UNIVERSITI PUTRA MALAYSIA

CHARACTERISATION OF COBALT, ALUMINIUM, AND MAGNESIUMPROMOTED MoVTeNbOx CATALYSTS SYNTHESISED BY MICROWAVEASSISTED SLURRY METHOD FOR PROPANE OXIDATION TO ACRYLIC ACID

WONG HONG REN

FS 2017 80

CHARACTERISATION OF COBALT, ALUMINIUM, AND MAGNESIUM-PROMOTED $MoVTeNbO_x$ CATALYSTS SYNTHESISED BY MICROWAVE-ASSISTED SLURRY METHOD FOR PROPANE OXIDATION TO ACRYLIC ACID

By

WONG HONG REN

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

April 2017

COPYRIGHT

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

CHARACTERISATION OF COBALT, ALUMINIUM, AND MAGNESIUM PROMOTED MoVTeNbO$_x$ CATALYSTS SYNTHESISED BY MICROWAVE-ASSISTED SLURRY METHOD FOR PROPANE OXIDATION TO ACRYLIC ACID

By

WONG HONG REN

April 2017

Chairman: Associate Professor Irmawati Ramli, PhD
Faculty: Science

The selective oxidation of propane to acrylic acid is potential to replace the current manufacture of acrylic acid which uses propene as feedstock, due to this light alkane is more abundant and lower cost. Up to date, the most promising catalyst that has been reported for this selective oxidation of propane is MoVTeNbO$_x$ metal mixed oxide, yet its' performance does not achieve the requirement of being commercialised. Thus, a series of metal-promoted MoVTeNbO$_x$ catalysts (MVTN-A, where A = Co, Al, Mg) were synthesised by microwave-assisted slurry method, and then followed by calcination in air at 553 K for 1 hour and then in nitrogen at 873 K for 2 hours. It appears that the as-synthesised samples were semi-crystalline Anderson-type structure. Once calcined, the phase transformed into mixed phases of orthorhombic M1 phase, hexagonal M2 phase and tetragonal $(V_{0.07}Mo_{0.93})_5O_{14}$ phase. Only when the samples were port-treated in hydrogen peroxide, the evolution of orthorhombic M1 phase was observed. Since there is no appreciable formation of orthorhombic M1 phase was obtained, the calcined catalysts were post-treated in 30 % hydrogen peroxide. The physicochemical properties of the catalysts were examined using X-ray Diffraction (XRD), Fourier-Transform Infrared (FT-IR), Brunauer-Emmett-Teller (BET) surface area measurement, Field Emission Scanning Electron Microscopy (FESEM) and Temperature Programmed Reduction in hydrogen (H$_2$-TPR). Characteristics of the as-synthesised, calcined and post-treated catalysts were obtained. According to XRD results, highly pure orthorhombic M1 phase, $Te_2M_{20}O_{57}$ (M = Mo, V or Nb), was formed when MoVTeNbO$_x$ was promoted with 0.06 mole of Mg, 0.02 mole of Al, or 0.10 mole of Al. An increase in specific surface area could be seen in those promoted with magnesium and aluminium, as compared to the un-promoted MoVTeNbO$_x$ (13.4 m^2/g). On contrary, the specific surface area of cobalt-promoted catalysts was close to the un-promoted catalyst. Temperature Programmed Reduction in hydrogen (H$_2$-TPR) results indicated the enhanced reducibility of the cobalt-, aluminium- and magnesium-promoted catalysts as opposed to the unpromoted ones, signifying the apparent high activity of the catalyst. The propane conversion increased as follow: MVTN < MVTN-Al(0.02) < MVTN-Al(0.10) < MVTN-Mg(0.06). The selectivity of acrylic acid, however, progressively rose in this order: MVTN-Al(0.02) < MVTN < MVTN-Al(0.10) < MVTN-Mg(0.06). Among the tested catalysts, MVTN-Mg(0.06) gave the highest propane conversion (49.9 %) and acrylic acid's selectivity (34.9 %). Meanwhile, for aluminium promoted MoVTeNbOx, the higher propane conversion and selectivity of acrylic acid is found for higher loading of metal promoter.

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

PENCIRIAN MANGKIN MoVTeNbO$_x$ YANG DIPROMOSIKAN DENGAN KOBALT, ALUMINIUM DAN MAGNESIUM YANG DIHASILKAN MELALUI KAEDAH BUBURAN DIBANTU OLEH PENYINARAN GELOMBANG MIKRO UNTUK PENGOKSIDAAN TERPILIH PROPANA KEPADA ASID AKRILIK

Oleh

WONG HONG REN

April 2017

Pengerusi: Profesor Madya Irmawati Ramli, PhD
Fakulti: Sains

Pengoksidaan terpilih propana kepada asid akrilik berpotensi untuk menggantikan pembuatan semasa asid akrilik yang menggunakan propena sebagai bahan mentah kerana kekayaan sumber propana dan kemurahan kos propana. Sehingga hari ini, MoVTeNbO$_x$ oksida logam campuran telah dilaporkan sebagai mangkin yang terbaik untuk pengoksidaan terpilih propana ini. Tetapi, prestasi mangkin ini tidak mencapai keperluan untuk dikormersialkan. Oleh itu, satu siri mangkin MoVTeNbO$_x$ yang dipromosikan dengan unsur logam (MVTN-A, A = Co, Al, Mg) telah dihasilkan melalui kaedah buburan dibantu oleh penyinaran gelombang mikro. Prekursor telah dikalsinkan dalam udara pada suhu 553 K selama satu jam dan seterusnya dalam nitrogen pada suhu 873 K selama dua jam. Data menunjukkan mangkin prekursor adalah dalam struktur Anderson-type. Setelah dikalsin, transformasi fasa campuran belaku dengan menghasilkan fasa ortorombik M1, fasa heksagonal M2 dan fasa tetragonal $(V_{0.07}Mo_{0.93})_5O_{14}$. Evolusi fasa M1 didapati apabila mangkin yang telah dikalsin dirawat dengan hidrogen peroksida. Memandangkan pembentukan fasa ortorombik M1 yang ketara tidak dapat diperolehi, mangkin yang dikalsin seterusnya dirawat dengan 30 % hidrogen peroksida. Sifat-sifat fisikokimia mangkin telah dikaji dengan menggunakan pembelauan sinar-x (XRD), spektroskopi inframerah transformasi fourier (FTIR), Brunauer-Emmett-Teller (BET pengukuran luas permukaan, medan electron-mikroskopi imbasan elektron (FESEM) dan penurunan terprogram suhu dengan hidrogen (H_2-TPR). Pencirian mangkin prekursor, mangkin selepas dikalsin dan mangkin selepas dirawat telah diperolehi. Data XRD menunjukkan fasa ortorombik M1, $Te_2M_{20}O_{57}$ (M = Mo, V or Nb), dibentukkan apabila mangkin dipromosikan dengan 0.06 mol magnesium, 0.02 mole aluminium atau 0.10 mol aluminium. Peningkatan jumlah luas permukaan telah ditunjukkan oleh mangkin yang dipromosikan dengan magnesium dan aluminium berbanding dengan mangkin tanpa promosi (13.4 m^2/g). Manakala, mangkin dipromosikan kobalt memanifestasikan junlah luas permukaan yang lebih kurang sama dengan mangkin tanpa promosi. Keputusan penurunan terprogram suhu dengan hidrogen (H_2-TPR) mendedahkan penambahbaikan kebolehturunan mangkin MoVTeNbOx yang dipromosikan dengan ketiga-tiga unsur logam berbanding dengan mangkin tanpa promosi. Kadar ketukaran propana meningkat seperti berikut: MVTN < MVTN-Al(0.02) < MVTN-Al(0.10) <

MVTN-Mg(0.06). Manakala, kadar keterpilihan asid akrilik meningkat secara progesif seperti berikut: MVTN-Al(0.02) < MVTN < MVTN-Al(0.10) < MVTN-Mg(0.06). Antara pemangkin yang telah diuji, MVTN-Mg(0.06) mempunyai kadar ketukaran propana (49.9 %) and kadar keterpilihan asid akrilik (34.9 %) yang paling tinggi. Mangkin yang dipromosikan dengan lebih banyak aluminium mempunyai kadar ketukaran propana and kadar keterpilihan asid akrilik yang lebih tinggi.

ACKNOWLEDGEMENT

Firstly, I would like to express my utmost gratitude to my supervisor – Associate Prof. Dr. Irmawati Ramli for her guidance, advices and supervision during my entire works in this research. Her advices and encouragements enabled me to build up a better condition for completing the tasks. Also, I would like to deliver my appreciation to my co-supervisor, Prof. Dr. Taufiq Yap Yun Hin. His support and opinion have helped a lot in this work.

Secondly, I would like to acknowledge the postgraduates – Miss Haslinda, Miss Syazwani and Mr. Affandi for their favourable assistance and discussion. On top of that, I would like to thank the science officers for their assisting and helping in carrying out the analysis of FTIR, ICP-OES and FESEM.

Most especially, I convey my great appreciation to my family members for giving me encouragement and concern during the hard works I had faced.

