UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERISATION OF MOLYBDENUM-VANADIUM OXIDE CATALYSTS PREPARED BY REFLUX METHOD

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By

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

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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

SYNTHESIS AND CHARACTERISATION OF MOLYBDENUM-VANADIUM OXIDE CATALYSTS PREPARED BY REFLUX METHOD

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Reflux method was used to prepare MoV oxide catalysts for one controlled sample where no additional species was added, then EDTA, hexane, hydrazine sulphate and urea as organic species were added during the synthesis procedure for another 4 samples. The catalysts obtained based on different calcination environment conditions and temperatures have been compared in order to determine their influence on the physicochemical properties of the catalyst. The precursors were characterised using thermogravimetry analysis (TGA) and x-ray diffraction (XRD), and the calcined samples were characterised using XRD, scanning electron microscopy (SEM) and BET surface area measurements (S_{BET}).

It has been found that the organic-metal salt complexes facilitate well dispersed, organised structure and high S_{BET} MoV oxide based formation. This is only true for hydrazine sulphate- and urea- metal salt complexes with S_{BET} of 5.5 and 10.9 m^2g^{-1} respectively, as EDTA- and hexane- metal salt complexes lead to aggregated and low S_{BET} oxide formation with the S_{BET} of 0.1 and 1.8 m^2g^{-1} respectively.

Catalytic test of the MoV oxide, MoVTe oxide and MoVTeNb oxide shows notable effects of the addition of tellurium and niobium to the molybdenum vanadate matrix. It is found that MoV oxide is sufficiently active for propane selective oxidation to acrylic acid with high conversion percentage of 45 to 62%. When tellurium is added the catalytic activity remains almost constant but the selectivity decreases from 31% to 7%. However, niobium is found to increase the catalyst stability in high heat pre-treatment whereby the quaternary oxides showed better selectivity than the ternary oxides and increases from 7% to 32%. Niobium has a significant role in the insertion of oxygen into the hydrocarbon intermediate, although the metal itself is not part of the crystal system. Thus niobium is needed for the selectivity of the reaction. In overall, the MoV and MoVTeNb is active and selective when bear the mixture of orthorhombic structure where molybdenum is part of the lattice and a phase where vanadium is present.

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

SINTESIS DAN PENCIRIAN MANGKIN MOLIBDENUM VANADIUM-OKSIDA YANG DISEDIAKAN OLEH KAEDAH REFLUKS

Oleh

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Kaedah refluks telah digunakan untuk menyediakan mangkin berasaskan MoV oksida untuk satu sample kawalan di mana tiada spesis organik ditambah, kemudian EDTA, heksana, hidrazin sulfat dan urea sebagai spesis organik yang ditambah sewaktu prosedur sintesis bagi 4 lagi sampel berasingan. Mangkin yang terhasil yang berasaskan keadaan sekeliling dan suhu pengkalsinan yang berbeza telah dibandingkan untuk mengetahui pengaruhnya terhadap sifat fizikal dan sifat kimia mangkin tersebut. Pelopor-pelopor telah dicirikan dengan menggunakan Analisis Thermogravimetry dan Pembelauan Sinar-X, dan sampel terkalsin dicirikan menggunakan Pembelauan Sinar-X, Mikroskopi Pengimbasan Elektron dan pengukuran luas permukaan dengan menggunakan kaedah BET.

Didapati bahawa kompleks garam organik-logam memudahkan pembentukan berasaskan MoV oksida yang mempunyai penyebaran yang sekata, struktur yang tersusun dan luas permukaan yang tinggi. Ini hanya benar bagi kompleks garam hidrazin sulfat-logam dan urea-logam dengan S_{BET} 5.5 dan 10.9 m^2g^{-1} masing-masing, kerana kompleks garam EDTA-logam dan heksana-logam terarah kepada

pembentukan oksida terkelompok dan mempunyai luas permukaan yang rendah dengan S_{BET} 0.1 dan 1.8 m^2g^{-1} masing-masing.

