



UNIVERSITI PUTRA MALAYSIA

**CHARACTERIZATION OF MOLYBDENUM -VANADIUM OXIDE
CATALYST PREPARED BY
HOMOGENEOUS PRECIPITATION METHOD
USING UREA HYDROLYSIS**

WOI PEI MENG

FS 2007 16

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**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

2007



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USING UREA HYDROLYSIS**

By

WOI PEI MENG

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

May 2007



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

**CHARACTERIZATION OF MOLYBDENUM-VANADIUM OXIDE
CATALYST PREPARED BY HOMOGENEOUS PRECIPITATION
METHOD USING UREA HYDROLYSIS**

By

WOI PEI MENG

May 2007

Chairman: Irmawati Ramli, PhD

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Molybdenum-vanadium oxide (Mo-V-O) has been constantly reported as an active and selective catalyst for the direct propane transformation to acrylic acid. In this study, crystalline molybdenum-vanadium oxide catalysts have been successfully synthesized by homogeneous precipitation method using urea hydrolysis. A new approach was taken whereby the solid obtained were further refluxed in the presence of additives which are adipic acid (AA), maleic acid (MA) and polyvinyl alcohol (PVA). The precursors which upon drying were subjected to various calcination temperatures.

The effect of additives and calcination temperatures on the formation and properties of Mo-V-O characteristics were monitored by Thermogravimetric Analysis (TGA), Powder X-ray diffraction (XRD), Photon Cross Correlation Spectroscopy (PCCS), Inductively Couple Plasma-Atomic Emission Spectroscopy



(ICP-AES), BET Surface Area Measurements (S_{BET}), Scanning Electron Microscopy (SEM) and Hydrogen-Temperature Programmed Reduction (H_2 -TPR).

It was found that without the presence of additives, the precursor was in a semicrystalline form of ammonium molybdate anorthic phase. However, in the presence of additives, the precursors were highly crystalline with the presence of desirable orthorhombic, monoclinic and tetragonal MoVO_x species. Heat treatment that imposed on the materials has successfully transformed the precursor into a more stable phase. The desirable orthorhombic phase was found to be achieved when sample was calcined at 873 K in nitrogen atmosphere.

SEM analysis showed a rather randomly distributed particle with defined size and shape. Total surface area, S_{BET} for sample prepared by complexing MoV salts with PVA (MoVPVA_{873}) was found to be the highest, *i.e.* $20.5 \text{ m}^2 \text{ g}^{-1}$. This property consequently contributed to the highest total amount of oxygen species removed from the oxide, hence an indication of the highly active and selective characteristics borne by the oxide. This is further confirmed by catalytic test of propane oxidation to acrylic acid which done on the sample. The test showed that samples treated with organic species (AA, MA, PVA) give better acrylic acid selectivity and yield.

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

PENCIRIAN MOLIBDENUM VANADIUM OKSIDA MELALUI KAEDAH PEMENDAKAN HOMOGEN MENGGUNAKAN HIDROLISIS UREA

Oleh

WOI PEI MENG

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Molibdenum-vanadium oksida (Mo-V-O) telah dilaporkan penggunaannya sebagai mangkin yang aktif dan memilih dalam proses tindak balas pertukaran propana secara terus kepada asid akrilik. Dalam kajian ini, mangkin molibdenum-vanadium oksida hablur telah berjaya disintesis melalui kaedah pemendakan homogen secara hidrolisis urea. Satu pendekatan baru telah diambil dimana pepejal prekursor yang diperolehi akan direflukskan dengan kehadiran bahan tambah seperti asid adipik (AA), asid maleik (MA) dan polivinil alkohol (PVA). Prekursor yang diperolehi selepas pengeringan akan dikalsinkan pada pelbagai suhu.