Last but not least, I gratefully acknowledge the financial support from Fundamental Research Grant Scheme (FRGS) and Graduate Research Fellowship (GRF).

I certify that a Thesis Examination Committee has met on 27 April 2017 to conduct the final examination of Wong Hong Ren on his thesis entitled "Characterisation of Cobalt, Aluminium, and Magnesium-Promoted $MoVTeNbO_X$ Catalysts Synthesised by Microwave-Assisted Slurry Method for Propane Oxidation to Acrylic Acid" 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.

Members of the Thesis Examination Committee were as follows:

Norhazlin binti Zainuddin, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Tan Yen Ping, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Zainab binti Ramli, PhD
Associate Professor
Universiti Teknologi Malaysia
Malaysia
(External Examiner)

NOR AINI AB. SHUKOR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 6 July 2017

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:

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)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity in upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature:____________________ Date:__________________

Name and Matric No.:_______________________________________

Declaration by Member of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 201-2013) are adhered to.

Signature: ____________________________________
Name of
Chairman of
Supervisory
Committee: ____________________________________

Signature: ____________________________________
Name of
Member of
Supervisory
Committee: ___________________________________

TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENTS	v
APPROVAL	vi
DECLARATION	viii
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	

CHAPTER

1 INTRODUCTION	1
1.1 Acrylic Acid	1
1.1.1 Global Consumption and Demand	1
1.1.2 Current Manufacture of Acrylic Acid – Two Step Production	2
1.1.3 Proposed Manufacture of Acrylic Acid- Single Step Production	4
1.2 Problem Statement	5
1.3 Scope of Study	6
1.4 Objectives	7
2 LITERATURE REVIEW	8
2.1 Mo-V-O Based Oxides as Catalysts in Selective Oxidation of Propane	8
2.1.1 Function of Each Constituent Elements	8
2.1.2 Structural Aspect	9
2.2 Preparation Methods of Mo-V Based Mixed Oxide Catslysts	14
2.2.1 Hydrothermal Method	14
2.2.2 Slurry Method	15
2.2.3 Solution Method	16
2.2.4 Microwave-assisted Method	17
2.2.5 Reflux Method	17
2.3 Temperature Programmed Reduction in hydrogen (H_2-TPR) of each constituent elements in MoVTeNb mixed oxide	18
2.4 Addition of Metal Promoters into MoV Based Mixed Oxides	19
3 MATERIALS AND METHODOLOGY	21
3.1 Chemicals and Gases	21
3.2 Catalysts Preparation	21
3.3 Catalysts Characterisation	22
3.3.1 Fourier-Transform Infrared Spectroscopy (FTIR)	23
3.3.2 Field Emission Scanning Electron Microscopy (FESEM)	23
3.3.3 Temperature Programmed Reduction in Hydrogen (H_2-TPR)	23
3.3.4 X-ray Diffraction	24
3.3.5 Inductively Coupled Plasma/Optical Emission Spectroscopy	24

3.3.6 Brunauer-Emmett-Teller Surface Area (S_{BET}) Analysis 25
3.4 Catalytic Test 25

4 RESULTS AND DISCISSION 26
4.1 X-ray Diffraction 26
4.1.1 As-synthesised Promoted MoVTeNb Mixed Oxide Catalysts 26
4.1.2 Calcined Promoted MoVTeNb Mixed Oxide Catalysts 28
4.1.3 Washed Promoted MoVTeNb Mixed Oxide Catalysts 31
4.2 Fourier-Transform Infrared Spectroscopy 33
4.2.1 As-synthesised Promoted MoVTeNb Mixed Oxide Catalysts 33
4.2.2 Calcined Promoted MoVTeNb Mixed Oxide Catalysts 37
4.2.3 Washed Promoted MoVTeNb Mixed Oxide Catalysts 41
4.3 Inductively Coupled Plasma/Optical Emission Spectroscopy 44
4.3.1 As-synthesised Promoted MoVTeNb Mixed Oxide Catalysts 44
4.3.2 Calcined Promoted MoVTeNb Mixed Oxide Catalysts 45
4.3.3 Washed Promoted MoVTeNb Mixed Oxide Catalysts 46
4.4 Field Emission Scanning Electron Microscopy 47
4.5 Brunauer-Emmett-Teller Surface Area (S_{BET}) Analysis 52
4.6 Temperature Programmed Reduction in Hydrogen 53
4.6.1 Calcined Promoted MoVTeNb Mixed Oxide Catalysts 53
4.6.2 Washed Promoted MoVTeNb Mixed Oxide Catalysts 57
4.7 Catalyst Screening 61
4.8 Catalytic Performance 61
4.8.1 Propane Conversion 64
4.8.2 Acrylic Acid Selectivity and Yield 66

5 CONCLUSION 71
5.1 Conclusion 71
5.2 Suggestion for Future Works 72

REFERENCES 73
APPENDICES 81
BIODATA OF STUDENT 83
PUBLICATION 84

LIST OF TABLES

Table		**Page**
3.1	List of chemicals and gases used.	21
4.1	Functional groups of the as-synthesised catalysts	36
4.2	Functional groups of the calcined catalysts	40
4.3	Functional groups of the washed catalysts	43
4.4	Elemental composition of as-synthesised MoVTeNb mixed oxide catalysts.	44
4.5	Elemental composition of calcined MoVTeNb mixed oxide catalysts.	45
4.6	Elemental composition of washed MoVTeNb mixed oxide catalysts.	46
4.7	BET surface area of washed MoVTeNb mixed oxides.	52
4.8	Reduction energy and total number of oxygen removed of the calcined catalysts.	56
4.9	Reduction energy and total number of oxygen removed of the washed catalysts.	60
4.10	Selective oxidation of propane over $MVTN_w$ catalyst.	62
4.11	Selective oxidation of propane over $MVTN\text{-}Mg(0.06)_w$ catalyst.	62
4.12	Selective oxidation of propane over $MVTN\text{-}Al(0.02)_w$ catalyst.	63
4.13	Selective oxidation of propane over $MVTN\text{-}Al(0.10)_w$ catalyst.	63

LIST OF FIGURES

Figure		**Page**
1.1	Influence of the Te/Mo atomic ratio of the catalysts on the propylene conversion (a) and on the selectivity to acrolein + acrylic acid (b) Reaction temperature 380˚C; W/F = 540 g_{cat} h $(mol_{C3})^{-1}$.	3
2.1	Reaction step and nature of active and selective sites in the oxidation of propane to acrylic acid on MoVTeNbO catalysts.	10
2.2	Structure models for Mo-V-O-based complex metal oxides along the [001] (upper) and [100] (lower) directions. (a) Orthorhombic, (b) hexagonal, (c) tetragonal Mo_5O_{14}, (d) orthorhombic $Mo_{17}O_{47}$ and (e) disordered. (●) Te or Sb occupying the central position of the hexagonal channel.	11
2.3	Ideal structure of three distinct types of Mo-V-O based catalysts and their catalytic performance for propane and propene oxidations.	12
2.4	XRD patterns of calcined (a) Mo-V-O, (b) Mo-V-Sb-O, (c) Mo-V-Te-O, (d) Mo-V-Sb-Nb-O, and (e) Mo-V-Te-Nb-O catalysts.	14
4.1	XRD patterns of precursors: (a) $MVTN_p$, (b) MVTN-Mg$(0.02)_p$, (c) MVTN-Mg$(0.04)_p$, (d) MVTN-Mg$(0.06)_p$, (e) MVTN-Mg$(0.08)_p$, and (f) MVTN-Mg$(0.10)_p$.	26
4.2	XRD patterns of precursors: (a) $MVTN_p$, (b) MVTN-Al$(0.02)_p$, (c) MVTN-Al$(0.04)_p$, (d) MVTN-Al$(0.06)_p$, (e) MVTN-Al$(0.08)_p$, and (f) MVTN-Al$(0.10)_p$.	27
4.3	XRD patterns of precursors: (a) $MVTN_p$, (b) MVTN-Co$(0.02)_p$, (c) MVTN-Co$(0.04)_p$, (d) MVTN-Co$(0.06)_p$, (e) MVTN-Co$(0.08)_p$, and (f) MVTN-Co$(0.10)_p$.	27
4.4	XRD patterns of calcined catalysts: (a) $MVTN_c$, (b) MVTN-Mg$(0.02)_c$, (c) MVTN-Mg$(0.04)_c$, (d) MVTN-Mg$(0.06)_c$, (e) MVTN-Mg$(0.08)_c$, and (f) MVTN-Mg$(0.10)_c$.	29
4.5	XRD patterns of calcined catalysts: (a) $MVTN_c$, (b) MVTN-Al$(0.02)_c$, (c) MVTN-Al$(0.04)_c$, (d) MVTN-Al$(0.06)_c$, (e) MVTN-Al$(0.08)_c$, and (f) MVTN-Al$(0.10)_c$.	29
4.6	XRD patterns of calcined catalysts: (a) $MVTN_c$, (b) MVTN-Co$(0.02)_c$, (c) MVTN-Co$(0.04)_c$, (d) MVTN-Co$(0.06)_c$, (e) MVTN-Co$(0.08)_c$, and (f) MVTN-Co$(0.10)_c$.	30
4.7	XRD patterns of washed catalysts: (a) $MVTN_w$, (b) MVTN-Mg$(0.02)_w$, (c) MVTN-Mg$(0.04)_w$, (d) MVTN-Mg$(0.06)_w$, (e) MVTN-Mg$(0.08)_w$, and (f) MVTN-Mg$(0.10)_w$.	32
4.8	XRD patterns of washed catalysts: (a) $MVTN_w$, (b) MVTN-Al$(0.02)_w$, (c) MVTN-Al$(0.04)_w$, (d) MVTN-Al$(0.06)_w$, (e) MVTN-Al$(0.08)_w$, and (f) MVTN-Al$(0.10)_w$.	32
4.9	XRD patterns of washed catalysts: (a) $MVTN_w$, (b) MVTN-Co$(0.02)_w$, (c) MVTN-Co$(0.04)_w$, (d) MVTN-Co$(0.06)_w$, (e) MVTN-Co$(0.08)_w$, and (f) MVTN-Co$(0.10)_w$.	33
4.10	FTIR spectra of precursors: (a) $MVTN_p$, (b) MVTN-Mg$(0.02)_p$, (c) MVTN-Mg$(0.04)_p$, (d) MVTN-Mg$(0.06)_p$, (e) MVTN-Mg$(0.08)_p$, and (f) MVTN-Mg$(0.10)_p$.	34
4.11	FTIR spectra of precursors: (a) $MVTN_p$, (b) MVTN-Al$(0.02)_p$,	35

