

UNIVERSITI PUTRA MALAYSIA

PREPARATION, CHARACTERIZATION AND CATALYTIC BEHAVIOR OF MoVTeNbOx CATALYSTS PREPARED BY REFLUX METHOD

SHAFIZAH MASURI

FS 2012 111

PREPARATION, CHARACTERIZATION AND CATALYTIC BEHAVIOR OF MoVTeNbOx CATALYSTS PREPARED BY REFLUX METHOD



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

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

PREPARATION, CHARACTERIZATION AND CATALYTIC BEHAVIOR
OF MoVTeNbOx CATALYSTS PREPARED BY REFLUX METHOD

By

SHAFIZAH BINTI MASURI

Chairman: Irmawati Ramli, PhD

Faculty : Science

MoVTeNbOx catalyst was prepared using reflux method at Mo:V:Te:Nb molar ratio of 1:0.3:0.16:0.12. In order to form the desired structure of orthorhombic M1 phase, three parameters considered were pH, number of washing and niobium source. The first two parameters were observed unsuccessful in forming orthorhombic structure but instead formed tetragonal $(V_{0.07}Mo_{0.93})_5O_{14}$ and monoclinic $TeMo_5O_{16}$ phases. The monoclinic $TeMo_5O_{16}$ phase was found to become more dominant as the pH of the solution increased. Meanwhile, washing had an effect on the crystallinity of the tetragonal $(V_{0.07}Mo_{0.93})_5O_{14}$ and monoclinic $TeMo_5O_{16}$ phases. The peaks for both phases were seen to be more intense as the numbers of washing were increased. The desired orthorhombic M1 phase was only formed when using niobium(V) chloride instead of ammonium niobium oxalate as the niobium source. This can be clearly seen by the appearance of the three peaks at $2\theta = 6.6^{\circ}$, 7.7° and 8.6° . The catalyst was then further investigated on the effect of calcination period on the orthorhombic formation. Longer calcination period as in this case was 2h, formed better

orthorhombic phase with monoclinic $TeMo_5O_{16}$ phase was found diminished. However, the tetragonal $(V_{0.07}Mo_{0.93})_5O_{14}$ phase in the catalyst was still present. Catalytic testing for propane oxidation into acrylic acid found that catalyst contain less orthorhombic phase showed less activity and selectivity towards the formation of acrylic acid. This was due to the existence of monoclinic $TeMo_5O_{16}$ and tetragonal $(V_{0.07}Mo_{0.93})_5O_{14}$ phase that hindered the propane to be oxidized to acrylic acid. While for the high orthorhombic content catalyst gave high activity with selectivity towards acrylic acid reached 22%.

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

PENYEDIAAN, PENCIRIAN DAN PENYIFATAN PEMANGKINAN BAGI MANGKIN MoVTeNbOx YANG DISEDIAKAN MELALUI KAEDAH REFLUKS

Oleh

SHAFIZAH BINTI MASURI

Pengerusi : Irmawati Ramli, PhD

Fakulti : Sains

Mangkin MoVTeNbOx telah disediakan melalui kaedah refluks pada nisbah molar bagi Mo:V:Te:Nb: adalah 1:0.3:0.16:0.12. Dalam proses untuk membentuk struktur fasa M1 ortorombik yang diinginkan, tiga parameter telah dipertimbangkan iaitu pH, bilangan pembersihan dan sumber niobium yang digunakan. Dua parameter pertama didapati tidak dapat menghasilkan struktur M1 ortorombik yang diingini akan tetapi menghasilkan fasa tetragonal $(V_{0.07}Mo_{0.93})_5O_{14}$ dan fasa monoklinik $TeMo_5O_{16}$. Fasa monoklinik $TeMo_5O_{16}$ ini menjadi dominan apabila pH bagi larutan tersebut meningkat. Sementara itu, pembersihan pula menunjukkan kesan terhadap kristaliniti bagi fasa tetragonal $(V_{0.07}Mo_{0.93})_5O_{14}$ and monoclinic $TeMo_5O_{16}$. Puncak bagi keduadua fasa ini didapati menjadi lebih tinggi apabila bilangan pembersihan meningkat. Fasa M1 ortorombik yang diinginkan didapati hanya terbentuk apabila niobium(V) klorida digunakan berbanding ammonium niobium oxalat sebagai sumber bagi niobium. Ini dapat dilihat melalui kemunculan tiga puncak pada $2\theta = 6.6^{\circ}$, 7.7° dan

8.6° di dalam graf. Mangkin yang dihasilkan dikaji dengan lebih lanjut terhadap kesan tempoh proses kalsinasi kepada pembentukan struktur ortorombik. Tempoh kalsinasi yang lebih panjang, dalam kajian ini adalah selama 2 jam membentuk struktur fasa M1 ortorombik yang lebih jelas dan fasa monoklinik TeMo₅O₁₆ didapati telah dihapuskan. Walau bagaimanapun, fasa tetragonal (V_{0.07}Mo_{0.93})₅O₁₄ masih lagi wujud di dalam mangkin. Ujian katalitik untuk proses pengoksidaan propana kepada asid akrilik menunjukkan bahawa mangkin yang mengandungi kurang fasa ortorombik menunjukkan aktiviti dan pemilihan yang rendah terhadap penghasilan asid akrilik. Ini disebabkan oleh kehadiran fasa TeMo₅O₁₆ dan tetragonal (V_{0.07}Mo_{0.93})₅O₁₄ yang menghalang propana untuk dioksidakan menjadi asid akrilik. Sementara itu, mangkin yang mempunyai banyak struktur ortorombik menunjukkan kadar aktiviti dan pemilihan yang tinggi dalam penghasilan asid akrilik yang mampu mencapai sehingga 22%.

ACKNOWLEDGEMENT

Praise be to Allah Almighty who has bestowed upon with wisdom and knowledge that enables me to complete this thesis. By that time, I have worked with a great number of people whose contribution in assorted ways to the research and the making of the thesis deserved special mention. It is a pleasure to convey my gratitude to them all in my humble acknowledgment.

First of all, I owe my deepest gratitude and especially thanks to my supervisor, Assoc. Prof. Dr. Irmawati Ramli for her encouragement, guidance and support from the initial to the final level of this research as well as giving me extraordinary experiences through out the work. Her truly intuition has made her as a constant of ideas and passions in science, which exceptionally inspire and enrich my growth as a student, a researcher and a scientist want to be. I am indebted to her more than she knows.

I would also acknowledge my co-supervisor, Prof. Dr. Taufiq Yap Yun Hin for his willingness to share their bright thoughts with me, which were very fruitful for shaping up my ideas and research. Collective and individual acknowledgments are also owed to my colleagues at PutraCAT who never failed to give ideas, knowledges and also memorable joy being there to do my reaserch. Many thanks also to Ueda Sensei and other colleagues at Hokkaido University for giving me such a pleasant time when working together with them there.

