

**Improving the Physicochemical Properties of SbVZrCe Catalyst Prepared By
Reflux Method**

by

Mohd Faris bin Ab Halim

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

JULY 2009

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

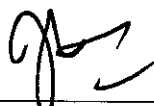
**Improving the Physicochemical Properties of SbVZrCe Catalyst Prepared By
Reflux Method**

by

Mohd Faris bin Ab Halim

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,



(AP Dr. Anita Ramli)

DR ANITA RAMLI
Associate Professor
Fundamental & Applied Sciences Department
Universiti Teknologi PETRONAS, PERAK

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2008

CERTIFICATION OF ORIGINALITY

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



MOHD FARIS BIN AB HALIM

Abstract

Antimony-vanadium-oxide is known to be an active and selective catalyst for the ammoxidation of propane to Acrylonitrile (ACN) and doping with Zr-Ce can enhance the performance of this catalyst. Unfortunately the yield of 21.3% is too low to be used commercially. Sb-V-Zr-Ce catalyst is prepared by using slurry method for the ammoxidation of propane to ACN. In an attempt to increase the yield of propane to ACN, modifications methods solely focus on reflux method are introduced into the catalyst preparation method for this process. A combination of various physicochemical techniques such as FTIR, physical adsorption of N₂, BET surface area, X-ray Diffraction (XRD), scanning electron microscopy (SEM) and Temperature Programmed Desorption Reduction & Oxidation (TPDRO) are used to characterize the modified catalyst.

ACKNOWLEDGEMENTS

First of all, I would like to thank Allah, the Most Gracious, the Most Merciful, and the Creator of all, that with His will, this project was completed. May this project shall be benefited to all.

Secondly, my utmost gratitude is for my supervisor, AP. Dr. Anita Ramli for being such a tutor, a guider, a provider, and a helper throughout the project. Her inspirations were behind the project and the knowledge that comes with the ideas greatly strengthened the project. Her sacrifices of time and energy were priceless to the outcome of this project.

Special thanks go to Dr. Mohd Khalik as final year project coordinator for the successful project cooperation which benefits me all final year final semester student. Not to forget the technicians who have made this project a success..

And not forgetting my family and friends, especially my parents, for giving their utmost support for whatever that I do. May God repay all of the deeds.

TABLE OF CONTENTS

CERTIFICATION OF APPROVAL	i
CERTIFICATION OF ORIGINALITY	ii
ABSTRACT	iii
ACKNOWLEDGEMENT	iv
LIST OF FIGURES	vi
LIST OF	
ABBREVIATIONS AND NOMENCLATURES	vii
CHAPTER 1: INTRODUCTION	1
1.1 Background of Study	1
1.2 Problem Statement	2
1.3 Objectives	4
1.4 Scope of Study	4
CHAPTER 2: LITERATURE REVIEW	5
2.1 Catalyst	5
2.2 Catalyst Preparation	8
2.3 Catalyst Characterization	11
CHAPTER 3: METHODOLOGY	14
3.1 Project Activities	14
3.2 Research Methodology	15
CHAPTER 4: RESULTS AND DISCUSSION	18
4.1 SEM	18
4.2 TPDRO	20
CHAPTER 5: CONCLUSION AND RECOMMENDATION	23
5.1 Conclusion	23
REFERENCES	28
APPENDICES	24

LIST OF TABLES

Table 1:	United State Pattern Catalyst for Propane Ammoxidation to ACN	5
Table 2:	Catalytic Performance of the Sb-V Promoted Catalysts in the Ammoxidation of Propane	8

ABBREVIATIONS AND NOMENCLATURES

Acrylonitrile.....	ACN
Acrylonitrile-butadiene-styrene.....	ABS
The Standard Oil Company.....	Sohio
British Petroleum.....	BP
Hydrogen Sulfide.....	H ₂ S
Methyl Bromide.....	CH ₃ Br
Antimony.....	Sb
Vanadium.....	V
Zirconium.....	Zr
Cerium.....	Ce
Fourier transform infra red spectrometry.....	FTIR
Physical adsorption of N ₂	BET
X-ray diffraction.....	XRD
Scanning electron microscopy.....	SEM
Temperature Programmed Desorption Reduction Oxidation.....	TPDRO
Surfaced Area.....	A _{sam} [m ² /g]
L.....	Avogadro Number
n _{rec}	Amount of gas reacted.[mmole/g]
Fs.....	Stoichiometric factor
a _{met}	square section of atom [metal mole/gas mole]

INTRODUCTION

1.1 Background of Study

Chances are that acrylonitrile touches everyone in some way every day. Acrylonitrile (ACN) is the key ingredient in the acrylic fiber used to make clothing and carpeting; in acrylonitrile-butadiene-styrene (ABS), a durable material used in automobile components, telephone and computer casings, and sports equipment; and in nitrile rubber, which is used in the manufacture of hoses for pumping fuel.

Acrylonitrile is used to produce plastics that are impermeable to gases and are ideal for shatterproof bottles that hold chemicals and cosmetics, clear “blister packs” that keep meats fresh and medical supplies sterile, and packaging for many other products. It is also a component in plastic resins, paints, adhesives, and coatings.

The acrylonitrile in those products was made by a process discovered and developed in the 1950s by scientists and engineers at The Standard Oil Company, or Sohio, which became part of British Petroleum (BP) in 1987. The process is a single-step direct method for manufacturing acrylonitrile from propylene, ammonia, and air over a fluidized bed catalyst.

Sohio's discovery led to the production of plentiful and inexpensive acrylonitrile of high purity as a raw material and to dramatic growth in the thermoplastics, synthetic fiber, and food packaging industries. Today more than 95% of the world's acrylonitrile is produced by BP or made under its license.

Acrylonitrile, first synthesized in 1893 by Charles Moureu, did not become important until the 1930s, when industry began using it in new applications such as acrylic fibers for textiles and synthetic rubber.

Although by the late 1940s the utility of acrylonitrile was unquestioned, existing manufacturing methods were expensive, multistep processes. They seemed reserved for the world's largest and wealthiest principal manufacturers: American Cyanamid, Union Carbide, DuPont, and Monsanto. At such high production costs, acrylonitrile could well have remained little more than an interesting, low-volume specialty chemical with limited applications.

In the late 1950s, however, Sohio's research into selective catalytic oxidation led to a breakthrough in acrylonitrile manufacture. The people who invented, developed, and commercialized the process showed as much skill in marketing as in chemistry. The result was such a dramatic lowering of process costs that all other methods of producing acrylonitrile, predominantly through acetylene, soon became obsolete.