Ujian pemangkinan oksida-oksida MoV, MoVTe dan MoVTeNb menunjukkan dengan jelas kesan penambahan telurium dan niobium pada matrik molibdenum vanadat. Adalah didapati bahawa MoV oksida adalah cukup aktif untuk pengoksidaan propana secara terpilih terhadap asid akrilik dengan peratus pertukaran dalam julat 45 ke 62%. Apabila telurium ditambahkan, aktiviti mangkin hampir malar tetapi sifat kepilihan terhadap asid akrilik menurun daripada 31% ke 7%. Walau bagaimanapun, niobium didapati meningkatkan kestabilan mangkin dalam pengkalsinan suhu tinggi di mana oksida kuaternari menunjukkan kepilihan yang lebih tinggi daripada oksida ternari dengan peningkatan daripada 7% ke 32%. Niobium mempunyai peranan yang penting dalam penyisipan oksigen ke dalam bahan perantaraan hidrokarbon, walaupun logam itu sendiri bukan sebahagian daripada sistem kekisi. Maka, niobium adalah diperlukan untuk tindak balas yang memilih. Secara keseluruhannya, MoV dan MoVTeNb adalah aktif dan mempunyai keupayaan kepilihan yang tinggi apabila ia mempunyai campuran fasa berstruktur ortorombik dengan molibdenum sebahagian daripada kekisinya dan satu fasa dengan kehadiran vanadium.

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DECLARATION

I hereby declare that the thesis is based on my original work except for the 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.

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LIST OF ABBREVIATIONS

AHM	Ammonium heptamolybdate tetrahydrate
BET	Brunauer-Emmet-Teller surface area measurements
EDTA	Ethylenediaminetetra-acetic acid
FWHM	Full width at half maximum
JCPDS	Joint Committee of Powder Diffraction Standards
GC	Gas Chromatography
IUPAC	International Union of Pure and Applied Chemistry
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometer
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Introduction to Catalyst

Catalytic processes have already been applied for a long period of time but it was not until 1836 when Berzelius introduced the term ‘catalysis’ (Bond, 1987). He derived it from the Greek words kata, which stands for down, and lysein, which means to split or break. Later, in 1895, William Ostwald was the first to write down the definition of a catalyst as such: ‘A catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products’. It is important to note that a catalyst does not influence the thermodynamic equilibrium of reactants and products. Therefore, the current definition is slightly better, though close to Ostwald’s description: ‘A catalyst is a substance that increases the rate of approach to thermodynamic equilibrium of a chemical reaction without being substantially consumed (Clarendon Press).

1.2 Heterogeneous catalyst

A heterogeneous catalyst presents in a different phase from the reactant. A heterogeneous catalyst is commonly a solid and it usually functions by promoting a reaction on its surface. One or more of the reactant molecules are adsorbed onto the surface of the catalyst where an interaction with the surface increases their reactivity Heterogeneous catalysts are extensively used in many commercial processes. Industrial processes such as ammonia synthesis, petroleum refining and

petrochemical production are achieved by the use of heterogeneous catalysts. The advantages of a heterogeneous catalyst is that it has extremely high selectivity which yields a single product, so extra steps and costs are not needed to separate the products from the catalyst.

According to the Maxwell-Boltzmann distribution, only those particles represented by the area to the right of the activation energy in Figure 1.1 (a) will react when they collide (Brady *et al.*, 2000). To increase the rate of a reaction, the number of successful collisions must be increased. One possible way of doing this is to provide an alternative way for the reaction to happen which has lower activation energy as in Figure 1.1 (b). This can be done by a suitable catalyst.