It is a pleasure to express my gratitude to my parents for their inseparable support and prayers. My Father, Masuri Symon, in the first place is the person who put the fundament my learning character, showing me the joy of intellectual pursuit ever since I was a child. My Mother, Saidah Saman, is the one who sincerely raised me with her caring and gently love. Also the most gratitude to my special supporter, Md. Sodiqin who never fails to cheer and enhance me to complete the thesis. Lastly to Norsafikah, Hazmi and Norsyuhaidah thanks for being supportive and caring siblings. Finally, I would like to thank everybody who was important to the successful realization of thesis, as well as expressing my apology that I could not mention personally one by one.

I certify that a Thesis Examination Committee has met on 24 September 2012 to conduct the final examination of Shafizah binti Masuri on her thesis entitled "Preparation, Characterization, and Catalytic Behavior of MoVTeNbOx Catalysts Prepared by Reflux Method" in accordance with the Universities and University College 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.

Members of the Thesis Examination Committee were as follows:

Gwendoline Ee Cheng Lian, PhD

Professor Faculty of Science Universiti Putra Malaysia (Chairman)

Nor Azah binti Yusof, PhD

Associate Professor Faculty of Science Universiti Putra Malaysia (Internal Examiner)

Tan Yen Ping, PhD

Senior Lecturer Faculty of Science Universiti Putra Malaysia (Internal Examiner)

Zaharah Ayiub, PhD

Professor Faculty of Science Universiti Malaya (External Examiner)

SEOW HENG FONG, PhD

Professor and Deputy Dean School of Graduate Studies Universiti Putra Malaysia

Date: 19 December 2012

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

Irmawati Binti Ramli, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia

(Chairman)

Taufiq Yap Yun Hin, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD

Professor and Dean School of Graduate Studies Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



TABLE OF CONTENTS

				Page
ABST	RAC	T		i
ABST	RAK	,		iii
ACK	NOW	LEDGEMENTS	S	v
APPR	ROVA	L		vi
DECI	LARA	TION		vii
LIST	OF F	IGURES		xii
LIST	OF T	ABLES		xv
LIST	OF S	CHEMES		xvi
LIST	OF A	BBREVIATIO	NS I was the same of the same	xvii
CHA		RODUCTION		
	1.1	Background		1
	1.2	Propane		3
	1.3	Acrylic acid		4
	1.4	Partial oxidati	on of propane	7
	1.5	Catalyst for se	elective propane oxidation to acrylic acid	9
	1.6	Problem state	ment	13
	1.7	Objectives		14
2	LIT	ERATURE REV	VIEW	
	2.1	Bulk structure	of MoVTeNb oxide catalyst	15
	2.2	Mechanistic p	athway of MovTeNbOx catalyst	19
	2.3	Synthesis met	hod	23
		2.3.1	Hydrothermal method	23
		2.3.2	Slurry method	25
		2.3.3	Reflux method	26

		2.4.2 Effect of washing	30
		2.4.3 Effect of niobium source	30
		2.4.4 Effect of calcination period	32
3	MAT	ERIALS AND METHODOLOGY	
	3.1	Materials and gases	33
	3.2	Catalyst Preparation	34
		3.2.1 Effect of pH	37
		3.2.2 Effect of washing	37
		3.2.3 Effect of niobium source	38
		3.2.4 Effect of calcination period	38
	3.3	Catalysts Characterization	40
		3.3.1 X-ray Diffraction Analysis (XRD)	40
		3.3.2 Brunauer-Emmett-Teller surface area	ı <mark>Anal</mark> yzer 41
		(BET)	
		3.3.3 Temperature Programmed Reduction	(TPR) 42
		3.3.4 Scanning Electron Microscopy (SEM	I) 44
		3.3.5 Energy Dispersive X-ray Spectroscop	py (EDS) 45
		3.3.6 Inductive Coupled Plasma Atomic En	mission 46
		Spectroscopy (ICP-AES)	
	3.4	Catalyst Test	48
4	RESU	ILTS AND DISCUSSION	
	4.1	Synthesis of MoVTeNbO _x	53
		4.1.1 Effect of pH	53
		4.1.2 Effect of washing	57
		4.1.3 Effect of niobium source	60
		4.1.4 Summary	63
		X	

2.4

Preparation parameters

2.4.1 Effect of pH

28

28

	4.2	Effects of calcination period 0		
		4.2.1	XRD analysis of the calcined samples	64
		4.2.2	BET surface area and elemental composition	n 68
		4.2.3	SEM surface morphology	70
		4.2.4	TPR analysis	71
		4.2.5	Summary	76
	4.3	Cataly	rst Test	77
5	CON	CLUSI	ON AND RECOMMENDATION	
	5.1	Concl	usion	84
	5.2	Recon	nmendation for further studies	86
BIBLIOGRAPHY			88	
BIODATA OF STUDENT			95	
LIST OF PUBLICATIONS			96	

	LIST OF FIGURES	Page
Figure 1.1:	Malaysia natural gas reserves	1
Figure 1.2:	The top 5 ranking of natural gas in Asia Pacific (source: Oil and Gas Journal, 2010)	2
Figure 1.3:	The structure of acrylic acid which consists of a vinyl group and carboxylic acid group.	4
Figure 1.4:	Acrylic acid usage in industry	6
Figure 2.1:	Refined structural models of (a) orthorhombic M1 phase and (b) hexagonal M2 phase, according to Grasselli et al. (2003)	17
Figure 3.1:	Synthesis of catalyst	35
Figure 3.2:	The side view of vertical furnace used for calcination process	36
Figure 3.3:	Calcination process to activate the catalyst in nitrogen flow	39
Figure 3.4:	Schematic view of Bragg-Brentano system	41
Figure 3.5:	The TPR profile of concentration vs. Time (or temperature) Trace A displays the TCD signal output as the function of time and B displays the temperature as the function of time during heating process	43
Figure 3.6:	SEM principle of imaging the sample	44
Figure 3.7:	The principle of the electron transfer in EDS	46
Figure 3.8:	Map of the gas lines and connection in the online system	49
Figure 3.9:	Gases flow through the samples loop in reactor system	50
Figure 3.10:	Route for reactant gases to be send to GC (i) and products in sample loop (ii)	51
Figure 3.11:	Products route to GC and analyzed	52