1.2 Problem Statement

There is presently worldwide interest in developing heterogeneous catalysts that are active for the partial oxidation of alkanes, enabling the replacement of the corresponding olefins as feedstocks in chemicals production (Wittcoff, H. A., 1990). A driving force for this trend is the competition that exists for light olefins between various sectors, including partial oxidation, polymerization, and refinery processes. As a result, in various parts of the world there is a considerable difference in price between C₂-C₄ olefins and the corresponding alkanes, which is in favor of the alkanes. Partial oxidation of an alkane is already in practice for the manufacture of maleic anhydride, where butane oxidation has replaced older technologies using butene or benzene as feedstock. Currently, BP/SOHIO is active in developing a process for the direct manufacture of acrylonitrile from propane, as an alternative to their well-known ammoxidation process starting from propylene. BP has announced (29 May 1997) the successful operation of a first-stage demonstration plant. According to BP, the propane process offers 20% lower production costs compared to the route from propylene. Moreover, on an overall cost basis, BP claims that the one-step propane process is advantaged over two-step facilities which in a first step generate their propylene feedstock via propane dehydrogenation. Chances are that Acrylonitrile (ACN) touches everyone in some way every day. ACN is the key ingredient in the acrylic fiber used to make clothing, carpeting and many more.

Current method on producing ACN is ammoxidation of propylene using the SOHIO method and it is proved efficient. However the risk of propylene shortage and much cheaper price of propane compared to propylene initiates researchers to improve the ammoxidation of propane to ACN. Synthesis of ACN from propane requires a modification of the catalysts used for propylene ammoxidation, because the latter catalysts are not active enough with alkane feed. Ramli *et al.* (2005) state that the yield of ACN from ammoxidation of propane using Sb-V-Zr-Ce as catalyst is 21.3% which is higher than other vanadium-antimony group catalysts, Sb-V-Ti, Sb-V-Fe-Zn and Sb-V. In this project, a study to increase the ACN yield by using the reflux method will be done with the aim to increase the ACN yield from 21.3% to more significant value to be used in the industry.

1.3 Objectives

1. To study the characteristics of the physicochemical properties of SbVZrCe catalyst using fourier transform infra red spectrometry (FTIR), X-ray diffraction (XRD) scanning electron microscopy (SEM) and TPDRO.
2. To identify the potential of reflux method in synthesis SbVZrCe catalyst.

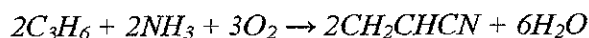
1.4 Scope of Study

The project will be focusing on modifying catalyst preparation method and characterize the modified catalyst of ammoxidation reaction of propane to ACN. Catalyst use will be antimony-vanadium oxide based with addition of zirconium and cerium as promoter (Sb-V-Zr-Ce). Preparation of catalyst will be studied in one specific preparation method (reflux). The characterization of the catalyst will be studied to investigate the effects of the promoters (Zr-Ce) and the modified preparation method on the physicochemical properties and catalytic performance.

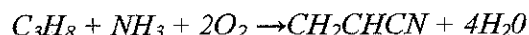
2. LITERATURE REVIEW

2.1 Catalyst

ACN is the chemical compound with the formula CH_2CHCN . This pungent-smelling colorless liquid often appears yellow due to impurities. It is an important monomer for the manufacture of useful plastics. In-terms-of its molecular structure, it consists of a vinyl group linked to a nitrile. ACN has been industrially produced as intermediates for the preparation of synthetic resins, synthetic rubbers, fibres and other important products using propylene as the feedstock. ACN is probably the nitrile manufactured on the largest scale. Most industrial ACN is produced through the Sohio process, the catalytic ammoxidation of propylene:



The cost of propane feedstock is about 5-6 times less than the cost of propylene thus the development of a process based on propane as the main material appears to be more direct evolution of propylene ammoxidation process.



The synthesis of ACN from propane requires a modification of the catalysts used for propylene ammoxidation, because the latter catalysts are not active enough with alkane feed. In recent years a large number of patents have been filed on new classes of catalysts (refer to Table 1). Many catalysts have been tested for the ammoxidation of propane to ACN and the most effective of them fall into two main classes: antimonates and molybdates (Grasselli, 1999). Among the antimonates, the most studies belong to the family VSb_xM_y , where M can be many different elements, posses the rutile or trirutile structure (Pal *et al.*, 2001).

Table 1: United State Pattern Catalyst for Propane Ammoxidation to ACN

Catalyst	Conversion of C ₃ H ₈ (%)	Selectivity to ACN (%)
VSb ₅ Zr ₅ O _x	18	35
VSb ₅ Zr ₅ Nb ₂ O _x	14	30
VSb ₅ Zr ₅ Mg _{0.3} O _x	12	30
VSb ₅ Zr ₅ Mo _{0.05} O _x	5	22

Multi component-oxides based on Antimony (Sb) and Vanadium (V) with rutile-type structures are generally considered most promising for direct conversion of propane into ACN. In the mixed vanadium-antimony group, phases are said to be most active and selective for ACN formation i.e. VSbO₄ (Nilsson *et al.*, 1994). In addition to a VSbO₄ rutile phase, Sb₂O₄, V₂O₅, Sb₆O₁₃, amorphous V and Sb oxides can also be formed, depending on the preparation method and the Sb/V ratio (Centi *et al.*, 1997). According to Centi *et al.* (1997) and Nilsson *et al.* (1994), it is accepted that a cation-deficient rutile VSbO₄ and α -Sb₂O₄ are the crucial phases for an efficient catalyst.

Although the possible benefit of additive elements during ammoxidation of propane is notorious, only little is known how the various promoter elements influenced the physicochemical and its respective catalytic properties (Grasselli *et al.*, 1990). Antimony that is used as main metal in the Sb-V catalyst system act as NH₃ activation and the NH insertion in the formation of ACN while vanadium act as paraffin activation where in the Sb-V catalyst system, it will activate the propane ammoxidation process. Centi *et al.* (1997) and Nilsson *et al.* (1994) have shown that an excess of antimony brings about an activity decrease, but also a large increase in the selectivity and in the yield of ACN and propylene.