Kesan bahan tambah dan suhu pengkalsinan ke atas pembentukan dan sifat-sifat Mo-V-O telah diperhatikan melalui analisis gravimetri terma (TGA), pembelauan sinar-X (XRD), spektroskopi korelasi silang foton (PCCS), spektroskopi pengandungan plasma teraruh-pancaran atom (ICP-AES), pengukuran luas

permukaan BET (S_{BET}), mikroskopi pengimbasan elektron (SEM) dan penurunan berprogramkan suhu hidrogen (H_2 -TPR).

Prekursor tanpa kehadiran bahan tambah didapati berada dalam bentuk semikristal ammonia molibdat fasa anortik. Walau bagaimanapun, dengan kehadiran spesies organik, prekursor berada dalam keadaan kehabluran tinggi dengan kehadiran fasa ortorombik, monoklinik dan tetragon spesis Mo-V-O_x yang dikehendaki. Rawatan haba ke atas sampel berjaya menukarkan prekursor kepada fasa yang lebih stabil. Fasa ortorombik yang diinginkan berjaya dicapai apabila sampel dikalsinkan pada suhu 873 K dalam atmosfera nitrogen.

Analisis SEM menunjukkan penaburan partikel yang agak berselerak tetapi dengan saiz dan bentuk yang jelas. Luas permukaan (S_{BET}) bagi sampel MoV yang dirawat dengan PVA (MoVPVA_{873}) memberikan nilai yang tertinggi iaitu $20.5 \text{ m}^2 \text{ g}^{-1}$. Ciri ini menyumbangkan kepada jumlah oksigen tertinggi yang disingkirkan dari oksida, maka menandakan oksida mempunyai ciri kepilihan yang tinggi. Ujian pemangkinan untuk pertukaran propana ke asid akrilik yang dijalankan ke atas sampel telah mengesahkan hal tersebut. Ujian ini menunjukkan bahawa sampel yang dirawat dengan spesies organik (AA, MA, PVA) memberikan kepilihan dan hasil kepada asid akrilik yang lebih baik.

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I certify that an Examination Committee met on 23th May 2007 to conduct the final examination of Woi Pei Meng on her Master of Science thesis entitled "Characterization of Molybdenum-Vanadium Oxide Catalyst prepared by Homogeneous Precipitation Method using Urea Hydrolysis" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

WOI PEI MENG

Date: 13th JUNE 2007

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LIST OF ABBREVIATIONS

2 θ	2 Theta
Å	Angstrom
AA	Adipic acid
BET	Brunauer-Emmett-Teller
E_r	Reduction activation energy
ICP-AES	Inductively Couple Plasma-Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
JEOL	Japan Electron Optics Laboratory
MA	Maleic acid
Mo-V-O	Molybdenum-vanadium oxide
PCCS	Photon Cross Correlation Spectroscopy Analysis
PVA	Polyvinyl alcohol
SEM	Scanning Electron Microscopy
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
TGA-DTG	Thermogravimetric analysis-derivative thermal gravimetric
TPR	Temperature-programmed reduction
XRD	X-ray diffraction



Table 4.26: The performance of MoVO_x catalysts for propane oxidation with feed compositions of C₃H₈/O₂/N₂/H₂O = 8/10/37/45.

Catalysts	Propane Conversion (%)	Acrylic Acid Selectivity (%)	Acrylic Acid yield (%)	Acetic Acid Selectivity (%)	CO₂ Selectivity (%)	CO Selectivity (%)
MoV _{cont} ₈₇₃	8.3	72.4	6.0	7.8	2.0	0.0
MoVAA ₈₇₃	10.6	78.8	8.4	6.3	6.9	0.0
MoVMA ₈₇₃	9.6	85.0	8.2	5.1	4.2	0.0
MoVPVA ₈₇₃	7.2	90.1	6.5	1.7	4.2	0.0

CHAPTER 1

INTRODUCTION

1.1 The Catalysis Phenomenon

Humans have known about catalysis for many centuries, even though they knew nothing about the chemical process that was involved. The making of soap, the fermentation of wine to vinegar, and the leavening of bread are all processes involving catalysis. It was until 1836, a Swedish chemist Jöns Jakob Berzelius introduced the term ‘catalysis’. This word comes from two Greek terms, *kata* which stands for down, and *lysein*, which means to split or break. Berzelius assumed that catalysts possess special powers that can influence the affinity of chemical substances (Thomas and Thomas, 1996). In 1895, William Ostwald comes out with a definition of catalyst that still valid today: ‘A catalyst accelerates a chemical reaction without affecting the position of equilibrium’ (Gates, 1992).