Figure 4.1:	XRD patterns for precursor at; pH 1 (b) pH 2 (c) pH 3	54
Figure 4.2:	Schematic representation of Anderson-type heteropolyanion proposed by Anderson (1937).	55
Figure 4.3:	XRD patterns of calcined catalysts at (a) pH 1 (b) pH 2 (c) pH 3	57
Figure 4.4:	XRD patterns for precursors of washed samples (a) two times washing (b) three times washing (c) four times washing	58
Figure 4.5:	XRD patterns for washed catalyst samples with deionized water (a) two times washing (b) three times washing (c) four times washing	59
Figure 4.6:	XRD patterns of precursors using different niobium sources (a) ammonium niobate(V) oxalate hydrate (b) niobium(V) chloride	60
Figure 4.7:	XRD patterns for niobium sources after calcination (a) ammonium niobate(V) oxalate hydrate(b) niobium(V) chloride	62
Figure 4.8:	XRD patterns of MoVTeNbOx samples after calcined (a) precursor (b) A (c) B (d) C	65
Figure 4.9:	Morphology of MoVTeNbOx catalysts at different calcination period; (a) A (b) B (c) C	71
Figure 4.10:	The H ₂ -TPR profiles for the samples (a) A (b) B (c) C	73
Figure 4.11:	Proposed pathway of propane selective oxidation	80
Figure 4.12:	Graph of selectivity of propylene versus reaction temperatures	81
Figure 4.13:	Selectivity to acrylic acid at reaction temperatures	82
Figure 4.14:	Relation between selectivities of CO _x and propylene at reaction	83

	LIST OF TABLES	Page
Table 1.1:	Composition of natural gas	3
Table 4.1:	Calculated relative intensities of characteristic peaks for the calcined samples from the XRD patterns	67
Table 4.2:	Physicochemical properties of MoVTeNbOx mixed metal oxide catalysts	69
Table 4.3:	Values of reduction activation energy and oxygen removed from the samples	75
Table 4.4:	The activity and selectivity of the catalyst samples	78

	LIST OF SCHEME	Page
Scheme 1:	Radical resonance of M1 structure	19
Scheme 2:	Radical attack on the secondary hydrogen and αH abstraction of propane	20
Scheme 3:	Formation of π –allylic intermediate	20
Scheme 4:	Oxygen insertion at Mo ⁶⁺ site and re-oxidization of Te ³⁺ to Te ⁴⁺	21
Scheme 5:	Formation of acrolein and oxidation of Mo ⁴⁺ to Mo ⁶⁺	22

LIST OF ABBREVIATIONS

TcF trillion cubic feet

VPO vanadium pyrophosphate

MMO multi-component mixed metal oxide

DIW deionized water

ANO ammonium niobium oxalate

AA acrylic acid

AcA acetic acid

Ace Acetone

E_r reduction activation energy

CHAPTER 1

INTRODUCTION

1.1 Background

In a report published by Gas Malaysia in January 2008, it was stated that Malaysia has the world's 14th largest natural gas reserves of which about 38% of the natural gas is found off the East Coast of Peninsular Malaysia, 48% at offshore Sarawak and the remaining 14% is found at offshore Sabah as illustrated in Figure 1.1. This gas reserve stood at 88 trillion cubic feet (TcF) or 14.67 billion barrels equivalent of oil which was about three times the size of crude oil reserves of 5.46 billion barrels.

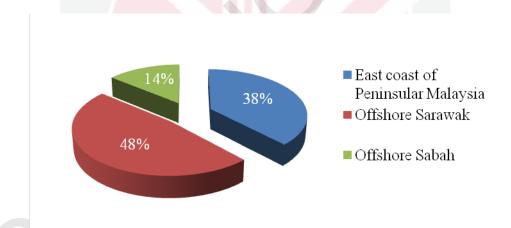


Figure 1.1: Malaysia natural gas reserves.

Recently in January 2010, Malaysia seized about 83 TcF natural gas reserve as reported by Oil and Gas Journal. Hence, it has made Malaysia the world's tenth largest natural gas reserve and among the top 5 in Asia Pacific after Australia, China

and Indonesia as shown in Figure 1.2. The change in this position is due to an increment in the world's demand on natural gas and the declining of some other country's reserves.

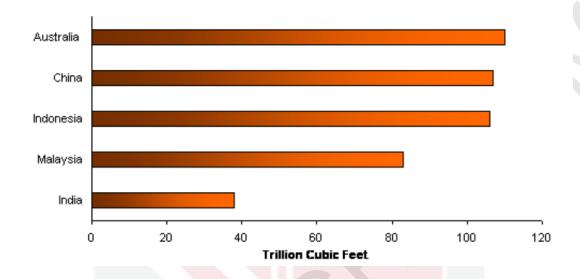


Figure 1.2: The top 5 ranking of natural gas in Asia Pacific (source: Oil and Gas Journal, 2010).

There are many usage of natural gas, such as for power plant station and industrial sector thus it tells that this gas must be consisted by a number of gases. Commonly, the natural gas mainly consists of methane with other minor compounds like ethane, propane and butane. The details on the type of compounds and their compositions in natural gas can vary widely as shown in Table 1.1. Since there are various compounds reside in natural gas, thus refining process is done to separate each compound so that the compound can be used or sold separately including propane and butane.

Table 1.1: Composition of natural gas.

Compound	Chemical formula	Percentage (%)
Methane	CH ₄	70-90
Ethane	C_2H_6	
Propane	C_3H_8	0-20
Butane	C_4H_{12}	
Carbon dioxide	CO_2	0-8
Oxygen	O_2	0-0.2
Nitrogen	N_2	0-5
Hydrogen sulfide	H_2S	0-5
Rare gas	Ar, He, Ne, Xe	Trace

1.2 Propane

Since propane is one of the compounds that can be found in natural gas, thus it can be used as the replacement of energy source instead of methane. It is more favorable due to its portability and ability to be compressed which is 270 times more compact than in its gas form. Though there are limited domestic used of propane, so, most of the gas being exported and used extensively in many other countries such as Japan, Taiwan and South Korea.

Nowadays, propane is highly needed as it is used in houses to fuel stoves, water heaters, clothes dryers, and other household appliances. Propane is also used as fuels for transportation due to its clean burning properties and portability, hence, make it popular as an alternative transportation fuel. The propane-fueled engines performed better where the emissions of carbon dioxide and carbon monoxide are much fewer if compared to gasoline. Propane also is being used in the industries as their raw materials. For an example, the semiconductor manufacturing uses propane as their source for silicon carbide deposition, hence becoming the feedstock in propyl alcohol production and it is also widely used as solvent. Hence, it proves that propane has many practices which will trigger the interest of researcher to maximize the usage.

1.3 Acrylic acid

Acrylic acid is a common name for 2-propenoic acid; an organic compound consists of three carbon atoms, four hydrogen atoms and two oxygen atoms. The formula molecule is CH₂=CHCOOH which is known as a simple unsaturated hydrocarbon with a vinyl group bonded together with carboxylic group as illustrate in Figure 1.4.

Figure 1.3: The structure of acrylic acid which consists of a vinyl group and carboxylic acid group.