The best catalyst for the synthesis of ACN from propane has a large excess of antimony (Sb/V = 5). This excess seems to facilitate the transformation of the intermediate propylene to ACN. An excess of vanadium on the other hand, increase the activity but also cause low selectivity to ACN due to the production of propylene and carbon dioxide. Vanadium ions are the primary active sites for the dehydrogenation of propane. However, the more severe reaction condition required

for the first step of propane activation (higher reaction temperature, longer contact times) enhance the possibility of side reactions causing a significant lowering of the selectivity to ACN from propane with respect to propylene (Nilsson *et al.*, 1994). The control of the rate of the side reaction of NH_3 unselective oxidation to N_2 , in particular, is a key factor in determining the selectivity to ACN such that the catalytic performance of Sb-V oxide catalyst for propane ammoxidation depend critically on the preparation methodology and the reaction condition.

It has been found that the substitution of other cations for vanadium can improve the selectivity of a catalyst for ACN (J. Nilsson *et al.*, 1999). For example, a catalyst test of Sb-V-Al oxides showed much better catalytic properties compare with the Sb-V-O system. The hypothesis is that they contribute to the isolation of the vanadium site in the catalyst, thus improving the selectivity towards ACN (A. Wickman *et al.*, 2000). On the other hand, a study on VSbFeO_4 showed that iron helps to stabilize the surface composition thus limiting the formation of surface antimony oxide during reaction (H. Roussel *et al.*, 2002). It was suggest that this effect might lead to more active but less selective catalysts. These results show that the substitution may play several roles, with different effects on catalytic properties.

A comparison of the activity data which has been reported for the different catalyst systems indicate that the Al-Sb-V-W-O rutile system is a most promising catalyst candidate, which gives a yield of 40% ACN at 70% propane conversion. However, the Al-Sb-V-W-oxide system is complex. According to the patents, SbVO_4 is a crucial catalyst component, and the presence in the finished catalyst of excess antimony oxide (Sb: V=3–7) as Sb_2O_3 results in superior catalytic performance. Aluminum in the form of alumina was considered a catalyst support, while tungsten was considered an element of the active material. The data given in the patents show a remarkable successive improvement in the catalytic properties when excess Sb, Al, and W, respectively, are added to the Sb–V–oxide. Examples show that the yield to acrylonitrile is about 4% over $\text{VSbO}_x/\text{SiO}_2$ and 10–12% over both unsupported and silica-supported VSb_5O_x . The yield is higher, 20–30%, for VSb_5O_x on an Al-rich support (80 wt% alumina and 20 wt% silica). When tungsten is added the yield to acrylonitrile is further improved and reaches 25–40% for $\text{VSb}_5\text{WO}_x/\text{Al}_2\text{O}_3\text{–SiO}_2$.

It has been reported that the addition of zirconia (ZrO_2) and ceria (CeO_2) in the ZrO_2 - CeO_2 catalyst for methane oxidation leads to improvements in its redox properties and thermal resistance as well as better activity at lower temperatures (Pengpanich *et al.*, 2002). Ramli *et al.* (2005) state that the yield of ACN from ammoxidation of propane using Sb-V-Zr-Ce as catalyst is 21.3% which is higher than other catalysts; Sb-V-Ti, Sb-V-Fe-Zn and Sb-V (refer to Table 2). This research concludes that the promotion of the Sb-V catalyst with Ti, Zr-Ce and Fe-Zn improves the conversion of C_3H_8 but decreases the selectivity to ACN due to the decrease of surface area (Sb-V-Zr-Ce) or the absence of α - Sb_2O_4 phase (Sb-V-Ti, Sb-V-Fe-Ce).

Table 2: Catalytic Performance of the Sb-V Promoted Catalysts in the Ammoxidation of Propane

Catalyst	Conversion of C_3H_8 (%)	Selectivity to ACN (%)	Yield in ACN (%)
Sb-V-Ti	68	21	14
Sb-V-Zr-Ce	54	39	21.3
Sb-V-Fe-Ce	60	18	11
Sb-V	15	77	11

2.2 Catalysts Preparation

The phase composition of Sb-V oxide catalysts depends on several factors, including the method of preparation adopted for the synthesis of Sb-V oxides which do not only influence the phase composition, but also features of the catalyst such as the microstructure and non-stoichiometry of the $VSbO_4$ phase. According to Haber *et al.* (1995) methods of catalyst preparation are very diverse and each catalyst may be produced via different routes. Preparation usually involves several successive steps. Many supported metal and oxide catalysts are prepared by the succession of impregnation, drying, calcination, activation; zeolite catalysts are prepared by precipitation of gel, crystallization, washing, ion exchange, drying. The properties of heterogeneous catalysts depend on all their previous history. Three fundamental stages of catalyst preparation may be distinguished:

- a) Preparation of the primary solid (or first precursory solid) associating all the useful components (impregnation or co-precipitation, or, in the case of zeolites, crystallization).
- b) Processing of that primary solid to obtain the catalyst precursor, for example by heat treatment.
- c) Activation of the precursor to give the active catalyst: reduction to metal (hydrogenation catalysts), formation of sulfides (hydrodesulphurization), deammoniation (acidic zeolites). Activation may take place spontaneously at the beginning of the catalytic reaction (selective oxidation catalysts).

2.2.1 Preparation of the Primary Solid

All experimental parameters are critical for determining the characteristics of the solid obtained after the first step:

- a) Aggregate morphology of the carrier used, if any.
- b) Quantities used (solutions, carrier).
- c) Concentrations.
- d) Stirring conditions (shape and volume of vessel are important).
- e) Temperature and temperature changes.
- f) Sequence and duration of all operations.

Four main routes exist for preparing the primary solid: deposition, precipitation and co-precipitation, gel formation and selective removal. Most of the methods used to produce Sb-V oxides catalysts are precipitation and co-precipitation.

2.2.1.1 Precipitation and co-precipitation

In all precipitations it is essential to carefully control all the details of the process including:

- a) Order and rate of addition of one solution into the other.
- b) Mixing procedure.
- c) pH and variation of pH during the process.
- d) Maturation process.

Precipitation involves two distinct processes, namely nucleation and growth. Nucleation requires that the system is far from equilibrium (high supersaturation, or,

in the case of ionic species, a solubility product far exceeding the solubility constant of the solid to be precipitated). Growth of the new phase takes place in conditions which gradually approach the equilibrium state.

In the co-precipitation of a phase associating two (or several) elements, if one of them is contained in an anion and the second in a cation, the precipitate will have a fixed or at least very inflexible composition. If both are cations (or both anions) the characteristics of the reactions with a common anion (or cation) of the solution, the solubility constants, and the supersaturation values will all be different, and the properties of the precipitate will change with time. Consequently, co-precipitation does not in general give homogeneous precipitates.