While it was formerly assumed that the catalyst remained unchanged in the course of reaction, it is now known that the catalyst is involved in chemical bonding with the reactants during the catalytic process (Hagen, 1999). Thus, catalysis is a cyclic process (Figure 1.1). The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give product, P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle



in its original state. Every catalytic reaction is a sequence of elementary steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle (Chorkendorff and Niemantsverdriet, 2003).

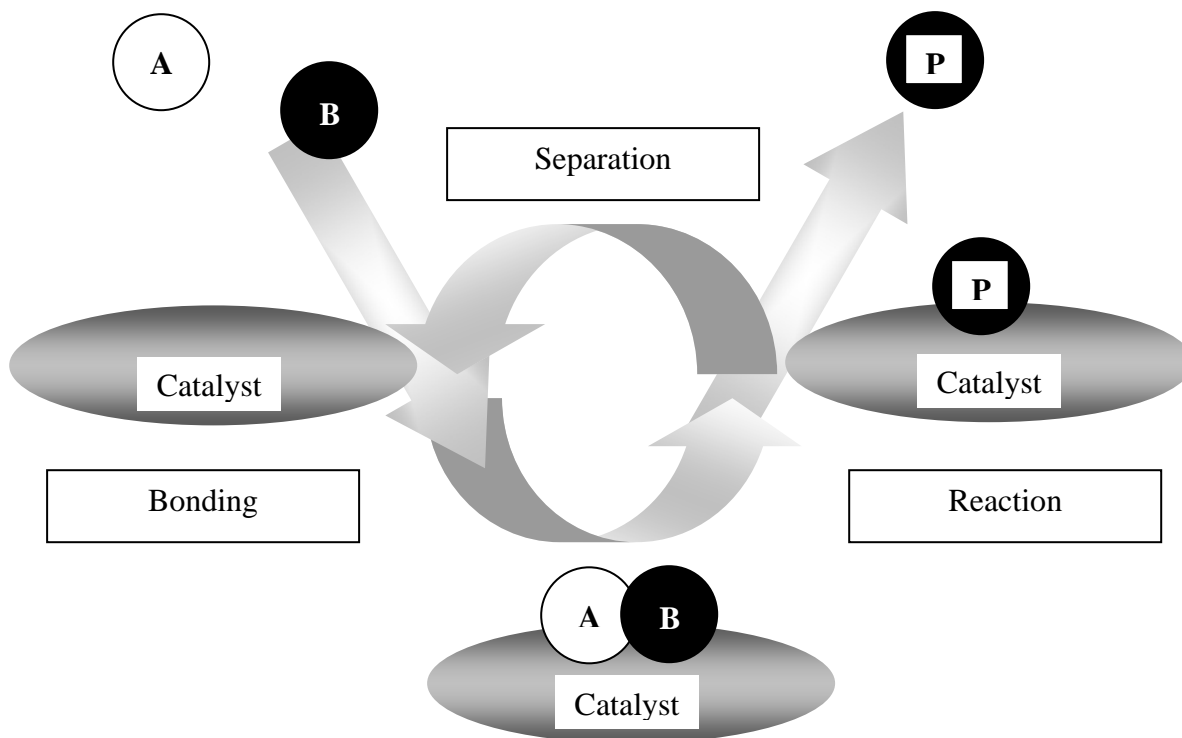


Figure 1.1: Catalytic cycle (Chorkendorff and Niemantsverdriet, 2003).