(c) MVTN-Al(0.04)$_p$, (d) MVTN-Al(0.06)$_p$, (e) MVTN-Al(0.08)$_p$, and (f) MVTN-Al(0.10)$_p$.
4.12 FTIR spectra of precursors: (a) MVTN$_p$, (b) MVTN-Co(0.02)$_p$, (c) MVTN-Co(0.04)$_p$, (d) MVTN-Co(0.06)$_p$, (e) MVTN-Co(0.08)$_p$, and (f) MVTN-Co(0.10)$_p$. 35
4.13 FTIR spectra of calcined catalysts: (a) MVTN$_c$, (b) MVTN-Mg(0.02)$_c$, (c) MVTN-Mg(0.04)$_c$, (d) MVTN-Mg(0.06)$_c$, (e) MVTN-Mg(0.08)$_c$, and (f) MVTN-Mg(0.10)$_c$. 37
4.14 FTIR spectra of calcined catalysts: (a) MVTN$_c$, (b) MVTN-Al(0.02)$_c$, (c) MVTN-Al(0.04)$_c$, (d) MVTN-Al(0.06)$_c$, (e) MVTN-Al(0.08)$_c$, and (f) MVTN-Al(0.10)$_c$. 38
4.15 FTIR spectra of calcined catalysts: (a) MVTN$_c$, (b) MVTN-Co(0.02)$_c$, (c) MVTN-Co(0.04)$_c$, (d) MVTN-Co(0.06)$_c$, (e) MVTN-Co(0.08)$_c$, and (f) MVTN-Co(0.10)$_c$. 38
4.16 FTIR spectra of washed catalysts: (a) MVTN$_w$, (b) MVTN-Mg(0.02)$_w$, (c) MVTN-Mg(0.04)$_w$, (d) MVTN-Mg(0.06)$_w$, (e) MVTN-Mg(0.08)$_w$, and (f) MVTN-Mg(0.10)$_w$. 41
4.17 FTIR spectra of washed catalysts: (a) MVTN$_w$, (b) MVTN-Al(0.02)$_w$, (c) MVTN-Al(0.04)$_w$, (d) MVTN-Al(0.06)$_w$, (e) MVTN-Al(0.08)$_w$, and (f) MVTN-Al(0.10)$_w$. 42
4.18 FTIR spectra of washed catalysts: (a) MVTN$_w$, (b) MVTN-Co(0.02)$_w$, (c) MVTN-Co(0.04)$_w$, (d) MVTN-Co(0.06)$_w$, (e) MVTN-Co(0.08)$_w$, and (f) MVTN-Co(0.10)$_w$. 42
4.19 FESEM images of washed catalysts: (a) MVTN$_w$, (b) MVTN-Mg(0.02)$_w$, (c) MVTN-Mg(0.04)$_w$, (d) MVTN-Mg(0.06)$_w$, (e) MVTN-Mg(0.08)$_w$, and (f) MVTN-Mg(0.10)$_w$. 48
4.20 FESEM images of washed catalysts: (a) MVTN$_w$, (b) MVTN-Al(0.02)$_w$, (c) MVTN-Al(0.04)$_w$, (d) MVTN-Al(0.06)$_w$, (e) MVTN-Al(0.08)$_w$, and (f) MVTN-Al(0.10)$_w$. 49
4.21 FESEM images of washed catalysts: (a) MVTN$_w$, (b) MVTN-Co(0.02)$_w$, (c) MVTN-Co(0.04)$_w$, (d) MVTN-Co(0.06)$_w$, (e) MVTN-Co(0.08)$_w$, and (f) MVTN-Co(0.10)$_w$. 50
4.22 Schematic drawing of *a*-*b* plane of the rod-shaped particles. 51
4.23 H$_2$-TPR profiles of calcined catalysts: (a) MVTN$_c$, (b) MVTN-Mg(0.02)$_c$, (c) MVTN-Mg(0.04)$_c$, (d) MVTN-Mg(0.06)$_c$, (e) MVTN-Mg(0.08)$_c$, and (f) MVTN-Mg(0.10)$_c$. 54
4.24 H$_2$-TPR profiles of calcined catalysts: (a) MVTN$_c$, (b) MVTN-Al(0.02)$_c$, (c) MVTN-Al(0.04)$_c$, (d) MVTN-Al(0.06)$_c$, (e) MVTN-Al(0.08)$_c$, and (f) MVTN-Al(0.10)$_c$. 54
4.25 H$_2$-TPR profiles of calcined catalysts: (a) MVTN$_c$, (b) MVTN-Co(0.02)$_c$, (c) MVTN-Co(0.04)$_c$, (d) MVTN-Co(0.06)$_c$, (e) MVTN-Co(0.08)$_c$, and (f) MVTN-Co(0.10)$_c$. 55
4.26 H$_2$-TPR profiles of washed catalysts: (a) MVTN$_w$, (b) MVTN-Mg(0.02)$_w$, (c) MVTN-Mg(0.04)$_w$, (d) MVTN-Mg(0.06)$_w$, (e) MVTN-Mg(0.08)$_w$, and (f) MVTN-Mg(0.10)$_w$. 57
4.27 H$_2$-TPR profiles of washed catalysts: (a) MVT$_w$, (b) MVTN-Al(0.02)$_w$, (c) MVTN-Al(0.04)$_w$, (d) MVTN-Al(0.06)$_w$, (e) MVTN-Al(0.08)$_w$, and (f) MVTN-Al(0.10)$_w$. 58
4.28 H$_2$-TPR profiles of washed catalysts: (a) MVTN$_w$, (b) MVTN-Co(0.02)$_w$, (c) MVTN-Co(0.04)$_w$, (d) MVTN-Co(0.06)$_w$, (e) MVTN-Co(0.08)$_w$, and (f) MVTN-Co(0.10)$_w$. 58

4.29 The conversion of propane for $MVTN_w$, MVTN-Mg$(0.06)_w$, MVTN-Al$(0.02)_w$ and MVTN-Al$(0.10)_w$ at different temperature. 64

4.30 The consumption of oxygen for $MVTN_w$, MVTN-Mg$(0.06)_w$, MVTN-Al$(0.02)_w$ and MVTN-Al$(0.10)_w$ at different temperature. 66

4.31 The selectivity of acrylic acid for $MVTN_w$, MVTN-Mg$(0.06)_w$, MVTN-Al$(0.02)_w$ and MVTN-Al$(0.10)_w$ at different temperature. 66

4.32 The selectivity of propene for MVT_w, MVTN-Mg$(0.06)_w$, MVTN-Al$(0.02)_w$ and MVTN-Al$(0.10)_w$ at different temperature. 67

4.33 The selectivity of CO_x for $MVTN_w$, MVTN-Mg$(0.06)_w$, MVTN-Al$(0.02)_w$ and MVTN-Al$(0.10)_w$ at different temperature. 68

4.34 The yield of acrylic acid for $MVTN_w$, MVTN-Mg$(0.06)_w$, MVTN-Al$(0.02)_w$ and MVTN-Al$(0.10)_w$ at different temperature. 70

LIST OF ABBRIVIATIONS

SAP	Superabsorbent polymer
CAGR	Compound annual growth rate
BASF	Badische Anilin-und Soda-Fabrik
OPEC	Organisation of Petroleum Exporting Countries
PETRONAS	Petroliam Nasional Berhad
IPCs	Integrated petrochemical complexes
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
XRD	X-ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier-Transform Infrared Spectroscopy
BET	Brunauer-Emmett-Teller surface area measurement
H_2-TPR	Temperature Programmed Reduction in Hydrogen
HTB	Hexagonal tungsten bronze
TTB	Tetragonal tungsten bronze
AMV	Ammonium metavanadate
AHM	Ammonium heptamolybdate tetrahydrate

CHAPTER 1

INTRODUCTION

1.1 Acrylic Acid

Acrylic acid, also known as prop-2-enoic acid, is the simplest unsaturated carboxylic acid, with molecular formula $H_2C{=}CHCOOH$. This colourless liquid is miscible with water, alcohols, ethers, and chloroform. The carboxyl group of acrylic acid enables it to form ester derivatives with other substance containing O-H group. The vinyl group (C=C) attached at the carboxylic acid terminus allows this organic compound acts as monomer that undergo polymerization. Polyacrylic acid is produced when acrylic acid monomer is grouped with the same acrylic acid monomer, whereas copolymerization of acrylic acid is taken place when this organic acid monomer meets with other monomers or its ester derivatives.