Back in time, the acrylic acid was first synthesized in the mid nineteenth century which then had been formulated to form methacrylic acid in 1865. This methacrylic acid was used to react with methanol for the formation of ester methyl methacrylate. Then in 1877, German chemist Fittig and Paul discovered a polymerization process which successfully turns methyl methacrylate to polymethyl methacrylate.

Due to that, the demand on acrylic acid has increased every year. This acrylic acid has been used for more than 30 years as the crucial building block in the production of some of the most commonly used industrial and consumer products. Two-third of the acrylic acid manufactured is used to produce acrylic esters such as methyl acrylate, butyl acrylate, ethyl acrylate and 2-ethylhexyl acrylate which are very useful when being polymerized and used as one of the ingredient in paints, coatings, textiles, adhesives, plastics and numerous other applications. The remaining one-third is used to generate polyacrylic acid or cross-linked polyacrylic acid compound which have been used in the production of hygienic products, detergents, and waste water treatment chemicals (Figure 1.5).

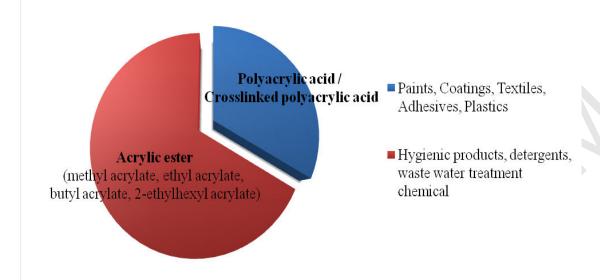


Figure 1.4: Arylic acid usage in industry.

The manufacturing of acrylic acid by means of hydrocarboxylation acetylene process (Eq.1) which required nickel-based catalyst react in a high pressure of carbon monoxide with the present of water was developed by Reppe in Germany in 1930s. Regarding to that, large scale production of acrylic acid was commercially began which utilized in production of acrylic safety glass and extensively used for submarine periscopes, windshields, canopies, and gun turrets for airplanes during World War II.

$$C_2H_2 + H_2O + CO$$

Ni(CO)₄-CuBr-THF

CH₂=CHCOOH

Acrylic acid

(Eq.1)

Nowadays, acrylic acid is manufactured worldwide using the propylene as starting materials in two steps via acrolein in a gas phase oxidation process. The first stage is the oxidation of propylene to acrolein using various type of promoter such as Fe, Co, W and Pt on the molybdenum-bismuth catalyst at a reaction temperature of about $623 \text{ K} \pm 50 \text{ K}$ (Eq.2). In the second stage, the intermediate product which is the acrolein is passed over a promoted molybdenum-vanadium oxide catalyst (promoters, e.g., W, Cu, Sn, and Sb) at lower temperatures of about 543 K (Eq.3). These two oxidation steps are strongly exothermic.

Stage 1

$$H_2C=CHCH_3 + O_2$$
 Promoted Mo-Bi catalyst $H_2C=CHCHO + H_2O$ (Eq.2) propylene $\Delta H= -340.8 \text{ kJ/mol}$ acrolein

Stage 2

$$H_2C=CHCHO + 1/2 O_2$$

Promoted Mo-V catalyst
 $H_2C=CHCOOH$

acrolein

 $\Delta H= -254.1 \text{ kJ/mol}$

acrylic acid

1.4 Partial oxidation of propane

Due to economic reason and high cost of propylene production, it had triggered the industrialist interest to find alternative way in producing acrylic acid. In some way the researchers are actively doing the activities which focus on substituting the propylene as feedstock in the production. The most probable way is by using propane as the replacement (see Eq.4). By undergoing a partial oxidation of propane, it shows

that the utilization of propane as a raw material to be transform to acrylic acid in a single step appears as potential route in the future.

$$H_3CCH_2CH_3 + 2O_2$$
 \longrightarrow
 $H_2C=CHCOOH + H_2O$

propane

acrylic acid

(Eq.4)

A reason to use propane is that the propane exhibits similar number of carbon as propylene and acrylic acid. Thus, there will be no reaction involved on inserting or removing the carbon atom. Hence, it will suggest the reducing of production cost for acrylic acid. However, when considering the catalytic oxidation of propane, two main difficulties arise. First, the reactivity of the reactants is lower compared to the products formed. The activation needs tremendous operating condition to react which then can affect the stability of the products. As to solve this matter, a catalyst with specific properties which are able to activate propane at low reaction condition and can restrain the products from over oxidized are crucially needed (Kim *et al.*, 1991 and Mamedov *et al.*, 2005). The second problem is the design of suitable catalyst was interrupted because lack of information regarding reaction mechanism involved (Kim *et al.*, 1990 and Kim *et al.*, 1992).

Another issue in oxidation of propane is regarding the selectivity of intermediate products that formed during the oxidation process. When propane is partially oxidized, it would form an intermediate C3 molecule which is needed to be preserved but this intermediate is an active molecule. The intermediates C3 formed like propylene, acrolein and acetone yet not all of the intermediates would lead to the

formation of acrylic acid. Thus, the catalyst used must be able to block or suppress the intermediate molecule from further oxidization in order to form a high selective acrylic acid (Lin, 2001).

1.5 Catalysts for selective propane oxidation to acrylic acid

For propane selective oxidation to acrylic acid, there are several systems that are highly potential for this reaction. Those are VPO-type catalyst, which is successfully used in industrial process for *n*-butane transformation to maleic anhydride. Second is the heteropoly acid or salts which is said to be effective for alkane oxidative dehydrogenation and lastly the multi-component metal oxide where it is utilized in propylene oxidation, alkane oxidative dehydrogenation and efficient in propane ammoxidation.

VPO type catalyst is an effective catalyst in n-butane oxidation and highly selective towards maleic anhydride formation. It is usually in a form of crystal phase mainly consists of V^{4+} and V^{5+} ions which known as its active species. The V^{5+} species acts in activating n-butane by abstracting the H atom from compound. While the V^{4+} species contribute in the formation of by-product of n-butane oxidation. However, the catalyst is not very effective in propane oxidation to acrylic acid. Although propane is the homologue for n-butane with only one less CH_2 , it was reported that none of this VPO type catalyst can offer the yield of acrylic acid >15%. It was due to the condition like high reaction temperature used by VPO type catalyst which cannot

actively convert propane to acrylic acid. This is because of the condition preferred to be further oxidized to the active intermediate products like propylene and acrolein rather than converting propane. Moreover, the performance of VPO catalyst is rather structure specific towards the length of hydrocarbon chain; hence it is not able to preserve the partial oxidation products of propane like acrolein or even the acrylic acid from over-oxidize to other products.