2.2.2 Treatment of Intermediate Solids or Precursors

These treatments include drying, thermal decomposition of the salts, calcination, etc. The product obtained is a reasonably inert solid (usually an oxide) which can be stored easily.

Many recommendations are common to all treatments. The main recommendation is that in all these processes all the particles of catalyst be subjected statistically to exactly the same succession of conditions.

A second recommendation is to supply a sufficient quantity of gas or liquid to the reactor to ensure complete reaction (dry air or nitrogen for complete evaporation, air or oxygen for quantitative formation of oxides, etc.). In this respect special consideration should be given to mass and heat transfer. Drying may result in a loss of uniformity in the distribution of a given element in the catalyst. This occurs if the compound in which this element is contained is not sufficiently strongly attached to the solid (carrier). Very slow drying avoids these problems. Marked improvement is often achieved by the application of freeze drying. The same recommendations are valid for all types of calcination treatment.

2.3 Catalysts Characterization

2.3.1 Scanning electron microscopy (SEM)

Topographical images in a SEM (refer to Figure 2) are formed from back-scattered primary or low-energy secondary electrons. The best resolution is about 2-5 nm but many routine studies are satisfied with a lower value and exploit the ease of image interpretation and the extraordinary depth of field to obtain a comprehensive view of the specimen. With non-crystalline catalysts, SEM is especially useful for examining the distribution and sizes of mesopores. An energy dispersive X-ray spectroscopy device is a frequent attachment in the instrument.

In electron microscopy as in any field of optics the overall contrast is due to differential absorption of photons or particles (amplitude contrast) or diffraction phenomena (phase contrast). The method provides identification of phases and structural information on crystals, direct images of surfaces and elemental composition.



Figure 1: SEM

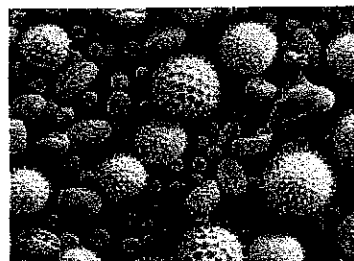


Figure 2: Image from SEM

2.3.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Samples are analyzed as powders with grains in random orientations to insure that all crystallographic directions are "sampled" by the beam. When the Bragg conditions for constructive interference are obtained, a "reflection" is produced, and the relative peak height is generally proportional to the number of grains in a preferred orientation. Based on the principle of X-ray diffraction, a wealth

of structural, physical and chemical information about the material investigated can be obtained (refer to Figure 4). A host of application techniques for various material classes is available, each revealing its own specific details of the sample studied.



Figure 3: XRD

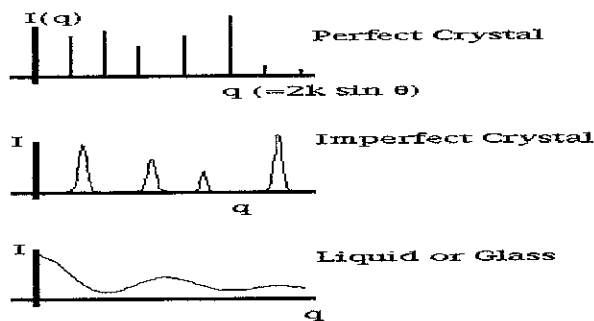


Figure 4: Graph from XRD

The advantages of X-ray Powder Diffraction are:

- a) Rapid identification of materials
- b) Ease of sample preparation
- c) Computer-aided material identification
- d) Large library of known crystalline structures
- e) Multi-sample stage

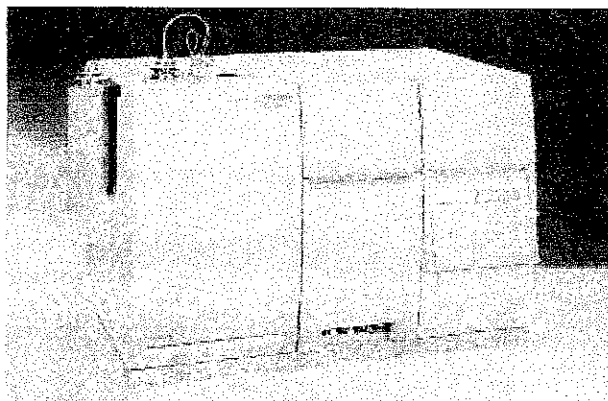
2.3.3 BET Method

BET method to provide information about the total surface area of a catalyst, the surface area of the phase carrying the active sites, or possibly even the type and number of active sites. Physical adsorption is used in the BET method to determine total surface areas. The interaction between the adsorbate and the physical adsorbent (physiorption) in nature and ideally should be a surface-specific interaction. It is necessary to be aware, however, that in some cases the interaction between the adsorbate and the adsorbent can lead to a chemical reaction in which more than just the surface layer of the adsorbent is involved. For example, when using oxidizing compounds as adsorbates (O_2 or N_2O) with metals such as copper or nickel or sulfides, sub-surface oxidation may occur.

2.3.4 Fourier Transform Infra Red Spectrometry (FTIR)

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

2.3.5 Temperature Programmed Desorption, Reduction & Oxidation



Probably the most time consuming step in catalyst development is represented by a proper and accurate characterization of surface properties and reactivity. Fundamental parameters such as free metal surface, metal dispersion and surface reactivity can be achieved very often by long procedures that have to be exactly repeated to obtain reproducible results. The TPDRO joins in a single instrument the most commonly used techniques of temperature programmed desorption (TPD), reduction (TPR), oxidation (TPO) and pulse chemisorption, using a wide range of pure gases and mixtures. It can perform activation of one catalyst while analyzing another on the same instrument which comes as standard with two electrically heated oven.

3. METHODOLOGY

3.1.1 Stage 1: Literature review

The important of the literature review is to understand the core concept and some theories of the project and to direct the orientation of this project. The literature review cover:

- a) Background study of acrylonitrile.
- b) Research by other researcher on catalyst for ammoxidation of propane to ACN.
- c) Catalyst preparation method.

3.1.2 Stage 2: Material requisition

From the ongoing research, all the necessary materials for the preparation of Sb-V-Zr-Ce catalyst were ordered.

3.1.3 Stage 3: Catalyst preparation

The catalyst will be prepared by using slurry method with some modification on the procedure namely by reflux, changing the solvent and the calcinations temperature.