Generally, there are two categories of commercially available acrylic acid: (1) Technical Grade Acrylic Acid (also known as Crude Acrylic Acid) and (2) Glacial Grade Acrylic Acid. They have different end applications due to the composition and purity of acrylic acid. In crude acrylic acid, there is about 94 % acrylic acid content with minimal amount of maleic anhydride, acetic acid, propionic acid and furfural. On the contrary, although glacial acrylic acid contains a higher degree of purity of acrylic acid which is between 98 % and 99.7 %, the commercial glacial grade acrylic acid is known to contain 99.5 % to 99.7 % purity. Due to the desirable qualities of polymeric materials such as low temperature flexibility, acid and base resistance, colour stability, clarity, ageing and heat resistance along with good weather-ability, the commodity acrylate esters (methyl, ethyl, *n*-butyl, and 2-ethylhexyl acrylate) produced from crude acrylic acid is mainly used in adhesives, plastic additives, surface coating, sealants, and paper treatment. Glacial acrylic acid, however, concentrates in the production of superabsorbent polymer (SAP), dispersants, detergents and water treatment.

1.1.1 Global Consumption and Demand

Acrylic acid and its ester derivatives have been commercially utilized for about 30 years because they are readily to homopolymerize and copolymerize. These highly valued homopolymers and copolymers are useful in applications such as superabsorbent polymers, surface coating, adhesive and sealants, thickeners, textiles, plastic additives, fibres and synthetic resins.

In parallel with the increasing population of humankind, improving lifestyle and other factors, the demand for acrylic acid is growing. In year 2014, the global acrylic acid demand was 5,750.0 kilo tonnes and is expected to make up to 8,750.0 kilo tonnes by 2022. The demand is growing at a Compound Annual Growth Rate (CAGR) of 5.6 % during the forecast period between year 2015 and 2022. The booming demands of superabsorbent polymers is expected to shape up the personal care industry (Research, 2013). The global consumption of acrylic acid is estimated to achieve 8,169 kilo tonnes by year 2020 (Clark, 2014). Acrylate ester was the largest product segment for the market where 50 % of total acrylic acid consumed was used for production of acrylate ester in year 2014 (Chommanad, 2015).

As the global demand and consumption of acrylic acid is expected to increase, the global acrylic acid market was valued at $11,006.6 million in year 2013 and is estimated to reach $18,824.0 million by year 2020, growing at a CAGR of 7.6 % from year 2014 to 2020 (Clark, 2014). Another reported global market value of acrylic acid was USD 13.6 billion in 2013 and is expected to achieve USD 20.0 billion by year 2018, growing at a CAGR 6.5 % from year 2012 to 2018). Meanwhile, the global acrylic acid market will be valued at USD 22.55 billion by year 2022 (Research, 2013).

In year 2014, 40 % of the global acrylic acid market share is controlled by four top manufacturers, namely BASF, Dow Chemical, Nippon and Arkema (Research, 2013). BASF, the global leader in the acrylic acid value chain, inaugurated its €600 million-invested world-scale manufacture complex for acrylic acid, butyl acrylate and superabsorbent polymers in Camaçari, Bahia, Brazil. This complex is the first plant to manufacture acrylic acid and superabsorbent polymers in South America. The annual production of the acrylic acid is expected to be 160,000 tonnes (BASF, 2015).

1.1.2 Current Manufacture of Acrylic Acid – Two Step Production

Tracing back to history, the first available commercialised acrylic acid was developed in correspondence to the production route which based on the reaction of acetylene with water or alcohol and carbon monoxide, in the presence of acids such as hydrochloric acid and nickel tetracarbonyl. A crude product comprising acrylate ester, nickel chloride and hydrogen was formed. Another early stage process was the pyrolysis of acetone or acetic acid, reacted with formaldehyde to produce acrylic acid. When acetone is used, the pyrolysis process would result in a crude product made up of acrylic acid and methane. When acetic acid is used, the crude product would consist of acrylic acid and water. To present, these processes, however, are obsolete in the aspects of economic, environmental and other reasons (Acton, 2013).

The current manufacture of acrylic acid is based on the principle of a two-step gas phase catalytic oxidation process, using propylene as the starting material. Due to the presence of unsaturated C=C bond of propylene, the electrons of C1 and C2 are delocalized, causing C-H bond of propylene to be in a high polarity state and reactive in oxidation. At the first stage, propylene is converted into propenal (acrolein). The propylene and air are mixed and passed through a heated catalyst (often mixture of bismuth(III) and molybdenum(VI) oxide on silica) at *ca.* 650 K. The next stage is carried out by passing propenal with air over another heated catalyst (often molybdenum(VI) and vanadium(V) oxide on silica) at *ca.* 550 K .

The chemistry of the fundamental steps of stated catalytic oxidation processes are summarized by the following chemical equations (Jeffrey, 2010):

$H_2C{=}CHCH_3 + O_2 \xrightarrow{\text{catalyst}} H_2C{=}CHCHO + H_2O$ (Equation 1.1)
propene acrolein $\Delta H = -340.8$ kJ/mol

$H_2C{=}CHCHO + \frac{1}{2}O_2 \xrightarrow{\text{catalyst}} H_2C{=}CHCOOH$ (Equation 1.2)
acrolein acrylic acid $\Delta H = -254.1$ kJ/mol

Over the past several years, the development and modification of a family of catalysts had been carried out – the promoted molybdenum-bismuth system for the oxidation of propylene to acrolein (Equation 1.1) and promoted molybdenum-vanadium system for the oxidation of acrolein to acrylic acid (Equation 1.2). Regarding to this, the influence of tellurium on catalytic behaviour of hydrothermally prepared Mo-based tetragonal tungsten bronze structure catalyst in selective oxidation of propene had been discussed. The existence of tellurium increased the selectivity to acrolein up to a maximum of ca. 90% (Figure 1.1) when the Te/Mo ratio hiked to ca. 0.03. However, the similar effect on the increment of selectivity to acrylic acid is not practical whereas the MoVTeNb mixed oxide catalyst with M2 phase, i.e. a pseudo-orthorhombic $Te_{0.33}MO_{3.33}$ (M = Mo, V and Nb) shows comparatively higher selectivity to acrylic acid. Therefore, acrolein is more likely to be formed in TTB (tetragonal tungsten bronze)-based catalyst. Meanwhile, the pseudo-orthorhombic $X_{0.33}MO_{3.33}$ (M = Mo, V and Nb; X = Te, Sb) HTB (hexagonal tungsten bronze)-type catalyst is more favourable in the formation of acrylic acid (Botella *et al.*, 2009).

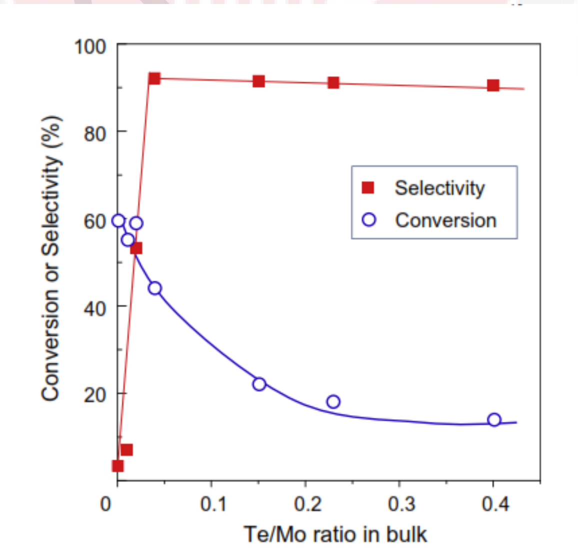

Figure 1.1: Influence of the Te/Mo atomic ratio of the catalysts on the propylene conversion (a) and on the selectivity to acrolein + acrylic acid (b) Reaction temperature 380˚C; W/F = 540 g_{cat} h $(mol_{C3})^{-1}$ (Botella *et al.*, 2009).

1.1.3 Proposed Manufacture of Acrylic Acid – Single Step Production

Since propylene is the feedstock in the current manufacture of acrylic acid, therefore the margin price of acrylic acid is significantly affected by the fluctuation of its market price. In year 2011, the global market price of propylene was USD 1800 per tonne. Due to supply constraints, the price is expected to rise further in future (Research, 2013). Therefore, an alternative feedstock that has similar geometrical shape and same number of carbon was searched. It was found that propane closely resembles propene although without carbon double bond (C=C) in its structure.