Second system of catalyst use for propane oxidation is heteropoly compound where this catalyst has well defined cage-like structure with central cation and surrounding polyanion. This type of catalyst also has variety of cage-like structure such as Keggin, Dawson and Anderson. It is formed through polymerization of oxoanions at low pH. Dissimilar to VPO type catalyst, the heteropoly catalyst can contain acidic proton and have strong acidity. The heteropoly-anions are multi-electron oxidants especially those that have Mo and V. The special properties in this heteropoly compound which is redox enable it to be used as catalyst in dehydrogenation of alcohols or amines also for the allylic oxidative dehydrogenation of aldehyde, ketones and nitriles. Apart from this, the study on the utilization of heteropoly compound as catalyst for propane oxidation in one step conversion to acrylic acid with molecular oxygen as the oxidants is done. However, the actual yield of acrylic acid is relatively low and has been left for more than a decade. The first one-step reaction using this catalyst is reported in 1990s by Trifiró and Centi where H₅PV₂Mo₁₀O₄₀ with Keggin structure showed reasonable activity and selectivity of propane but rapidly deactivated in about one to two hours. This is due to deep reduction with decomposition of Keggin structure and noticeable that the structure

lack of thermal stability which lead to the structural decomposition to occur at temperature below than 673 K. Then, some improvement is done on the heteropoly-compound especially in acidity and thermal stability of the catalyst. Neutralizing the acidic site with pyridine has increased the propane conversion and selectivity towards acrylic acid but in overall reaction shows the yield is still low. Also by replacing the protons with appropriate metal ions has made the catalyst that is used for oxidative dehydrogenation of ethane stable at 813K. The performance of the catalyst also improves as it is supported with Cs-salt which make thermally stable and increase the surface area. Regardless, the surface acidity is difficult to control and reproduce so that high surface area of salts is needed to support and stabilize the acid form.

The third potential system in propane oxidation is multi-component metal oxide (MMO) which primarily consists of transition metals. This MMO do not have specific defined structure so it may contain mixture of multiple crystal and amorphous phase. Usually this type of catalyst requires activation at high temperature since it has excellent thermal stability. The application of MMO starts in 1990s although the research has initially begun long time ago. Mo-V-Nb mixed oxide, the basis catalyst for high performing propane selective oxidation had at first been used in oxidation of ethane to acetic acid. The potential of Mo- and V-based mixed oxides for propane oxidation to acrylic acid has been studied by Bartek *et al.* (1993) and the most effective catalyst is Mo-V-Te-Nb-O as reported by Japanese researcher, Ushikubo and coworkers (1995) and Lin and Linsen (1999). This four component mixed oxide catalyst is also first found to be effective for the

ammoxidation of propane to acrylonitrile. It is unexpected that Mo-V-Te-Nb-O catalyst can be well functioned in two different reactions without undergoing any compositional modification. This is due to both reaction share some fundamental reaction steps for example the activation of propane and propane oxidative dehydrogenation. The performance of Mo-V-Te-Nb catalyst on propane to acrylic acid is considerable better than the other MMO type, VPO or heteropoly compound type catalyst because the selectivity towards acrylic acid has achieve about 60% higher than ever reported for the others. There are several reports that showed the importance of preparation method, as well as the composition of the catalyst especially for the same catalyst with the same composition. The performances of the catalyst, for example MoV_{0.3}Te_{0.23}Nb_{0.1}O_x may be very poor, mediocre (14% acrylic acid) and excellent (>40%) depending on the preparation method used. However, the difficulty in controlling the parameters is the major drawback also very sensitive to the preparation condition which will determine the structure of the catalyst. Thus, a fine consideration of structural aspect could guide to design and prepare the mixed metal oxide catalyst.

1.6 Problem Statement

MoVTeNbOx catalyst is successfully prepared using hydrothermal method and slurry method. The catalyst ability and performance towards propane transformation to acrylic acid cannot be denied and has been reported in many articles. However in hydrothermal method, high temperature and pressure is needed whereby the yield of catalyst obtained did not reach the industrial standard yield. The alternative way is considered in order to reduce its high cost of production but arrived at the same structure. While Lin (2001), Holmberg et al. (2004) and Botella et al. (2004) claimed that slurry method would result in poor control over the formation of desired M1 phase and lead to phase mixtures. Although majority study preferred to used this slurry method in synthesizing the MoVTeNbOx catalyst, hence it would end with poorly defined crystal morphologies. In this study, reflux method is used as the alternative method to synthesize this MoVTeNbOx catalyst. This method is used due to its low cost benefits and permit the species exist to homogeneously mixing in the solution under atmospheric pressure and at solvent's boiling temperature as compared to hydrothermal and slurry method. Thus far, there is only one reported work by Ramli et al. (2011) on synthesizing MoVTeNbOx catalysts using reflux method. The research group disclosed that orthorhombic structure can be derived from this method. This leave an opportunity to improve the synthesis parameter by reducing the period of reflux to a lesser day which in this work, the reflux period was fixed for three days. To derive the formation of orthorhombic structure of MoVTeNbOx, other parameters will be studied. These are pH, washing, niobium source and calcination period.

1.7 Objectives

The objectives of this study are:

- i. To synthesize MoVTeNbOx catalysts by reflux method.
- ii. To study the effect of pH, washing and niobium source towards then formation of orthorhombic stucture.
- iii. To characterize the chosen catalyst on the effect of calcination period towards the formation of orthorhombic M1 phase.
- iv. To obtain the catalytic activity of the obtained catalysts for the conversion of propane to acrylic acid.

BIBLIOGRAPHY

- Anderson J.S., (1937) Constitution of the Poly-acids, *Nature* 140:850-850.
- Baca M., Pigamo A., Dubois J.-L. and Millet J.M.M., (2003). Propane oxidation on MoVTeNbO mixed oxide catalysts: Study of phase composition of active and selective catalysts, *Topic in Catalysis* 23:39-46.
- Bartek J., Ebner A. and Bradzil J., (1993), US Patent 5,198,580.
- Bart J.C.J., Petrini G. and Giordano N., (1975) The binary oxide system TeO₂-MoO₃, *Zeitschrift für Anorganische und Allgemeine Chemie* 412:258-270.
- Bart J.C.J., Cariati F. and Sgamellotti S., (1979) Mixed-valence effects in tellurium-molybdenum oxides, *Inorganica Chimica Acta* 36:105-112.
- Beato P., Blume A., Girgsdies F., Jentoft R. E., Schlögl R., Timpe O., Trunschke A., Weinberg G., Basher Q., Hamid F. A., Hamid S. B. A., Omar E. and Mohd Salim L., (2006). Analysis of structural transformations during the synthesis of a MoVTeNb mixed oxide catalyst, *Applied Catalysis A: General* 307:137-147.
- Bordes E., (1987). Crystallochemistry of VPO phases and application to catalysis, *Catalysis Today* 1:499-526.
- Botella P., Solsona B., Martinez-Arias A. and López Nieto J.M., (2001). Selective oxidation of propane to acrylic acid on MoVNbTe mixed oxide catalysts prepared by hydrothermal synthesis, *Catalysis Letter* 74:149-154.
- Botella P., García-Gonzáles E., Dejoz A., López Nieto J.M., Vázquez M.I. and González-Calbet J., (2004). Selective oxidative dehydrogenation of ethane on MoVTeNbO mixed metal oxide catalysts, *Journal of Catalysis* 225:428-438.
- Botella P., Concepcion P., López Nieto J.M. and Moreno J., (2005). The influence of Te-precursor in Mo-V-Te-O and Mo-V-Te-Nb-O catalysts on their catalytic behaviour in the selective propane oxidation, *Catalysis Today* 99:51-57.
- Botto I.L., Cabello C.I. and Thomas H.J., (1997), (NH₄)₆[TeMo₆O₂₄].7H₂O Anderson phase as precursor of the TeMo₅O₁₆ catalytic phase:thermal and spectroscopic studies, *Materials Chemistry and Physics* 47:37-45.
- Centi G.and Trifiró F., (1988). Functionalization of paraffinic hydrocarbons by heterogeneous vapour-phase oxidation III. Conversion of C₁-C₇ alkane series, *Catalysis Today* 3:151-162.