3.1.4 Stage 4: Catalyst characterization

The modified catalyst will be characterized using FTIR to determine the functional group of the catalyst, BET to study the surface area, X-ray Diffraction (XRD) to study the crystal phase, scanning electron microscopy (SEM) for the morphology of the catalyst and TPDRO

3.1.5 . Stage 5: Catalyst activity test

The catalytic activity of all catalyst will be tested using a fixed-bed reactor with online GC at 420°C with feed composition (%V) of 5.8:7:17.4 for propane ammonia and oxygen respectively, with the Helium as carrier to give a total flow rate of 120 ml min⁻¹.

3.1.6 Stage 6: Result analysis

The result from catalyst activity test will be analyze to determine the effect of the modifying the preparation method and activation process on the physicochemical properties of the Sb-V-Zr-Ce catalyst for propane ammoxidation to acrylonitrile.

3.2 Research Methodology

3.2.1 Material

Ammonium metavanadate, NH_4VO_3 (99.9%), Antimony Trioxide, Sb_2O_3 (99%), Zirconium, $\text{N}_2\text{O}_7\text{-Zr}\cdot x\text{H}_2\text{O}$ (99.9%), Cerium, $\text{CeN}_3\text{O}_9\cdot 6\text{H}_2\text{O}$ (99.9%), Ethanol, $\text{C}_2\text{H}_5\text{OH}$ (99.9%)

3.2.2 Tool / Equipment Required

Lab glassware, hot plate stirrer, drying oven, furnace, FTIR, XRD, BET, TGA, SEM, micro reactor

3.2.3 Catalyst Preparation Method

The Sb-V catalysts with Zr-Ce as promoters are prepared by a reflux method. There are four modification methods for the preparation and the activation method of catalyst used in an attempt to improve the yield of ACN.

3.2.3.1 Reflux

1. 4.59g of ammonium metavanadate (NH_4VO_3 , 99.9%) is dissolved in 100ml distilled water.
2. The require promoter, 0.253g of zirconium ($\text{N}_2\text{O}_7\text{Zr}\cdot x\text{H}_2\text{O}$, 99.9%) and 0.289g of cerium, ($\text{CeN}_3\text{O}_9\cdot 6\text{H}_2\text{O}$, 99.9%) is added to the solution.
3. 3.35g of antimony trioxide (Sb_2O_3 , 99%) and 415ml of distilled water are added to an aqueous solution of ammonium metavanadate (NH_4VO_3 , 99.9%).
4. This solution is stir at 110°C (480rpm) for 3 hours in the closed beaker. After 3 hours, the beaker is opened and stirs for another 3 hours.

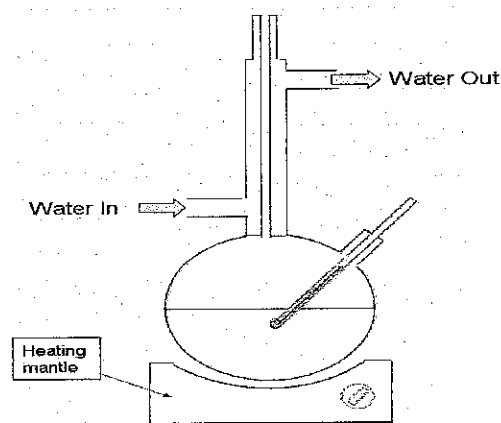
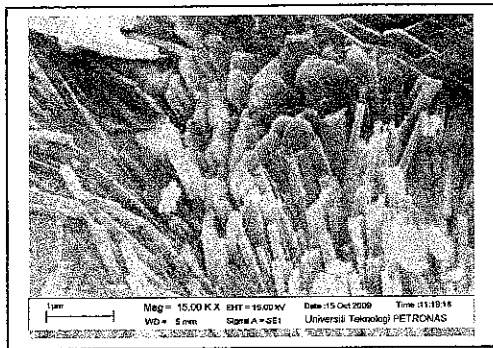


Figure 5: Set Up for Reflux

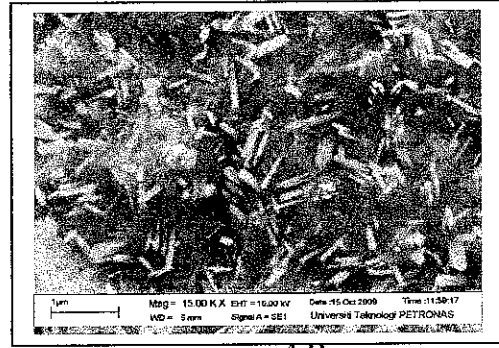
5. Set up the equipment as in Figure 5. Put the mixture inside the round flask. Set the heating mantle to 105°C . Reflux the mixture for 4 hours.
6. The mixture is filtered using filter paper.
7. The resulting mixture in the filter paper is dried for 17 hours at 120°C .
8. Run FTIR on the mixture.
9. The mixture is calcinated in air at temperature between 350°C to 600°C for 10 hours.
10. Run XRD, BET, SEM, TPDRO and FTIR again on the resulting mixture.
11. Rerun the steps with 8 hours of reflux, different calcinations temperature and change the solvent to ethanol for different sample.

RESULTS AND DISCUSSION

4.1 Scanning Electron Microscope (SEM)

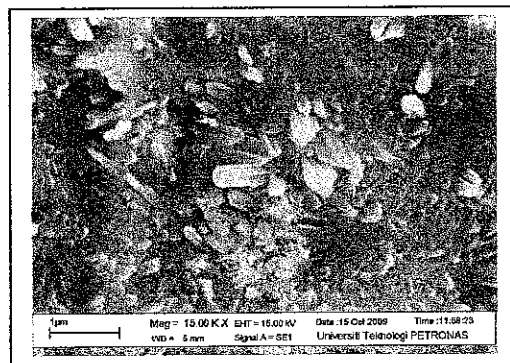


4.A



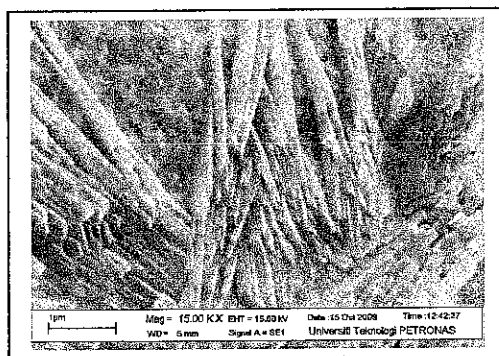
4.B

Figure presents the SEM micrographs of Sb-V-Zr-Ce. Both images exhibit a rather rod like morphology. Based on the SEM result as shown above and in the appendix, the mixed oxide catalysts exhibit an almost same shape of morphological structure and have a porous agglomerated form. 4.B is sample where the reflux time has been increase by another 4hours. Longer time forms porous structure



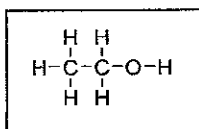
4.C

As the temperature increased, more agglomerate particle could be observed through SEM at magnification of 5 and 10kx. The average particle sizes tend to increase with calcinations temperatures.