Studies on propane as a raw material for acrylic acid production have received much attention. The conversion requires a single step process as shown in Equation 1.3. This selective oxidation of propane is highly proposed and recommended for the commercialised manufacture the acrylic acid. One of the key advantages of this oxidation is that propane is globally more abundant than propylene, hence it is cheaper. Besides that, acrylic acid can be directly produced from propane in a single step, thus reducing the cost of production. The oxidation process involves consecutive reaction mechanisms from propane to propylene, propylene to acrolein, and from acrolein to acrylic acid. The whole process requires the abstraction of four hydrogen atoms and insertion of two oxygen atoms with a transfer of eight electrons.

$$CH_3CH_2CH_3 + 2O_2 \xrightarrow{\text{catalyst}} H_2C{=}CHCOOH + 2H_2O \quad \text{(Equation 1.3)}$$
$$\Delta H = -715.8\text{kJ/mol}$$

Unfortunately, this potential alternative is not yet applicable in industry. This is mainly due to the properties of propane. The saturation of C-C bonds stabilizes propane reactivity, causing it to resist most of the reaction in mild conditions. Therefore, the activation of propane could not be effectively taken place, so this selective oxidation of propane had led to fatality. In order to activate propane, catalytic system has been introduced. Some of the reported catalysts showed positive results on propane activation, also known as oxidative dehydrogenation of propane (Koc *et al.*, 2005; Sarzi-Amade *et al.*, 2005; Liu *et al.*, 2006; Dinse *et al.*, 2008; Botella *et al.*, 2009; Amakawa *et al.*, 2013). For example, the vanadium oxide loaded on SiO_2 from V(*t*-BuO)$_3$O had been reported to present a high propylene selectivity of 88.3% and propane conversion of 26.5% (Fukudome *et al.*, 2011).

However, another challenge arises when the deep and deviated oxidation of desired C3 intermediates as well as the final product led to poor effectiveness of selective oxidation of propane. The oxidation of C3 intermediate, propylene, could be the formation of unwanted acetone, thereby suppressing the production of acrylic acid. As another C3 intermediate, acrolein tends to be oxidised to produce acetic acid. Even the desired final product (acrylic acid), with low stability due to its reactive acid groups, is prone to be further oxidised and transformed into smaller compounds, such as carbon monoxide.

Therefore, any effective catalysts in selective oxidation of propane must be able to oxidise propane to acrylic acid selectively, and “end” the oxidation in which acrylic acid is the final product. To synthesise required catalyst, the relationship between each elementary steps of propane oxidation and formation of active crystal structure of catalyst has to be examined and well-studied.

1.2 Problem Statement

Malaysia is a well-known country rich in natural resources, blessed with abundant petroleum oil bed, and is one of the largest non-OPEC (Organisation of Petroleum Exporting Countries) oil exporters in the world. This superiority prompts Malaysia’s state-owned national oil company – PETRONAS (Petroliam Nasional Berhad) to be greatly profitable in which it contributes 40% of its revenue to the country. In order to add value to this plentiful natural resource, PETRONAS has ventured into the petrochemical industry years ago. As evidence, the establishment of two Integrated Petrochemical Complexes (IPCs) – the Kertih IPC and the Gebeng IPC provided ready sites for chemical plants and became home to more than 20 petrochemical plants since year 1992.

In parallel to this bright prospect, the selective oxidation of propane has huge potential to be a low-cost alternative to convert the petroleum fraction to higher value petrochemical such as acrylic acid. In terms of global exporting prices, it worths more than crude oil. The cost of propane feedstock is about 5 – 6 times less than the cost of current feedstock (propylene) of acrylic acid production (Centi *et al.*, 1992). Undeniably, with adequate feedstock, the nation’s revenue could increase with the production and export of higher-value acrylic acid. Meanwhile, the production cost of domestic products using acrylic acid as raw material could also be reduced. This indirectly lowers the living cost of people.

To make this promising alternative practical in petrochemical industries, the first challenge that must be overcome is to effectively activate the saturated propane. Propane has no lone pair of electron and carbon π bond, thus making it less reactive. A catalyst is needed to make propane reacts. Among the metal oxide catalysts, MoVTeNb mixed oxide catalyst is a highly viable catalyst applied in propane oxidation. It is proposed to function as a sacrificial oxidizing agent by providing lattice oxygen which is able to activate the propane, and propagates the process to produce the desired product of acrylic acid. The metal-oxygen (M-O) bonds of functional lattice oxygen must be in intermediate strength to make the reaction happens. If the M-O bond is too strong, lattice oxygen will be hardly released during the reaction, thus no reaction may be observed (unreactive). On the contrary, when the M-O bond is too weak, further oxidation of desired product will occur (over-oxidation), leading to undesired by-products (unselective) (Grasselli, 2002).

However, the performance of this quaternary metal oxide catalyst has yet to achieve the industrial requirements, in the aspect of activation of propane and selectivity of acrylic acid. To improve the effectiveness of MoVTeNb mixed oxide catalyst, a metal promoter can be introduced in a small amount (several wt%). The addition of metal promoters may influence the properties of M-O bond by affecting the electron density around the metal and oxide ions (Grzybowska-Świerkosz, 2002). For instance, the positive charge on V (its' acidity) was reduced by the addition of K (Ishchenko *et al.*, 2016), but the negative charge on oxygen atoms (the basicity) was increased by the presence of K. While, the incorporation of P increased the positive charge of the neighbouring V atom, but it has no significant changes in the oxygen charges (Ramis *et al.*, 1993; Deo *et al.*, 1994).

As discussed earlier, an effective catalyst for selective oxidation of propane to acrylic acid should be capable to convert propane to propene (oxidative dehydrogenation of propane) and also selectively produce acrylic acid. Magnesium and cobalt-molybdenum mixed oxide has been reported to give high catalytic activity for oxidative dehydrogenation of propane to propene (Ueda *et al.*, 1997). Among the transition metal molybdates (Zn, Cu, Co, Fe and Mn), the best performing catalysts in converting propane to propene were cobalt, manganese and copper molybdates. A cobalt molybdate was the best and most stable one (Palacio *et al.*, 2005). Besides, magnesium promoted $MoVSbO_x$ catalyst showed promising catalytic behaviour with good activity and selectivity in the selective oxidation of propane to acrylic acid (Chaudhari *et al.*, 2010). In the case of $MoVTeNbO_x$ catalyst, V^{5+} sites in orthorhombic phase is responsible in oxidative dehydrogenation of propane to propene. Al^{3+} cation, the ionic radius and electronegativity of it are 0.054 nm and 1.6, respectively. Meanwhile, the ionic radius and electronegativity of vanadium ion (V^{5+}) are 0.054 nm and 1.63, respectively. With similar ionic radius and electronegativity to V^{5+}, the incorporation of aluminium might enhance the concentration of V^{5+} sites to convert propane to propene.

In the microwave-assisted slurry method, microwave irradiation is introduced as a source of energy in order to heat the precursor solution. As compared to conventional heating method, this unconventional heating process is cleaner and gives better yield of product. The microwave irradiation sufficiently heat the precursor solution as the core of the solution is heated up by the electromagnetic wave, and the heat generated diffuse outward to provide an effective and uniform heating. Another advantages of this heating technique are, it could save more time, energy and also the cost.

Therefore, this research will look into the effects of proposed metal promoters (aluminium, magnesium and cobalt) on the surface properties and the catalytic performance of catalysts, which are synthesised using the microwave-assisted slurry method. The extent of induction of metal promoters with different amount will also be investigated.

1.3 Scope of study

In this study, heterogeneous catalysts of $MoVTeNbO_x$ mixed oxides, without or with the metal promoters (Al, Mg, Co), for selective oxidation of propane to acrylic acid was synthesised using the microwave-assisted slurry method. The influence of catalysts' synthesis condition *i.e.* type of metal promoters and molar ratio of metal promoter to molybdenum was studied. Various characterisation methods (XRD, BET, FT-IR, FESEM, ICP-OES and H_2-TPR) were carried out in order to understand the physicochemical properties of catalysts. The structural characteristic and elemental composition of the catalysts was analysed using XRD and ICP-OES, respectively. Besides, the functional groups in the catalysts was identified using FT-IR and the surface morphologies of the synthesised catalysts was observed using FESEM. In addition, the reducibility of the catalysts was also studied using H_2-temperature programmed reduction (H_2-TPR). Then, the potential catalysts were selected according to the presence of active phase as revealed in XRD results, and its' catalytic performance in selective oxidation of propane to acrylic acid was evaluated. The effect of metal promoters in the catalytic behaviour of $MoVTeNbO_x$ was also discussed.

1.4 Objectives

The objectives of this study are:

1. To synthesise Al-, Mg-, and Co-promoted MoVTeNb mixed oxide catalysts by microwave assisted slurry method.
2. To characterise the effects of different metal promoters on the MoVTeNb mixed oxide catalysts' characteristics by (Inductively Coupled Plasma/Optical Emission Spectrometry (ICP-OES), X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Fourier-Transform Infrared (FTIR) Spectroscopy, Brunauer-Emmett-Teller Surface Area (S_{BET}) Analysis and Temperature Programmed Reduction in Hydrogen (H_2-TPR).
3. To evaluate the catalytic performance of promoted MoVTeNb mixed oxide catalysts in selective oxidation of propane to acrylic acid.