- Courtine P. and Bordes E., (1997) Synergistic effects in multicomponent catalysts for selective oxidation, *Studies in Surface Science and Catalysis* 110:177-184.
- Deng Z., Wang H., Chu W. and Yang W., (2008) Influence of reducing atmosphere on the structure and activity of Mo-V-Te-Nb-O catalysts for propane selective oxidation, *Chinese Journal of Catalysis* 29:1032-1036.
- Deniau B., Millet J.M.M., Loridant S., Christin N. and Dubois J.L., (2008) Effect of several cationic substitution in the M1 active phase of MoVTeNbO catalysts used for the oxidation of propane to acrylic acid, *Journal of Catalysis* 260:30-36.
- Gas Malaysia Sdn. Bhd., Accessed 1st July 2010, http://www.gasmalaysia.com/about gas/how industries use natural gas.php.
- Grasselli R.K., Burrington J.D., Buttrey D.J., DeSanto Jr. P., Lugmair P.C.G., Volpe Jr. A.F. and Weingand T., (2003). Multifunctionality of active centers in (amm)oxidation catalysts: From Bi-Mo-O_x to Mo-V-Nb-(Te,Sb)-O_x, *Topic in Catalysis* 23:5-22.
- Grasselli K., Buttrey D.J., DeSanto Jr. P., Burrington J.D., Lugmair C.G., Volpe Jr. A.F. and Weingand T., (2004), Active centres in Mo-V-Te-Nb-O_x (amm)oxidation catalysts, *Catalysis Today* 91-92:251-258.
- Guliants V.V., Bhandari R., Al-Saeedi J., Vasudevan V.K., Soman R.S., Guerrero-Pérez O. and Bañares M.A., (2004). Bulk mixed Mo-V-Te-O catalysts for propane oxidation to acrylic acid, *Applied Catalysis A: General* 274:123-132.
- Guliants V.V., Bhandari R., Swaminathan B., Vasudevan V.K., Brongersma H.H., Knoester A., Gaffney A.M. and Han S., (2005) Roles of surface Te, Nb and Sb oxides in propane oxidation to acrylic acid over bulk orthorhombic Mo-V-O phase, *Journal of Physical Chemistry B* 109:24046-55.
- Guo H. Y., Xiang H. W. and Li Y. W., (2010) The TPR reduction dynamics of Ru/SiO₂ catalyst, *Acta Petrolei Sinica (Petroleum processing section)* 26:231-234.
- Holmberg J., Grasselli R.K. and Anderson A., (2004) Catalytic behaviour of M1, M2 and M1/M2 physical mixtures of the Mo-V-Nb-Te-oxide system in propane and propene ammoxidation, *Applied Catalysis A:General* 270:121-134.
- Holmes S.A., Al-Saeedi J., Guliants V.V., Boolchand P., Georgiev D., Hackler U. and Sobkow E., (2001) Solid state chemistry of bulk mixed metal oxide catalysts for the selective oxidation of propane to acrylic acid, *Catalysis Today* 67:403-409.
- Hutching G.J., (2004). Vanadium phosphate: A new look at the active components of catalyst for the oxidation of butane to maleic anhydride, *Journal of Materials Chemistry* 14:3385-3395.

- Ivars F., Botella P., Dejoz A., López Nieto J.M., Concepción P. and Vazquez M.I., (2006) Selective oxidation of short-chain alkanes over hydrothermally prepared MoVTeNbO catalysts, *Topic in Catalysis* 38:59-67.
- Ischenko E.V., Andrushkevich T.V., Popova G.Ya., Bondareva V.M., Kardash T. Yu., Plyasova L.M., Dovlitova L.S. and Ischenko A.V., (2010) Formation of active component of MoVTeNb oxide catalyst for selective oxidation and ammoxidation of propane and ethane, *Studies in Surface Science and Catalysis* 175:479-482.
- Ivars F., Solsona B., Rodríguez-Castellón E. and López Nieto J.M., (2009) Selective propane oxidation over MoVSbO catalysts. On the preparation, characterizationand catalytic behavior of M1 phase, *Journal of Catalysis* 262:35-43.
- Ivars F., Solsona B., Hernándes S. and López Nieto J.M., (2010) Influence of gel composition in the synthesis of MoVTeNb catalysts over their catalytic performance in partial propane and propylene oxidation, *Catalysis Today* 149:260-266.
- Katou T., Vitry D. and Ueda W., (2003) Hydrothermal synthesis of a new Mo-V-O complex metal oxide and its catalytic activity for the oxidation of propane, *Chemistry Letters* 32:1028-1029.
- Katou T., Vitry D. and Ueda W., (2004) Structure dependency of Mo-V-O based complex oxide catalysts in the oxidations of hydrocarbons, *Catalysis Today* 91-92:237-240.
- Kihlborg L., (1963), Crystal structure studies on monoclinic and orthorhombic Mo₄O_N, Arkiv foer Kemi 21: 365-377.
- Kim Y.C., Ueda W. and Moro-oka Y., (1990). Selective oxidation of propane to acrolein and ammoxidation over Ag-doped bismuth vanadomolybdate catalysts, *Studies in Surface Science and Catalysis*, 55:491-504.
- Kim Y.C., Ueda W. and Moro-oka Y., (1991). Selective oxidation of propane involving homogeneous and heterogeneous steps over multicomponent metal oxide catalysts, *Applied Catalysis* 70:175-187.
- Kim Y.C., Ueda W. and Moro-oka Y., (1992). Catalytic (amm)oxidation of propane with molecular oxygen over complex metal oxides: Involvement of homogeneous reaction in gas phase, *Catalysis Today* 13:673-678.