In theory, an ideal catalyst would not be consumed, but this is not the case in practise. Owing to competing reactions, the catalyst undergoes chemical changes, and its activity becomes lower (catalyst deactivation). Hence, catalysts must be regenerated. Apart from accelerating reactions, catalysts have another important property: they can influence the selectivity of chemical reactions. This means that completely different

products can be obtained from a given starting material by using different catalyst systems (Hagen, 1999).

Catalysts can be in the form of gases, liquids or solids. Most industrial catalysts are liquids or solids, whereby the latter react only via their surface. The importance of catalysis in the chemical industry is shown by the fact that 75% of all chemicals are produced with the aid of catalysts; in newly developed processes, the figure is over 90%. Numerous organic intermediate products, required for the production of plastics, synthetic fibres, pharmaceuticals, dyes, resins and pigments, can only be produced by catalytic processes. Most of the processes involved in crude-oil processing and petrochemistry, such as purification stages, refining and chemical transformations, are also require catalysts (Hagen, 1999).

1.2 Functionality of Alkane in Selective Oxidation

Short chain alkanes (C_1 – C_5) are considered as cheap raw material for petrochemical catalytic processes, in particular for the production of olefins, alcohols, aldehydes, anhydrides or acids. The selective oxidation of alkane has been largely studied in the past 20 years for two main reasons. The first one is economical since alkanes are much cheaper and more abundant than the corresponding olefins. The second one is fundamental since the way by which the alkane is activated and functionalised into an oxygenate remains unclear and challenging (Védrine *et al.*, 2003). Moreover, the only process based on alkanes that met industrial applications at this moment, is the



oxidation of *n*-butane to maleic anhydride on vanadylpyrophosphate, $(VO)_2P_2O_7$ based catalysts (Centi *et al.*, 1988). Therefore, the developments of new catalytic systems for the gas phase oxidation of short chain alkanes have special interest from both fundamental and industrial point of view.

Alkanes are characterized by the absence of reactive sites such as hydrogen atoms, which can be easily abstracted and double bonds. Therefore, they are largely less reactive than most of the possible reaction products. Thus the solid catalysts used in the selective activation and transformation of alkanes must have very special surface properties in order to control the reactivity, bulk catalyst properties, and structural characteristics of the catalyst (Centi *et al.*, 2001).

1.3 Acrylic Acid and its Current Manufacturing Process

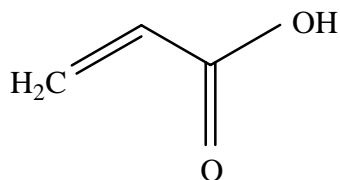


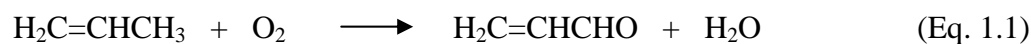
Figure 1.2: Structure of acrylic acid

Acrylic acid, $CH_2=CHCOOH$ (Figure 1.2) which also known as propenoic acid, ethylene carboxylic acid, 2-propenoic acid or acroleic acid is a colourless liquid or solid, with an irritating odour at room temperature and pressure. It is miscible with water and most organic solvents (Mamedov, 1995).

Acrylic acid is the main precursor in the production of super absorbent polymers, materials which absorb many times their own weight in liquid and are mainly used in diapers or other hygienic products. In addition, acrylic acid has also been used in the manufacturing of plastics, bonding and hydrogels used for contact lenses (Mamedov, 1995).

The acrylic acid demand in the global market grows at 4.0 percent per year through 2004, to 2.554 billion pounds. In Malaysia, a large-scale acrylic acid facility has been built in Gebeng, Pahang by Petronas/BASF. This acrylic acid plant produces 1600,000 t/y of acrylic acid (<http://www.petronas.com/>).

This desirable product is synthesized using the most widely accepted process which is the vapour phase oxidation of propylene. This two-step process starts with propylene and goes through acrolein as intermediate to make acrylic acid. The involved reactions are shown as follow:



1.4 Selective Oxidation of Propane to Acrylic Acid

In the coming century, the petrochemical industry will have to move to the direct use of natural gas as feedstock to fulfil the increasing demand in the intermediate