REFERENCES

Abello, M., Gomez, M., & Cadus, L. (1998). Selective oxidation of propane on MgO/γ- Al2O3- supported molybdenum catalyst: influence of promoters. *Catalysis letters, 53*(3-4), 185-192.

Acton, Q. A. (2013). *Aldehydes—Advances in Research and Application: 2013 Edition* (Q. Ashton Acton Ed.): ScholarlyEditions.

Alsaif, M. M., Field, M. R., Murdoch, B. J., Daeneke, T., Latham, K., Chrimes, A. F., Zoolfakar, A. S., Russo, S. P., Ou, J. Z., & Kalantar-Zadeh, K. (2014). Substoichiometric two-dimensional molybdenum oxide flakes: a plasmonic gas sensing platform. *Nanoscale, 6*(21), 12780-12791.

Amakawa, K., Kolen'ko, Y. V., Villa, A., Schuster, M. E., Csepei, L.-I., Weinberg, G., Wrabetz, S., Naumann d'Alnoncourt, R., Girgsdies, F., & Prati, L. (2013). Multifunctionality of crystalline MoV (TeNb) M1 oxide catalysts in selective oxidation of propane and benzyl alcohol. *ACS Catalysis, 3*(6), 1103-1113.

Aouine, M., Dubois, J., & Millet, J. (2001). Crystal chemistry and phase composition of the MoVTeNbO catalysts for the ammoxidation of propane. *Chemical Communications*(13), 1180-1181.

Baca, M., Aouine, M., Dubois, J., & Millet, J. (2005). Synergetic effect between phases in MoVTe (Sb) NbO catalysts used for the oxidation of propane into acrylic acid. *Journal of Catalysis, 233*(1), 234-241.

Bart, J., Cariati, F., & Sgamellotti, A. (1979). Mixed-valence effects in tellurium-molybdenum oxides. *Inorganica chimica acta, 36*, 105-112.

Bart, J., Petrini, G., & Giordano, N. (1975). Solid- state equilibrium relations in the Ternary Systems TeO2□ MoO3□ MoO2 and TeO2□ MoO3□ Te. *Zeitschrift für anorganische und allgemeine Chemie, 413*(2), 180-192.

BASF. (2015). BASF inaugurates world-scale acrylic acid complex in Camaçari, Brazil BASF. Camaçari, Brazil.[Press release]. Retrieved from https://www.basf.com/en/company/news-and-media/news-releases/2015/06/p-15-260.html

Bosch, H., Kip, B. J., Van Ommen, J. G., & Gellings, P. J. (1984). Factors influencing the temperature-programmed reduction profiles of vanadium pentoxide. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 80*(9), 2479-2488.

Botella, P., Concepción, P., Nieto, J. L., & Solsona, B. (2003). Effect of potassium doping on the catalytic behavior of Mo–V–Sb mixed oxide catalysts in the oxidation of propane to acrylic acid. *Catalysis letters, 89*(3-4), 249-253.

Botella, P., García-González, E., Nieto, J. L., & González-Calbet, J. (2005). MoVTeNbO multifunctional catalysts: Correlation between constituent crystalline phases and catalytic performance. *Solid state sciences, 7*(5), 507-519.

Botella, P., García-González, E., Solsona, B., Rodríguez-Castellón, E., González-Calbet, J., & Nieto, J. L. (2009). Mo-containing tetragonal tungsten bronzes. The influence of tellurium on catalytic behaviour in selective oxidation of propene. *Journal of Catalysis, 265*(1), 43-53.

Botella, P., Nieto, J. L., & Solsona, B. (2002a). Preparation, characterisation and catalytic behaviour of a new TeVMoO crystalline phase. *Catalysis letters, 78*(1-4), 383-387.

Botella, P., Nieto, J. L., & Solsona, B. (2002b). Selective oxidation of propene to acrolein on Mo-Te mixed oxides catalysts prepared from ammonium telluromolybdates. *Journal of Molecular Catalysis A: Chemical, 184*(1), 335-347.

Botella, P., Nieto, J. L., Solsona, B., Mifsud, A., & Márquez, F. (2002c). The preparation, characterization, and catalytic behavior of MoVTeNbO catalysts prepared by hydrothermal synthesis. *Journal of Catalysis, 209*(2), 445-455.

Botto, I., Cabello, C., & Thomas, H. (1997). (NH 4) 6 [TeMo 6 O 24]· 7H 2 O Anderson phase as precursor of the TeMo 5 O 16 catalytic phase: thermal and spectroscopic studies. *Materials chemistry and physics, 47*(1), 37-45.

Callahan, J., & Grasselli, R. (1963). A selectivity factor in vapor‐ phase hydrocarbon oxidation catalysis. *AIChE Journal, 9*(6), 755-760.

Centi, G., Grasselli, R. K., & Trifiro, F. (1992). Propane ammoxidation to acrylonitrile-an overview. *Catalysis today, 13*(4), 661-666.

Chaudhari, C. S., Sable, S. S., Gurav, H., Kelkar, A. A., & Rane, V. H. (2010). Oxidation of propane to acrylic acid and acetic acid over alkaline earth-doped Mo-V-Sb-O x catalysts. *Journal of Natural Gas Chemistry, 19*(6), 593-599.

Chen, N., Ueda, W., & Oshihara, K. (1999). Hydrothermal synthesis of Mo–V–M–O complex metal oxide catalysts active for partial oxidation of ethane. *Chemical Communications*(6), 517-518.

Chommanad, T. (2015).*Bio-based Acrylic Acid: Markets and Commercial Scale Development*.I. Nexant.

Chu, B., Truter, L., Nijhuis, T., & Cheng, Y. (2015). Performance of phase-pure M1 MoVNbTeO x catalysts by hydrothermal synthesis with different post-treatments for the oxidative dehydrogenation of ethane. *Applied Catalysis A: General, 498*, 99-106.

Clark, S. (2014).*Global Acrylic Acid Market (Derivatives Types, End Users and Geography) - Industry Analysis, Trends, Share, Opportunities and Forecast, 2013 - 2020*

Dang, J., Zhang, G.-H., Chou, K.-C., Reddy, R. G., He, Y., & Sun, Y. (2013). Kinetics and mechanism of hydrogen reduction of MoO 3 to MoO 2. *International Journal of Refractory Metals and Hard Materials, 41*, 216-223.

Deniau, B., Bergeret, G., Jouguet, B., Dubois, J., & Millet, J. (2008a). Preparation of single M1 phase MoVTe (Sb) NbO catalyst: Study of the effect of M2 phase dissolution on the structure and catalytic properties. *Topics in Catalysis, 50*(1-4), 33-42.

Deniau, B., Millet, J., Loridant, S., Christin, N., & Dubois, J. (2008b). Effect of several cationic substitutions in the M1 active phase of the MoVTeNbO catalysts used for the oxidation of propane to acrylic acid. *Journal of Catalysis, 260*(1), 30-36.

Deo, G., & Wachs, I. E. (1994). Effect of additives on the structure and reactivity of the surface vanadium oxide phase in V2O5/TiO2 catalysts. *Journal of Catalysis, 146*(2), 335-345.

DeSanto Jr, P., Buttrey, D. J., Grasselli, R. K., Lugmair, C. G., Volpe, A. F., Toby, B. H., & Vogt, T. (2003). Structural characterization of the orthorhombic phase M1 in MoVNbTeO propane ammoxidation catalyst. *Topics in Catalysis, 23*(1-4), 23-38.

DeSanto Jr, P., Buttrey, D. J., Grasselli, R. K., Lugmair, C. G., Volpe, A. F., Toby, B. H., & Vogt, T. (2004). Structural aspects of the M1 and M2 phases in MoVNbTeO propane ammoxidation catalysts. *Zeitschrift für*

Kristallographie/International journal for structural, physical, and chemical aspects of crystalline materials, 219(3/2004), 152-165.

Dinse, A., Frank, B., Hess, C., Habel, D., & Schomäcker, R. (2008). Oxidative dehydrogenation of propane over low-loaded vanadia catalysts: Impact of the support material on kinetics and selectivity. *Journal of Molecular Catalysis A: Chemical, 289*(1), 28-37.

Evans, J. H. T. (1968). Refined molecular structure of the heptamolybdate and hexamolybdotellurate ions. *Journal of the American Chemical Society, 90*(12), 3275-3276.

Fukudome, K., Ikenaga, N.-o., Miyake, T., & Suzuki, T. (2011). Oxidative dehydrogenation of propane using lattice oxygen of vanadium oxides on silica. *Catalysis Science & Technology, 1*(6), 987-998.

Girgsdies, F., Schlögl, R., & Trunschke, A. (2012). In-situ X-ray diffraction study of phase crystallization from an amorphous MoVTeNb oxide catalyst precursor. *Catalysis Communications, 18*, 60-62.