- Korovchenko P., Shiju N. R., Dozier A.K., Graham U.M., Guerrero-Pérez M.O. and Guliants V.V., (2008) M1 and M2 phase transformation and phase cooperation in bulk mixed metal mo-V-M-O (M=Te, Nb) catalysts for selective ammoxidation of propane, *Topic in Catalysis* 50:43-51.
- Lin M. and Linsen M., (1999), EP Patent 962,253,A2.
- Lin M.M., (2001). Selective oxidation of propane to acrylic acid with molecular oxygen, *Applied Catalysis A* 207:1-16.
- López Nieto J.M., Botella P., Solsona B. and Oliver J.M., (2003). The selective oxidation of propane on Mo-V-Te-Nb-O catalysts: The influence of Te precursor, *Catalysis Today* 81:87-94.
- Luo L., Labinger J.A. and Davis M.E., (2001) Comparison of reaction pathways for the partial oxidation of propane over vanadyl ion-exchanged zeolite beta and Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x, *Journal of Catalysis* 200:222-231.
- Mamedov E.A. and Cortés-Corberán V., (1995). Oxidative dehydrogenation of lower alkanes on vanadium oxide-based catalysts. The present state of the art and outlooks, *Applied Catalysis A: General* 127:1-40.
- Millet J.M.M., Baca M., Pigamo A., Vitry D., Ueda W. and Dubois J.L., (2003) Study of valence state and coordination of antimony in MoVSb catalysts determined by XANES and EXAFS, *Applied Catalysis A: General* 244:359-370.
- Muhamad E.N., Ramli I., Abdullah A.H., Taufiq-Yap Y.H. and Abd.Hamid S.B., (2007) The effect of number of washing on the nanocrystalline structure of copper oxide, *The Malaysian Journal of Analytical Science* 11:294-301.
- Müller A., Todea A.M., van Slageren J., Dressel M.,Bogge H., Schmidtmann M., Luban M., Engelhardt L. and Rusu M., (2005) Triangular geometrical and magnetic motifs uniquely linked on a spherical capsule surface, *Angewandte Chemie International Edition* 44:3857-3861.
- Müller A., Penk M., Krickemeyer E., Boegge H. and Walberg H.J., (1988) [V₁₉O₁₄(OH)₉]⁸⁻, An Ellipsoid-Shaped Cluster Anion Belonging to the Unusual Family of V^{IV}/V^V Oxygen Clusters, *Angewandte Chemie* 27: 1719-1721.
- Murayama H., Vitry D., Ueda W., Fuchs G., Anne M. and Dubois J.L., (2007) Structure characterization of orthorhombic phase in MoVTeNbO catalyst by powder X-ray diffraction and XANES, *Applied Catalysis A:General* 318:137-142.

- Moro-oka Y., (1999) The role of acidic properties of metal oxide catalysts in the catalytic oxidation, *Applied Catalysis A: General* 181:323-329.
- Naraschewski F.N., Chintala P.K., Jentys A. and Lercher J.A., (2011) Phase formation and selective oxidation of propane over MoVTeNbO_x catalysts with varying compositions, *Applied Catalysis A: General* 391:63-69.
- Oliver J.M., López Nieto J.M., Botella P. and Misfud A., (2004). The effect of pH on structural and catalytic properties of MoVTeNb catalysts, *Applied Catalysis A: General* 257:67-77.
- Oshihara K., Nakamura Y., Sakuma M. and Ueda W., (2001) Hydrothermal synthesis of novel crystalline Mo–V–M–O (M = Al, Ga, Fe) mixed oxide in the presence of triethylammonium chloride and their catalytic performance for selective ethane oxidation, *Catalysis Today* 71:153-159.
- Popova G.Ya., Andrushkevich T.V., Aleshina G.I, Plyasova L.M. and Khramov M.I., (2007) Effect of oxalic acid content and medium of thermal treatment on physicochemical and catalytic properties of MoVTeNb oxide catalysts in propane ammoxidation, *Applied Catalysis A: General* 328:195-200.
- Popova G.Ya., Andrushkevich T.V., Dovlitova L.S., Aleshina G.I, Chesalov Yu. A., Ishenko A.V., Ishenko E.V., Plyasova L.M., Malakov V.V. and Khramov M.I., (2009). The investigation of chemical and phase composition of solid precursor of MoVTeNb oxide catalyst and its transformation during the thermal treatment, *Applied Catalysis A: General* 353:249-257.
- Popova G.Ya., Andrushkevich T.V., Chesalov Yu. A., Plyasova L.M., Dovlitova L.S., Ishenko E.V., Aleshina G.I and Khramov M.I., (2009). Formation of active phase in MoVTeNb oxide catalysts for ammoxidation of propane, *Catalysis Today* 144:312-317.
- Ramli A., Jamil M.F. and Ibrahim S., (2007) The effect of support on the activity and selectivity of MoVTeNb catalysts for propane ammoxidation reaction, *The Malaysian Journal of Analytical Sciences* 11:124-132.
- Ramli I., Botella P., Ivars F., Woi P.M., Zawawi S.M.M., Ahangar H.A., Hernández S. and Nieto J.M.L., (2011) Reflux method as a novel route for the synthesis of MoVTeNbOx catalysts for selective oxidation of propane to acrylic acid, *Journal of Molecular Catalysis A: Chemical* 342-343:50-57.
- Sanfiz A.C., Hansen T.W., Girgsdies F., Timpe O., Rödel E., Ressler T., Trunschke A. and Schlögl R., (2008) Preparation of phase pure M1 MoVTeNb oxide

- catalysts by hydrothermal synthesis- Influence of reaction parameters in structure and morphology, *Topic in Catalysis* 50:19-32.
- Taufiq-Yap Y.H., Looi M.H., Waugh K.C. and Hussein M.Z., (2002). Investigation of Vanadyl Pyrophosphate Catalysts Synthesised from Three Different Routes, *Asian Journal of Chemistry* 14:1494-1502.
- Tsuji H. and Koyasu Y., (2002) Synthesis of MoVNbTe(Sb)O_x composite oxide catalysts via reduction of polyoxometallates in an aqueous medium, *Journal of the American Chemical Society* 124:5608-5609.
- Ueda W. and Oshihara K., (2000). Selective oxidation of light alkanes over hydrothermally synthesized Mo-V-M-O (M=Al, Ga, Bi, Sb and Te) oxide catalysts, *Applied Catalysis A General* 200:135-143.
- Ueda W., Oshihara K. and Hisano T., (2001) Catalytic oxidative activation of light alkanes over Mo-V-based oxides having controlled surface, *Topic in Catalysis* 15:153-160.
- Ueda W., Vitry D. and Katou T., (2004) Structural organization of catalytic functions in Mo-based oxides for propane selective oxidation, *Catalysis Today* 96:235-240.
- Ueda W., Vitry D. and Katou T., (2005) Crystalline Mo-V-O based complex oxides as selective oxidation catalysts of propane, *Catalysis Today* 99:43-49.
- Ushikubo T., Oshima K., Kayo A., Umezawa T., Kiyono K. and Sawaki I., (1992) European Patent 529,853, assigned to Mitsubishi Chemical corporation, Tokyo, Japan.
- Ushikobo T., Nakamura H., Koyasu Y. and Wajiki S., (1995). Method for producing an saturated carboxylic acid, US Patent 5,380,933.
- Vitry D., Morikawa Y., Dubois J.L. and Ueda W., (2003) Mo-V-Te-(Nb)-O mixed metal oxide prepared by hydrothermal synthesis for catalytic selective oxidations of propane and propene to acrylic acid, *Applied Catalysis A:General* 251:411-424.
- Watanabe H. and Koyasu Y., (2000). New synthesis route for Mo-V-Nb-Te mixed oxides catalyst for propane ammoxidation, *Applied Catalysis A:General* 194:479-485.
- Watanabe N. and Ueda W., (2006) Comparative study on the catalytic performance of single phase Mo-V-O-based metal oxide catalysts in propane ammoxidation to acrylonitrile, *Industrial & Engineering Chemistry Research* 45:607-614.

