$$CH_3CH_2CH_3\,(g) + 2O_2\,(g) \xrightarrow{\text{MoVTeNbOx}} H_2C{=}CH{-}COOH\,(g) + 2H_2O\,(g) \qquad \text{(Eq 1.4)}$$

Replacing alkenes as the starting materials by much cheaper alkanes can be highly profitable to the industries and end-users. The employing of alkenes as a starting material cost of around 50% or more of the total manufacturing costs. Hence, a great cost saving can be achieved by substituting propylene with much cheaper propane as the starting material to produce acrylic acid (Lin, 2003a).

1.2 Problem statement

In industry, there are two commercial sources of propylene, either a by-product of ethylene production or a by-product of refinery operations. The reduction of propylene supplies from steam crackers and refineries, resulting in the higher price levels. Utilising propane as a feedstock for the acrylic acid production could bring huge economic incentive since currently the olefin is approximately as twice as expensive than alkanes. However, lots of improvement is needed to ensure that the desirable transformation meets the industrial requirement.

The MoVTeNbOx catalyst is generally prepared using hydrothermal and slurry method. In the case of hydrothermal method, it requires high synthesis temperature and pressure to form active and selective catalyst. The synthesis is commonly done in an autoclave with the inside volume requires about 150-200 ml for a long initial heating period for at least 20 h and the yield of catalyst produced is relatively low, which is estimated in the range of 10 g. In addition, this method requires expensive autoclave and hence the huge production cost is required to upgrade this process to the industrial scale.

The microwave-assisted method that will be applied is an unconventional energy source that generates rapid heating of polar substances with resultant reductions in reaction times. This method easier to work up compared to conventional heating with cleaner reactions and usually produce greater yields. This method can be scaled-up for industrial chemical development since it gives faster reaction time with the improved product yield.

In this study, the effect of pH will be specifically investigated since the pH of the resultant slurry strongly effects both the crystallinity and the nature of the precursors. In addition, pH value of the resultant mixture is a crucial determinant in controlling the phase formation and morphology of phase produced.

1.3 Objectives of the study

The objectives of this study are:

1. To synthesise MoVTeNbOx catalyst through microwave-assisted slurry method at pH 1.0 to 7.0 (±0.01).
2. To characterise the precursor, calcined and washed MoVTeNbOx catalysts through XRD, FT-IR, TG-DTG, ICP-AES, FE-SEM, H_2-TPR and S_{BET}.
3. To evaluate performance of catalysts through selective oxidation of propane to produce acrylic acid.

1.4 Scope of the study

This study focused on the preparation of MoVTeNbOx mixed metal oxide catalyst which has been prepared by the slurry method followed by microwave irradiation. The effect of pH was studied by changing the pH of the resultant solution from 1.0 to 7.0 (±0. 01). The catalyst obtained after heat treatment and post-synthesis treatment was further analysed using XRD, FT-IR, TG-DTG, ICP-AES, FE-SEM, H_2-TPR and S_{BET} to investigate the physicochemical properties of the catalyst for selective oxidation of propane to acrylic acid. The performance of catalysts towards acrylic acid was evaluated using TPRn.

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