Grasselli, R., Lugmair, C., Volpe, A., Andersson, A., & Burrington, J. (2010). Enhancement of acrylic acid yields in propane and propylene oxidation by selective P Doping of MoV (Nb) TeO-based M1 and M2 catalysts. *Catalysis today, 157*(1), 33-38.

Grasselli, R. K. (2001). Genesis of site isolation and phase cooperation in selective oxidation catalysis. *Topics in Catalysis, 15*(2-4), 93-101.

Grasselli, R. K. (2002). Fundamental principles of selective heterogeneous oxidation catalysis. *Topics in Catalysis, 21*(1-3), 79-88.

Grasselli, R. K. (2005). Selectivity issues in (amm) oxidation catalysis. *Catalysis today, 99*(1), 23-31.

Grasselli, R. K., Burrington, J. D., Buttrey, D. J., DeSanto Jr, P., Lugmair, C. G., Volpe Jr, A. F., & Weingand, T. (2003). Multifunctionality of active centers in (amm) oxidation catalysts: from Bi–Mo–O x to Mo–V–Nb–(Te, Sb)–O x. *Topics in Catalysis, 23*(1-4), 5-22.

Grasselli, R. K., Buttrey, D. J., DeSanto Jr, P., Burrington, J. D., Lugmair, C. G., Volpe, A. F., & Weingand, T. (2004). Active centers in Mo–V–Nb–Te–O x (amm) oxidation catalysts. *Catalysis today, 91*, 251-258.

Grasselli, R. K., Lugmair, C. G., & Volpe, A. F. (2008). Doping of MoVNbTeO (M1) and MoVTeO (M2) phases for selective oxidation of propane and propylene to acrylic acid. *Topics in Catalysis, 50*(1-4), 66-73.

Grzybowska-Świerkosz, B. (2002). Effect of additives on the physicochemical and catalytic properties of oxide catalysts in selective oxidation reactions. *Topics in Catalysis, 21*(1-3), 35-46.

Guliants, V. V., Bhandari, R., Al-Saeedi, J. N., Vasudevan, V. K., Soman, R. S., Guerrero-Pérez, O., & Bañares, M. A. (2004). Bulk mixed Mo–V–Te–O catalysts for propane oxidation to acrylic acid. *Applied Catalysis A: General, 274*(1), 123-132.

Hävecker, M., Wrabetz, S., Kröhnert, J., Csepei, L.-I., d'Alnoncourt, R. N., Kolen'ko, Y. V., Girgsdies, F., Schlögl, R., & Trunschke, A. (2012). Surface chemistry of phase-pure M1 MoVTeNb oxide during operation in selective oxidation of propane to acrylic acid. *Journal of Catalysis, 285*(1), 48-60.

Hanato, M., & Kayou, A. (1988). European Patent No. 318,295.

Hatano, M., & Kayou, A. (1991). United States Patent No. 5,049,692.

Hinago, H., Komada, S., & Kogyo, A. K. (2000). United States Patent No. 6,603,728.

Holmberg, J., Grasselli, R. K., & Andersson, 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*(1), 121-134.

Holmes, S., Al-Saeedi, J., Guliants, V., Boolchand, P., Georgiev, D., Hackler, U., & Sobkow, E. (2001). Solid state chemistry of bulk mixed metal oxide catalysts for the selective oxidation of propane to acrylic acid. *Catalysis today, 67*(4), 403-409.

Irmawati, R., Ahmad Afandi, M., Ahmad Zaidi, I., & Hossein Abbastabar, A. (2011a).

Irmawati, R., Botella, P., Ivars, F., Meng, W. P., Zawawi, S. M. M., Ahangar, H. A., Hernández, S., & Nieto, J. M. L. (2011b). Reflux method as a novel route for the synthesis of MoVTeNbO x catalysts for selective oxidation of propane to acrylic acid. *Journal of Molecular Catalysis A: Chemical, 342*, 50-57.

Ischenko, E., Andrushkevich, T., Popova, G. Y., Bondareva, V., Chesalov, Y., Kardash, T. Y., Plyasova, L., Dovlitova, L., & Ischenko, A. (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.

Ishchenko, E., Kardash, T. Y., Gulyaev, R., Ishchenko, A., Sobolev, V., & Bondareva, V. (2016). Effect of K and Bi doping on the M1 phase in MoVTeNbO catalysts for ethane oxidative conversion to ethylene. *Applied Catalysis A: General, 514*, 1-13.

Ishchenko, E. V., Popova, G. Y., Kardash, T. Y., Ishchenko, A. V., Plyasova, L. M., & Andrushkevich, T. V. (2012). Role of MoVTeNb oxide catalyst constituent phases in propane oxidation to acrylic acid. *Catalysis for Sustainable Energy, 1*, 75-81.

Ivars-Barceló, F., Millet, J., Blasco, T., Concepción, P., Valente, J., & Nieto, J. L. (2014). Understanding effects of activation-treatments in K-free and K-MoVSbO bronze catalysts for propane partial oxidation. *Catalysis today, 238*, 41-48.

Ivars, F., Solsona, B., Botella, P., Soriano, M., & Nieto, J. L. (2009a). Selective oxidation of propane over alkali-doped Mo–V–Sb–O catalysts. *Catalysis today, 141*(3), 294-299.

Ivars, F., Solsona, B., Hernández, S., & Nieto, J. L. (2010). Influence of gel composition in the synthesis of MoVTeNb catalysts over their catalytic performance in partial propane and propylene oxidation. *Catalysis today, 149*(3), 260-266.

Ivars, F., Solsona, B., Rodríguez-Castellón, E., & Nieto, J. M. L. (2009b). Selective propane oxidation over MoVSbO catalysts. On the preparation, characterization and catalytic behavior of M1 phase. *Journal of Catalysis, 262*(1), 35-43.

Ivars, F., Solsona, B., Soriano, M., & Nieto, J. L. (2008). Selective Oxidation of Propane Over AMoVSbO Catalysts (A= Li, Na, K, Rb or Cs). *Topics in Catalysis, 50*(1-4), 74-81.

Jeffrey, S. P. (2010).*Acrylic Acid: Technology and Cost Estimates for Production Via Propylene Oxidation, 3HP Fermentation, (Glycerol Derived) Acrolein, (Ethylene-Oxide Derived) β-Propiolactone, Acetylene Complex. Regional supply, demand and trade forecast.*I. Nexant.

Katou, T., Vitry, D., & Ueda, W. (2004). Structure dependency of Mo-VO-based complex oxide catalysts in the oxidations of hydrocarbons. *Catalysis today, 91*, 237-240.

Kim, B.-S., Kim, E.-y., Jeon, H.-S., Lee, H.-I., & Lee, J.-C. (2008). Study on the reduction of molybdenum dioxide by hydrogen. *Materials transactions, 49*(9), 2147-2152.

Koc, S., Gurdag, G., Geissler, S., Guraya, M., Orbay, M., & Muhler, M. (2005). The oxidative dehydrogenation of propane over potassium-promoted molybdenum oxide/sol–gel zirconia catalysts. *Journal of Molecular Catalysis A: Chemical, 225*(2), 197-202.

Korovchenko, P., Shiju, N., Dozier, A., Graham, U., Guerrero-Pérez, M., & Guliants, V. (2008). M1 to M2 phase transformation and phase cooperation in bulk mixed metal Mo–V–M–O (M= Te, Nb) catalysts for selective ammoxidation of propane. *Topics in Catalysis*, *50*(1-4), 43-51.

Lemonidou, A., Nalbandian, L., & Vasalos, I. (2000). Oxidative dehydrogenation of propane over vanadium oxide based catalysts: Effect of support and alkali promoter. *Catalysis today, 61*(1), 333-341.

Lin, M. M. (2003a). Complex metal-oxide catalysts for selective oxidation of propane and derivatives: I. Catalysts preparation and application in propane selective oxidation to acrylic acid. *Applied Catalysis A: General, 250*(2), 305-318.

Lin, M. M. (2003b). Complex metal oxide catalysts for selective oxidation of propane and derivatives: II. The relationship among catalyst preparation, structure and catalytic properties. *Applied Catalysis A: General, 250*(2), 287-303.

Liu, Y.-M., Feng, W.-L., Li, T.-C., He, H.-Y., Dai, W.-L., Huang, W., Cao, Y., & Fan, K.-N. (2006). Structure and catalytic properties of vanadium oxide supported on mesocellulous silica foams (MCF) for the oxidative dehydrogenation of propane to propylene. *Journal of Catalysis, 239*(1), 125-136.

Ma, C. Y., Dou, B. J., Li, J. J., Cheng, J., Hu, Q., Hao, Z. P., & Qiao, S. Z. (2009). Catalytic oxidation of benzyl alcohol on Au or Au–Pd nanoparticles confined in mesoporous silica. *Applied Catalysis B: Environmental, 92*(1), 202-208.

Magneli, A. (1953). Studies on the Hexagonal Tungsten Bronzes of-Potassium. *Acta Chemica Scandinavica, 7*, 315-324.

Millet, J., Baca, M., Pigamo, A., Vitry, D., Ueda, W., & Dubois, J. (2003). Study of the valence state and coordination of antimony in MoVSbO catalysts determined by XANES and EXAFS. *Applied Catalysis A: General, 244*(2), 359-370.