4.D

4.D shows the result where ethanol has been used as solvent. Using 50:50 ratio. For this needle shape like to occur, this maybe due to the ethanol bigger molecular structure than water. It pushes the others metal further than water molecule can.



Ethanol molecular structure

Similar morphologies of the catalyst related to similar selectivities of ACN in the propane ammoxidation reaction. As can be predicted from the higher surface area of the catalyst, the conversion and yield to acrylonitrile obtained is higher (Salil Bhatt, 2006).

4.2 Temperature-programmed Desorption/ Reduction / Oxidation

TPD/R/O

Method Name: TPR FYP Jan09 Info:

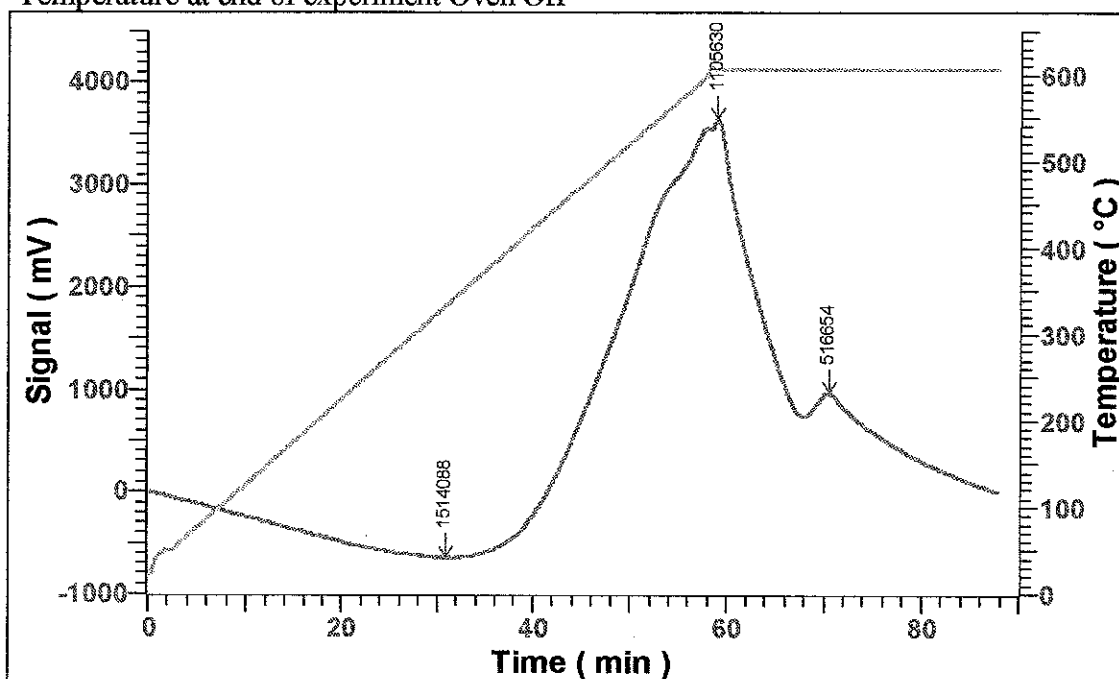
On Instrument: TPDRO 1100 with Ser.Nr.20033057 on Right Oven

Started 11/23/2009 at 5:14:37 PM finished 6:42:36 PM

With gas: Hydrogen 5% in Nitrogen and flow of 20 ccm/min

Start with oven off, heating rate 10 °/min, stop at 600 °C, hold for 30 min

Temperature at end of experiment Oven Off



Results

Amount gas adsorbed: 1897.71067 $\mu\text{mol/g}$

Peaks

#	Start[min]	Stop[min]	Maximum[min]	T[°C]	Integral[mVs]	[%]	[$\mu\text{mol/g}$]
1	30.3833	57.7333	30.7833	333	1514088.34	48.28	916.12260
2	58.4667	67.7333	58.9000	607	1105629.88	35.25	668.97848
3	68.1333	87.4500	70.4500	606	516654.15	16.47	312.60959

$$A_{\text{sam}} = L n_{\text{rec}} F_s a_{\text{met}} 10^{-23}$$

$$= 6.023 \times 10^{23} \times 1.897 \times 2 \times 8.9 \times 10^{-23}$$

$$= 203.38 \text{ m}^2/\text{g}$$

TPD/R/O

Method Name: TPR FYP Jan07 Info:

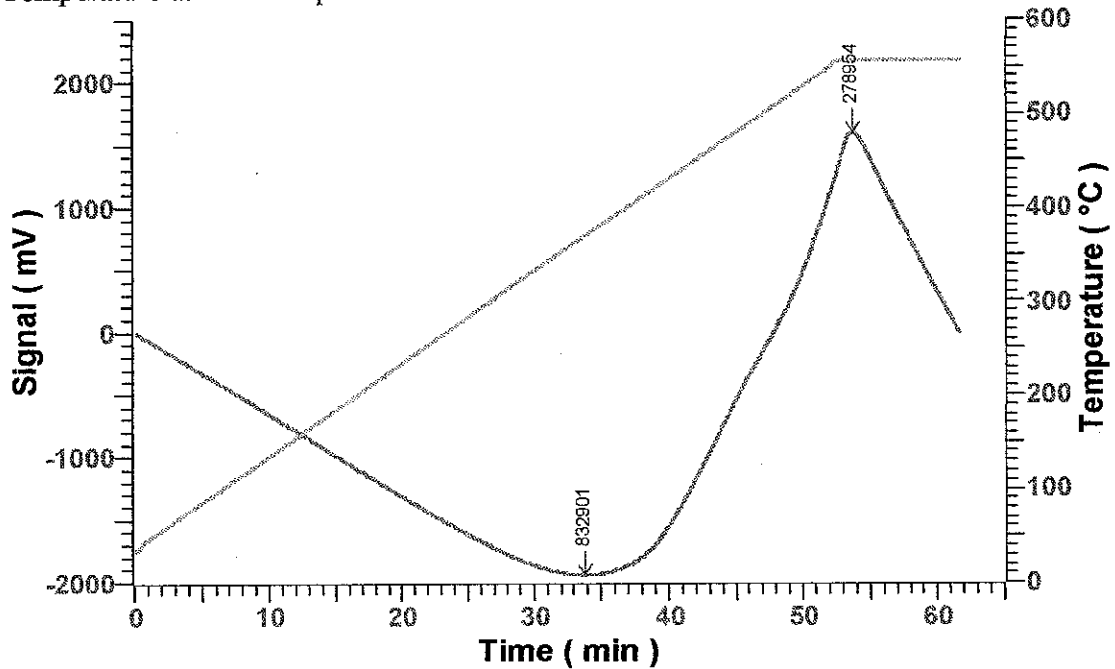
On Instrument: TPDRO 1100 with Ser.Nr.20033057 on Left Oven