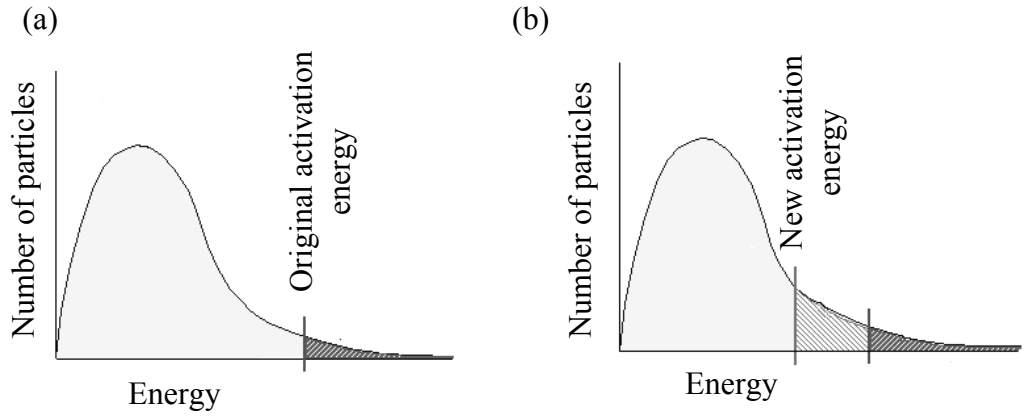

Figure 1.1: Maxwell-Boltzmann distribution (Brady *et al.*, 2000)

A catalyst provides an alternative route for the reaction. That alternative route has lower activation energy. This is shown on the following energy profile in Figure 1.2.

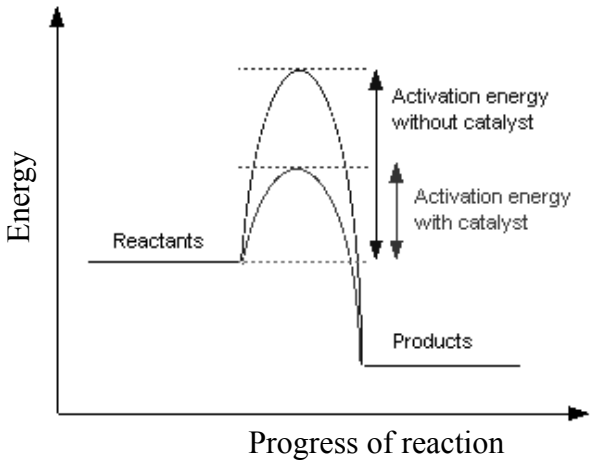

Figure 1.2: Comparison of activation energy (Brady *et al.*, 2000)

1.3 Molybdenum Vanadium Oxide Based Material

When mixing molybdenum and vanadium together, mixed phases or a single phase may form. Molybdenum vanadium binary oxide occurs in many types of crystal structures. Some of these common structures are the orthorhombic structure with the chemical formula $Mo_4V_6O_{25}$, the monoclinic structure with the chemical formulas $Mo_{056}V_{1.44}O_5$, MoV_2O_8 and $V_{3.6}Mo_{2.4}O_{16}$, the anorthic structure with the chemical formula $V_{0.95}Mo_{0.97}O_5$, the hexagonal structure with the chemical formula $(V_{0.12}Mo_{0.88})O_{2.94}$ and the tetragonal structure with the chemical formula $VOMoO_4$, These various structures has various usage and applications (Tichy, 1997).

1.4 Uses of Molybdenum Vanadium Oxide

Recently, an attempt has been made to produce thin films from MoV oxide. Molar ratio of Mo:V > 1 is suitable for this application. A study of optical properties of the films revealed that the oxides were optically homogeneous. These homogeneous thin

films are useful because of the possibility of integration into micro-electronic circuitry and its application in electrochromic devices. MoV oxide shows many advantages as a thin film optical coating because the optical absorption band is close to the sensitivity of the human eye (Al-Kuhaili *et al.,* 2004 and Gesheva *et al.,* 2006).

Besides the production of thin films, molybdenum has also been tested extensively as possible alternatives to replace toxic chromate as coatings for aluminium alloys. Due to strong oxidising power and stability of their reduction products, molybdenum seems to be a promising alternative to chromating. Moreover, such molybdenum based coating showed corrosion resistance (Hamdy, 2006).