Millet, J., Roussel, H., Pigamo, A., Dubois, J., & Jumas, J. (2002). Characterization of tellurium in MoVTeNbO catalysts for propane oxidation or ammoxidation. *Applied Catalysis A: General, 232*(1), 77-92.

Nakamoto, K. (1970). Infrared spectra of inorganic and coordination compounds.

Nieto, J. L., Botella, P., Solsona, B., & Oliver, J. (2003). The selective oxidation of propane on Mo-V-Te-Nb-O catalysts: The influence of Te-precursor. *Catalysis today, 81*(2), 87-94.

Oliver, J., Nieto, J. L., Botella, P., & Mifsud, A. (2004). The effect of pH on structural and catalytic properties of MoVTeNbO catalysts. *Applied Catalysis A: General, 257*(1), 67-76.

Oshihara, K., Hisano, T., & Ueda, W. (2001). Catalytic oxidative activation of light alkanes over Mo–V-based oxides having controlled surface. *Topics in Catalysis, 15*(2-4), 153-160.

Palacio, L. A., Echavarría, A., Sierra, L., & Lombardo, E. A. (2005). Cu, Mn and Co molybdates derived from novel precursors catalyze the oxidative dehydrogenation of propane. *Catalysis today, 107*, 338-345.

Pereira, E. B., Pereira, M. M., Lam, Y., Perez, C. A., & Schmal, M. (2000). Synthesis and characterization of niobium oxide layers on silica and the interaction with nickel. *Applied Catalysis A: General, 197*(1), 99-106.

Popova, G. Y., Andrushkevich, T., Aleshina, G., Plyasova, L., & Khramov, M. (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*(2), 195-200.

Popova, G. Y., Andrushkevich, T., Chesalov, Y. A., Plyasova, L., Dovlitova, L., Ischenko, E., Aleshina, G., & Khramov, M. (2009a). Formation of active phases in MoVTeNb oxide catalysts for ammoxidation of propane. *Catalysis today, 144*(3), 312-317.

Popova, G. Y., Andrushkevich, T., Dovlitova, L., Aleshina, G., Chesalov, Y. A., Ishenko, A., Ishenko, E., Plyasova, L., Malakhov, V., & Khramov, M. (2009b). 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*(2), 249-257.

Ramis, G., & Bregani, F. (1993). On the effect of dopants and additives on the state of surface vanadyl centers of vanadia-titania catalysts. *Catalysis letters, 18*(3), 299-303.

Ratheesh, R., Suresh, G., & Nayar, V. (1995). Infrared and Polarized Raman Spectra of M6 [TeMo6O24]· 7H2O [M= K, NH4] and (NH4) 6 [TeMo6O24]· Te (OH) 6· 7H2O Single Crystals. *Journal of Solid State Chemistry, 118*(2), 341-356.

Research, T. M. (2013).*Acrylic Acid Market (Acrylate Esters, Glacial Acrylic Acid & Others) for Superabsorbent polymers & Surface Coatings, Adhesives and Sealants, Textiles, Plastic Additives & Printing Ink Applications - Global Industry Analysis, Size, Share, Growth and Forecast, 2012 - 2018*.T. M. Research.

Rubia, I., & Sharifah, B. A. H. (2009). METAL-PROMOTER MoVTeNb OXIDE CATALYSTS FOR SELECTIVE OXIDATIVE OXIDATION: SYNTHESIS AND CHARACTERIZATION OF ACTIVE PHASE. *Borneo Science, 25*, 1-10.

Safonova, O. V., Deniau, B., & Millet, J.-M. M. (2006). Mechanism of the oxidation-reduction of the MoVSbNbO catalyst: In operando X-ray absorption spectroscopy and electrical conductivity measurements. *The Journal of Physical Chemistry B, 110*(47), 23962-23967.

Sanfiz, A. C., Hansen, T. W., Girgsdies, F., Timpe, O., Rödel, E., Ressler, T., Trunschke, A., & Schlögl, R. (2008). Preparation of Phase-Pure M1 MoVTeNb Oxide Catalysts by Hydrothermal Synthesis—Influence of Reaction Parameters on Structure and Morphology. *Topics in Catalysis, 50*(1-4), 19-32.

Sarzi-Amade, M., Morselli, S., Moggi, P., Maione, A., Ruiz, P., & Devillers, M. (2005). The effect of sol–gel promoters on the characteristics of mixed V–Nb oxides and their catalytic properties in propane oxidative dehydrogenation. *Applied Catalysis A: General, 284*(1), 11-20.

Schlögl, R. (2011). Active Sites for Propane Oxidation: Some Generic Considerations. *Topics in Catalysis, 54*(10-12), 627-638.

Schulmeyer, W. V., & Ortner, H. M. (2002). Mechanisms of the hydrogen reduction of molybdenum oxides. *International Journal of Refractory Metals and Hard Materials, 20*(4), 261-269.

Shiju, N. R., & Guliants, V. V. (2007). Microwave- Assisted Hydrothermal Synthesis of Monophasic Mo- V- Te- Nb- O Mixed Oxide Catalyst for the Selective Ammoxidation of Propane. *ChemPhysChem, 8*(11), 1615-1617.

Sun, Y., Liu, J., & Wang, E. (1986). Preparation and properties of some new 6-heteropoly-tellurate compounds of tungsten and molybdenum containing vanadium. *Inorganica chimica acta, 117*(1), 23-26.

Thomas, D. M., & McCarron, E. M. (1986). The composition and proposed structure of the alkali metal layered molybdenum bronzes. *Materials research bulletin, 21*(8), 945-960.

Tsuji, H., & Koyasu, Y. (2002). Synthesis of MoVNbTe (Sb) O x Composite Oxide Catalysts via Reduction of Polyoxometalates in an Aqueous Medium. *Journal of the American Chemical Society, 124*(20), 5608-5609.

Tsuji, H., Oshima, K., & Koyasu, Y. (2003). Synthesis of Molybdenum and Vanadium-Based Mixed Oxide Catalysts with Metastable Structure: Easy Access to the MoVNbTe (Sb) O x Catalytically Active Structure Using Reductant and Oxoacid. *Chemistry of materials, 15*(11), 2112-2114.

Ueda, W., Endo, Y., & Watanabe, N. (2006a). K-doped Mo–V–Sb–O crystalline catalysts for propane selective oxidation to acrylic acid. *Topics in Catalysis, 38*(4), 261-268.

Ueda, W., & Oshihara, K. (2000). Selective oxidation of light alkanes over hydrothermally synthesized Mo-VMO (M= Al, Ga, Bi, Sb, and Te) oxide catalysts. *Applied Catalysis A: General, 200*(1), 135-143.

Ueda, W., Oshihara, K., Vitry, D., Hisano, T., & Kayashima, Y. (2002). Hydrothermal synthesis of Mo-based oxide catalysts and selective oxidation of alkanes. *Catalysis Surveys from Asia, 6*(1-2), 33-44.

Ueda, W., Vitry, D., Kato, T., Watanabe, N., & Endo, Y. (2006b). Key aspects of crystalline Mo-VO-based catalysts active in the selective oxidation of propane. *Research on chemical intermediates, 32*(3), 217-233.

Ueda, W., Yoon, Y.-S., Lee, K.-H., & Moro-oka, Y. (1997). Catalytic oxidation of propane over molybdenum-based mixed oxides. *Korean Journal of Chemical Engineering, 14*(6), 474-478.

Umezawa, T., Kayou, A., Kiyono, K., Oshima, K., Sawaki, I., & Ushikubo, T. (1993). European Patent No. 529,853.

Ushikubo, T., Oshima, K., Kayou, A., & Hatano, M. (1997). Ammoxidation of propane over Mo-V-Nb-Te mixed oxide catalysts. *Studies in Surface Science and Catalysis, 112*, 473-480.

Vitry, D., Dubois, J.-L., & Ueda, W. (2004). Strategy in achieving propane selective oxidation over multi-functional Mo-based oxide catalysts. *Journal of Molecular Catalysis A: Chemical, 220*(1), 67-76.

Vitry, D., Morikawa, Y., Dubois, J., & Ueda, W. (2003). Mo-V-Te-(Nb)-O mixed metal oxides prepared by hydrothermal synthesis for catalytic selective oxidations of propane and propene to acrylic acid. *Applied Catalysis A: General, 251*(2), 411-424.

Wang, G., Guo, Y., & Lu, G. (2015). Promotional effect of cerium on Mo–V–Te–Nb mixed oxide catalyst for ammoxidation of propane to acrylonitrile. *Fuel Processing Technology, 130*, 71-77.

Watanabe, H., & 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., & Ueda, W. (2006). Comparative study on the catalytic performance of single-phase Mo-VO-based metal oxide catalysts in propane ammoxidation to acrylonitrile. *Industrial & engineering chemistry research, 45*(2), 607-614.

Yi, X., Sun, X., Zhang, X., Huang, C., Weng, W., & Wan, H. (2009). Highly dispersed MoVTeNbO/SiO 2 catalysts prepared by the sol–gel method for selective oxidation of propane to acrolein. *Catalysis Communications*, *10*(12), 1591-1594.