Started 11/24/2009 at 8:44:01 AM finished 9:45:44 AM

With gas: Hydrogen 5% in Nitrogen and flow of 20 ccm/min

Start with oven off, heating rate 10 °/min, stop at 550 °C, hold for 10 min

Temperature at end of experiment Oven Off



Results

Amount gas adsorbed: 444.59867 $\mu\text{mol/g}$

Peaks

#	Start[min]	Stop[min]	Maximum[min]	T[°C]	Integral[mVs]	[%]	[$\mu\text{mol/g}$]
1	33.3167	53.5500	33.6833	369	832900.51	74.91	333.05309
2	34.7167	61.2000	53.6000	556	278953.64	25.09	111.54558

$$\begin{aligned}
 A_{\text{sam}} &= L n_{\text{rec}} F_s a_{\text{met}} 10^{-23} \\
 &= 6.023 \times 10^{23} \times 0.444 \times 2 \times 8.9 \times 10^{-23} \\
 &= 47.6 \text{ m}^2/\text{g}
 \end{aligned}$$

From the calculation shown above, we can see that sample 1 has larger surface area. The SEM also shows the same thing. This will increase the catalyst performance. As can be predicted from the higher surface area of the catalyst, the conversion and yield to acrylonitrile obtained is higher (Salil Bhatt, 2006).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

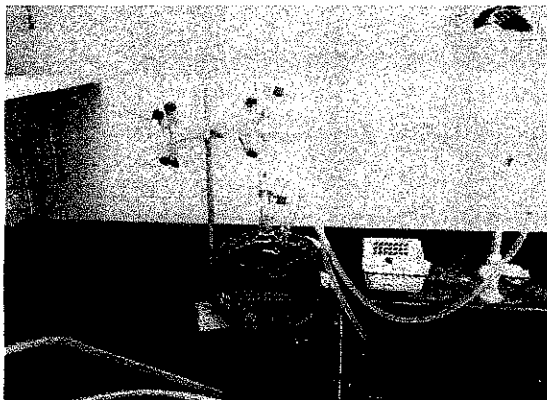
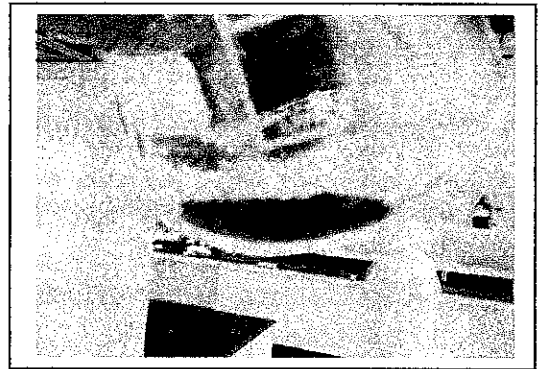
5.1 Conclusion

The objective of this project is to modify the preparation method of Sb-V-Zr-Ce catalyst and to characterize the modified catalyst using Fourier transform infra red spectrometry (FTIR), physical adsorption of N₂ (BET), X-ray diffraction (XRD) and scanning electron microscopy (SEM). However, XRD sample will be received on 16th december, for BET the sample has been sent to the Petronas Research in KL. From the SEM and TPDRO result we can deduct that the best result is between sample 1 and sample 4. We can expect an improvement to the physicochemical properties of SbVZrCe catalyst based on TPDRO and SEM.

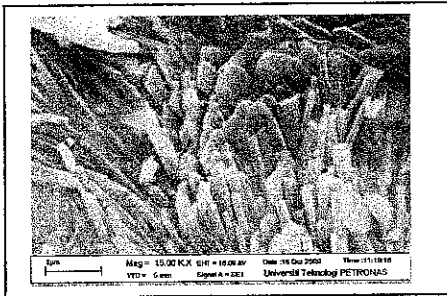
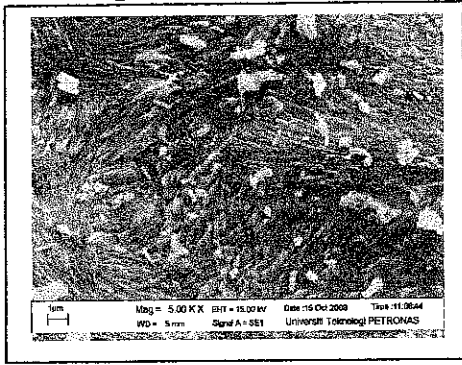
5.2 Recommendation

There are very wide scope to explore in other to improve the formation of the crystalline phases in Sb-V-Zr-Ce catalyst. The crystal formation can be affected by so many variables, by the type of support, particle size of the support, porosity of the support, temperature and pressure of impregnation, time of impregnation, method of drying, temperature and pressure of drying, rate of drying, temperature of calcination, rate of calcination, duration of calcination, temperature of reduction, duration of reduction to name a few. Each of these variables can be tested out to find the optimum method of crystal formulation.