- Yang X.J., Feng R.M., Ji W.J. and Au C.T., (2008) Characterization and evaluation of Mo-V-Te-Nb mixed oxide catalysts fabricated via hydrothermal process with ultrasonic pretreatment for propane partial oxidation, *Journal of Catalysis* 253:57-65.
- Yuhao S., Jingfu L., Enbo W., (1986) Preparation and properties of some new 6-heteropoly-tellurate compounds of tungsten and molybdenum containing vanadium, *Inorganica Chimica Acta* 117:23-26.
- Zheng W., Yu Z., Zhang P., Zhang Y., Fu H., Zhang X., Sun Q. and Hu X., (2008) Selective oxidation of propane to acrylic acid over mixed metal oxide catalysts, *Journal of Natural Gas Chemistry* 17:191-194.

BIODATA OF STUDENT

Shafizah binti Masuri was born in Johor Bahru, Johor, Malaysia on 8th February 1986. She acquired her early education at Sekolah Kebangsaan L.K.T.P. Belitong, Kluang before proceeding to Sekolah Menengah Agama Kerajaan Johor, Kluang. After completing her Sijil Pelajaran Malaysia (SPM) on 2003, she continued her studies in Kolej Matrikulasi Johor, Tangkak for 2004/2005 session. In July 2005, she embarked on Bachelor Science (Hons.) at Universiti Putra Malaysia majoring in Chemistry and graduated in 2008 with Second Class Upper degree level. Thereafter, she continued as a research assistant under supervision Assoc. Prof. Dr. Irmawati Ramli for six month before enrolled her Degree of Master in catalysis field at Faculty of Science, Universiti Putra Malaysia where she was awarded a National Science Fellowship (NSF) from Ministry of Science, Innovative and Technology (MOSTI). During her stay in Universiti Putra Malaysia, she's done well in her research and got chances to do three month attachment at Hokkaido Universiti, Sapporo, Japan under supervision of Professor Wataru Ueda.

LIST OF PUBLICATIONS

Publication to Journal

1) R. Irmawati, **M.Shafizah** (2009), Production of high purity hexagonal MoO₃ through acid washing of the as-prepared solid, *International Journal of Basic & Applied Sciences IJBAS Vol 9 No: 9*, pp: 241-244

Publication in Conferences / Seminars Proceeding

- 1) Shafizah Masuri, Irmawati Ramli and Ho Mun Yee, Effect of vanadium composition on the physicochemical properties of MoVTeNbOx synthesized by reflux method, *Fundamental Science Congress 2009, Auditorium Kejuruteraan Universiti Putra Malaysia,* 17th &18th June 2009, page 307
- 2) R. Irmawati, M. Shafizah, Production of high purity hexagonal MoO₃ through acid washing of the as-prepared solid, *ASIANALYSIS X & SKAM-22*, *Putra World Trade Center (PWTC) Kuala Lumpur*, 11th -13th August 2009, page 126
- 3) R. Irmawati, M. Shafizah, Y.H. Taufiq Yap, Effect of different niobium source on the characteristic of MoVTeNbO mixed oxide catalyst for propane conversion to acrylic acid, Seminar on Progress in Catalysis, Saintis Gemilang Room, Faculty of Science Universiti Putra Malaysia, 8th February 2010, page 4
- 4) R. Irmawati, M. Shafizah, I.A. Zaidi, Y.H. Taufiq-Yap, W. Ueda, Reflux synthesis of MoVTeNbO catalysts using niobium(V) chloride, *2nd Seminar on Catalysis Science and Technology: Catalysis for renewable and sustainable energy (2nd CAST), 24th November 2010, page 19*

National / International Seminars, Workshops or Conferences attended

- 1) 1st Seminar on Catalysis Science and Technology (1st CAST), Saintis Gemilang Room, Faculty of Science Universiti Putra Malaysia, 3rd December 2008
- 2) Inaugural Lecture Series: The Chemistry of Nanomaterial and Nanobiomaterial by Prof. Dr. Mohd Zobir Hussein, Dewan Taklimat, Bangunan Pentadbiran Universiti Putra Malaysia, 6th February 2009
- 3) Seminar ISO Pengurusan Makmal, Saintis Gemilang Room, Faculty of Science Universiti Putra Malaysia, 3rd March 2009
- 4) Fundamental Science Congress (FSC) 2009, Auditorium Kejuruteraan Universiti Putra Malaysia, 17th & 18th June 2009
- 5) Inaugural Lecture Series: Catalysis for a Sustainable World by Prof. Dr. Taufiq Yap Yun Hin, Dewan Taklimat, Bangunan Pentadbiran Universiti Putra Malaysia, 7th August 2009
- 6) ASIANALYSIS X & Seminar Kimia Analisis Malaysia ke-22 (SKAM-22), Putra World Trade Centre (PWTC) Kuala Lumpur, Malaysia, 11th -13th August 2009
- 7) Seminar on Progress in Catalysis, Saintis Gemilang Room, Faculty of Science Universiti Putra Malaysia, 8th February 2010
- 8) FHI CRC Joint International Symposium: Surface Science and Catalysis for Sustainable Society, Sousei Building 5F Conference Hall, Hokkaido University, Sapporo Japan, 1st & 2nd April 2010
- 9) Seminar on Bimetallic Catalysts for the Hydrogenation of Aromatic by Prof. Mohammed M. Bettahar, Saintis Gemilang Room, Faculty of Science Universiti Putra Malaysia, 4th October 2010
- 10)2nd Seminar on Catalysis Science and Technology: Catalysis for Renewable and Sustainable Energy (2nd CAST), Saintis Gemilang Room, Faculty of Science Universiti Putra Malaysia, 24th November 2010