Hanlon *et al*., 2003 reported the usage of MoV oxides as coatings on glass. A water soluble molybdenum compound added to the aqueous sol of V_2O_5 was used to produce such coatings. Materials where molybdenum is present showed higher conductivity than V_2O_5 thin films as the film changes from semiconductor to metal behaviour. Practical applications of these MoV oxides as coatings on glass include energy-efficient windows and optical switching.

Recently, the interest in amperometric glucose biosensor based on a surface treated inorganic metal oxide as an immobilisation matrix has arisen among researchers. Vanadium pentoxide has long been used for designing a glucose biosensor. Titanium dioxide and zinc oxide films have also been applied for such purposes. However, application of the above-mentioned ceramic was often limited by their brittleness. Efforts have been made to seek new materials, which could overcome the cracking.

Binary metal oxide such as MoV oxides has been proposed to be tested to replace these ceramics. Such research is only at preliminary levels (Azah *et al.*, 2006 and Azizul *et al.*, 2006).

MoV oxides based materials can also be used as catalysts for oxidation of alkanes and alkenes. MoVNb mixed oxide catalyst is used to catalyse ethane to ethene (Osawa *et al.*, 2000). Matar, 1989 reported the usage of MoVSb as a catalyst for the oxidation of propene to acrolein. Recent researches show that binary MoV oxide, ternary MoVTe oxide and quaternary MoVTeNb oxide are all high potential catalysts for the oxidation of propane to acrylic acid (Ueda *et al.*, 2004).

In this study, the usage of the MoV oxide based materials, as catalysts for propane oxidation are particularly the main interest. Studies of these materials synthesised via several methods have been carried out by many researchers.

1.5 Selective Oxidation Reaction

The selective oxidation of light alkanes to produce the mono- or dialkene compounds has been performed for close to one hundred years and has commonly been achieved either by dehydrogenation or by oxidative dehydrogenation. Common oxide catalysed selective oxidation reactions are shown in Table 1.1 (Matar *et al.*, 1989).

In standard dehydrogenation processes, the hydrocarbon feedstock is heated, in the absence of air, and introduced to the catalysts to produce the alkene and hydrogen

gas. In oxidative dehydrogenation, the alkanes are introduced to the catalyst in the presence of air, or a limited supply of oxygen, where it reacts to form alkene and water (Kung, 1986). Oxidation of hydrocarbon molecules proceeds as a multi-step process, consisting of consecutive abstractions of hydrogen atoms and addition of oxygen atoms (Horrath, 2002).

Table 1.1: Common oxide catalysed selective oxidation reactions (Matar *et al.*, 1989)

Reactions	Catalyst (s)
Ethylbenzene → Styrene	Fe-Cr-K-O
Isopentane, Isopentene → Isoprene	Sn-Sb-O
Butane, Butene → Butadiene	Promoted V-O
Methanol → Formaldehyde	Fe-Mo-O, MoO_3
Butane, Butene → Maleic Anhydride	V-P-O
Propene → Acrolein	Bi-Mo-O
Propene and NH_3 → Acetonitrile	Bi-Mo-O, U-Sb-O, Fe-Sb-O, Bi-
Propene → Acrolein , Acrylic acid, Acetaldehyde	Co-Mo-Te-O, Sb-V-Mo-O
Benzene → Malic Anhydride	V-P-O, V-Sb-P-O
O-sylene, Naphthalene → Phthalic Anhydride	Promoted V-O
Methane → Methanol, Formaldehyde	Mo-O, V-O
Ethylene → Ethylene Oxide	Fe-Mo-O, promoted Ag

1.6 Molybdenum Vanadium Oxide for the Oxidation of Propane

The potential use of alkanes as a source of the corresponding alkenes or their derivatives is increasing year by year. Alkanes are generally less reactive than alkenes because the molecules have only saturated C-H bonds. Although alkanes are poorly reactive resources because there are no lone pairs of electrons, no empty orbital and little polarity of the C-H bonds, interest in alkanes to replace alkenes as a source increases as it is highly abundant. In order to utilise the less reactive molecules, selective oxidation of alkanes has been widely investigated and many types of catalysts have been developed for this process (Oshihara *et al*., 2001).