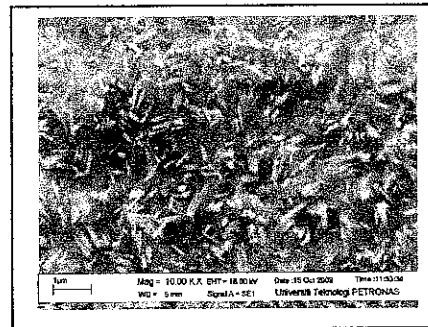
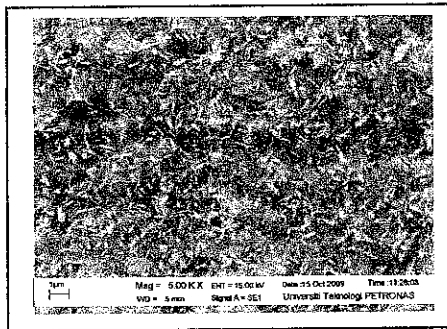
Appendix



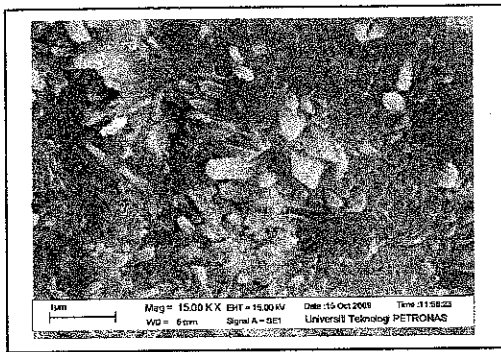
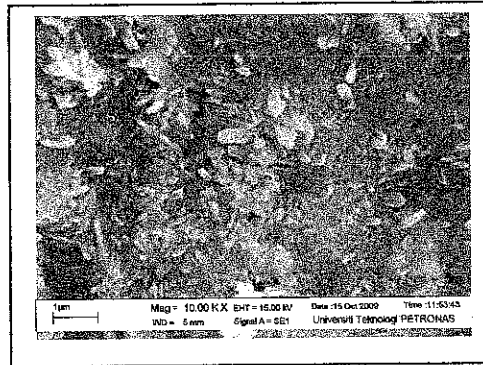
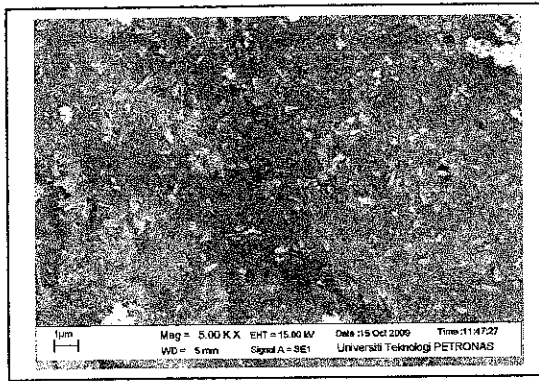
Appendix B
Sample Reflux 4hours, 400C



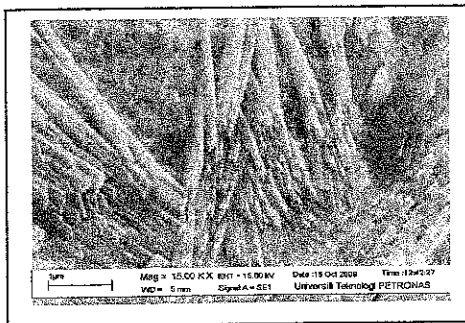
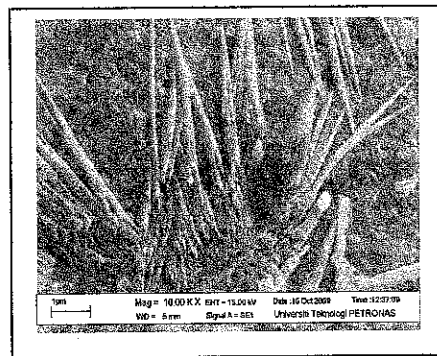
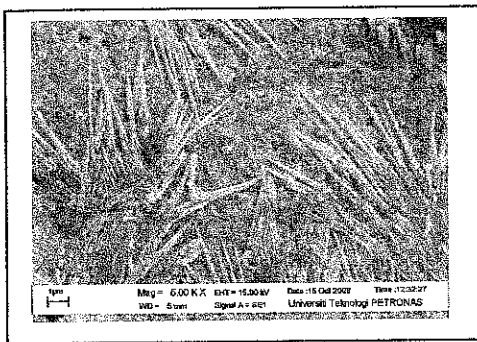
Sample Reflux 8hours, 400C



Sample Reflux 4hours, 450C



Sample Reflux Ethanol Solvent reflux 4hours, 400C



1. Sb-V doped catalysts for propane ammoxidation to ACN, Anita Ramli, Faridah Manaf, AMREC, SIRIM Berhad.
2. <http://aswebcontent.acs.org> - National Historic Chemical Landmarks Web
3. <http://en.wikipedia.org/wiki/ACN>
4. G. Centi, F. Marchi & S. Perathoner, 1997, "Effect of ammonia chemisorptions on the surface reactivity of V-Sb-Oxide catalysts for propane ammoxidation", *Appl. Catal. A*.
5. R.K Grasselli, 1999, "Advances and future trends in selective oxidation and ammoxidation catalysis", *Catal. Today*
6. Y. C. Kim, W. Ueda, & Y. Moro-oka, 1991, "Catalytic (amm)oxidation of propane with molecular oxygen over complex metal oxides: Involvement of homogeneous reaction in gas phase", *Appl. Catal.*
7. G. Centi & S. Perathoner, 1995, "Modification of the surface reactivity of vanadium antimonite catalysts during catalytic propane ammoxidation", *Appl. Catal. A*
8. http://en.wikipedia.org/wiki/Scanning_Electron_Microscope
9. <http://en.wikipedia.org/wiki/XRD>
10. V. D. Sokolovskii, A. A. Davydov, & O. Yu. Ovsitser, 1995, "Mechanism of selective paraffin ammoxidation", *Catal*
11. G. Centi, S. Perathoner & F. Trifiro, 1997, "V-Sb-oxide catalysts for ammoxidation of propane", *Appl. Catal*
12. H. Roussel, B. Mehlomakulu, F. Belhadj, E. Van Steen & J.M.M. Miller, 2002, "Active site characterization in mixed vanadium and iron antimonite oxide catalysts for propane ammoxidation", *J. Catal*
13. H. Roussel, B. Mehlomakulu, F. Belhadj, E. Van Steen & J.M.M. Miller, 2002, "Active site characterization in mixed vanadium and iron antimonite oxide catalysts for propane ammoxidation", *J. Catal*
14. Mohd Syamer Kadir, 2007
Modification of Preparation Method and Activation Process on the Physicochemical Properties of the Sb-V-Zr-Ce Catalyst for Propane Ammoxidation to Acrylonitrile

15. Salil Bhatt, 2006. *Synthesis, Characterization and Kinetic Studies of Mixed Metal MO-V-Nb-Te Oxide Catalysts for Propane Ammoxidation to Acrylonitrile*, University of Cincinnati