However, still, a great deal of research has to be done in order to achieve selective functionalisation of light alkanes, particularly by catalytic selective oxidation. The catalytic selective oxidation of light alkanes is still very difficult because the reactions are usually accompanied by many undesirable side-reactions as a result of low reactivity of the reactant (Ueda *et al.,* 2002).

Recently, a one-step oxidation of propane to acrylic acid was found possible. The oxidation of propane to acrylic acid using molecular oxygen as an oxidant has attracted much attention in industries for fundamental, academic and economical reasons.

Acrylic acid (Figure 1.3), CH_2=CHCOOH is a colourless liquid or solid that is used in the manufacturing of plastics, bondings and hydrogels used for contact lenses.

Synonyms for acrylic acid are acroleic acid, ethylenecarboxylic acid, propene acid, propenoic acid, 2-propenoic acid and vinylformic acid (Mamedov and Cortes, 1995).

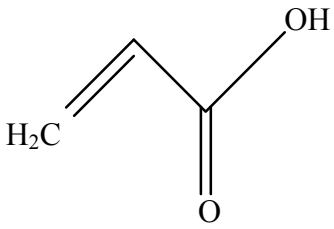

Figure 1.3: Structure of acrylic acid (Mamedov and Cortes, 1995)

As mentioned earlier, alkanes are more abundant compared to alkenes. Therefore, the high abundance of propane in natural gas lowers its price compared to propene. In the past, production of acrylic acid involves a two step process, which is the oxidation of propene to acrolein followed by the oxidation of acrolein to acrylic acid. The steps can be presented as below.

Step 1:

$$H_2C{=}CH\text{-}CH_3 + O_2 \xrightarrow{\text{Catalyst}} H_2C{=}CH\text{-}CHO + H_2O$$

$$\Delta H = -81.4 \text{ kcal mol}^{-1}$$

Equation 1.1

Step 2:

$$H_2C{=}CH\text{-}CHO + 0.5\ O_2 \xrightarrow{\text{Catalyst}} H_2C{=}CH\text{-}COOH$$

$$\Delta H = -60.7 \text{ kcal mol}^{-1}$$

Equation 1.2

For the oxidation of propane to acrylic acid in a single step, the process is still under heavy investigation. The one-step oxidation of propane in gas phase with molecular oxygen to acrylic acid follows equation below:

$$C_3H_8 + 2O_2 \xrightarrow{\text{Catalyst}} CH_2{=}CH\text{-}COOH\ (g) + 2H_2O$$

$$\Delta H = -\ 171\ \text{kcal mol}^{-1}$$

Equation 1.3

Recently, Mitsubishi Chemicals claimed their patents that MoVTeNb oxide system showed extremely high activity for the ammoxidation of propane and high selectivity to acrylic acid. The monophasic MoVM (where M=Al, Cr, Fe, Ga, Bi, Te and Sb) mixed oxides has been synthesised by hydrothermal method using the Anderson-type heteropolymolybdates as the precursor for building an organised structure. Structural arrangement of active sites is considered to be quite important to achieve selective oxidation. Selective oxidation pathway from alkanes to the desired oxygenates may consist of many reaction steps, for example, dehydrogenation, oxygen insertion, hydration and so on. These reactions should occur quickly and sequentially to avoid undesired oxidation to CO_x because intermediate products are generally more reactive than saturated hydrocarbon (Ueda *et al.*, 2004).

Therefore, when left uncontrolled at temperatures sufficient to activate propane, all its partial oxidation products can easily be further oxidised to carbon oxides while releasing large quantities of heat. As a result, without proper catalysts, propane is either unreacted, or totally oxidised to CO_x while generating large quantity of heat (Ai, 1986).

The oxidation of propane can take place via many different pathways, as illustrated in Figure. 1.4.