UNIVERSITI PUTRA MALAYSIA

MODIFICATION OF MICRO- AND NANO-STRUCTURES OF VANADIUM OXIDE-BASED CATALYST FOR PARTIAL OXIDATION OF *n*-BUTANE

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By

WONG YEE CHING

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

August 2009

Especially Dedicated To

My Dearest Mum & Dad	**Wong Lee Min Lim Ho**
My Dear Brother	**Wong Yee Seng**
My Dear Sister	**Wong Yee Chiek**

Without their love and continued support,
this thesis would not have been possible.

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

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Chairman: Professor Taufiq Yap Yun Hin, PhD, CChem, FRSC (UK)

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Sonochemical treatment on V_2O_5 and sonochemical synthesis were employed to produce $VOPO_4 \cdot 2H_2O$ both using ultrasound irradiation. Intercalation-exfoliation-reduction using different mixture of solvent as reducing agent to produce $VOHPO_4 \cdot 0.5H_2O$ and mechanochemical treatment were employed on both $VOPO_4 \cdot 2H_2O$ and $VOHPO_4 \cdot 0.5H_2O$. Besides, the effects of Bi dopant addition also have been studied. The catalysts were synthesised by calcining the precursor, $VOHPO_4 \cdot 0.5H_2O$ in a flow of *n*-butane in air (0.75% *n*-butane in air) for 18 h at 733 K. The physico-chemical properties of the catalysts were characterised by using X-ray diffraction (XRD), BET surface area measurement, redox titration, inductively coupled plasma-atomic emission spectroscope (ICP-AES), scanning electron microscope (SEM), transmission electron microscope (TEM) and temperature programmed reduction in H_2 flow (H_2-TPR). The catalytic properties of the selected catalysts were carried out by using temperature programmed reaction (TPRn) and on-line microreactor system. The experimental results indicated that V_2O_5 that undergoes ultrasound irradiation for 30 minutes showed an extremely high *n*-butane conversion (94%) due to its morphology which different from its bulk structures and with the present of kinetically reactive oxygen species. Moreover, nanostructured VPO catalyst produced using sonochemical treated V_2O_5 for 30 min as starting material also shows drastic increment in *n*-butane conversion (9%) compared to the reference catalyst synthesised via organic route. $VOPO_4 \cdot 2H_2O$ produced through sonochemical synthesis technique drastically reduced the synthesis time to only 15 min compared to the conventional reflux method that consumed the synthesis time up to 24 h. The VPO catalyst produced which undergo sonochemical synthesis for 120 min (VPDS120) shows a drastic increment in *n*-butane conversion (36%) due to its diameters and thickness of platelets which are smaller thus directly increase the active site of the catalyst for oxidation of *n*-butane. Furthermore, VPDS120 catalyst contains more V^{4+} percentage which directly lead to the increment of the total amount of active and mobile oxygen attached to V^{4+} phase (O^--V^{4+} pair). VPO catalyst produced through intercalation-exfoliation-reduction technique using mixture of 2-butanol and ethanol as reducing agent while doping 1 % bismuth as promoter, IERC(2Bu-Et)RBi1 gave the highest maleic anhydride (MA) selectivity due to reactive O^{2-} species released from the additional crystalline V^{5+} phase formed (O^{2-}-V^{5+} pair) at relative lower temperature. Mechanochemical treated VPO catalyst, VPDM30 shows both reduction peaks occurred at lower temperature compared to the reference catalyst with a suitable oxygen species ratio from V^{5+}/V^{4+} of around 0.25. The lattice oxygen species in the V^{5+} and V^{4+} phases which are more reactive, mobile and can be removed easily shown to be the main contribution for VPDM30 to gave high *n*-butane conversion. A high amount of active oxygen released from V^{4+} phase (O^--V^{4+} pair) was shown to be the main contribution for mechanochemical treated bismuth doped VPO catalyst, VPDBiMill to be the most active catalyst for *n*-butane oxidation.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

MODIFIKASI STRUKTUR MIKRO DAN NANO BAGI MANGKIN DASAR VANADIUM OKSIDA UNTUK PENGOKSIDAAN SEPARA *n*-BUTANA

Oleh

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Rawatan sonokimia pada V_2O_5 dan sintesis sonokimia untuk menghasilkan $VOPO_4 \cdot 2H_2O$ dimana kedua-duanya menggunakan pemancaran gelombang ultragema. Interkelasi-exfoliasi-penurunan menggunakan campuran pelarut berbeza sebagai agen penurunan untuk menghasilkan $VOHPO_4 \cdot 0.5H_2O$ dan rawatan mekanokimia juga diaplikasikan pada $VOPO_4 \cdot 2H_2O$ dan $VOHPO_4 \cdot 0.5H_2O$. Selain itu, kesan-kesan dari Bi sebagai dopan juga turut dikaji. Mangkin-mangkin telah disintesis dengan mengkalsinkan prekurser, $VOHPO_4 \cdot 0.5H_2O$ dalam aliran *n*-butana selebihnya udara (0.75 % *n*-butana dalam udara) selama 18 jam pada suhu 733 K. Sifat-sifat fizikal-kimia mangkin telah dicirikan dengan menggunakan pembelauan sinar-X (XRD), pengukuran luas permukaan BET, penitratan redox, plasma gandingan teraruh-spektoskop pancaran atom (ICP-AES), mikroskop elektron imbasan (SEM), mikroskop elektron pemancaran (TEM) dan penurunan suhu terprogram dalam aliran H_2 (H_2-TPR). Sifat pemangkinan untuk mangkin terpilih telah dijalankan dengan menggunakan tindak balas suhu terprogram (TPRn) dan sistem rektor mikro on-line. Keputusan-keputusan eksperimen telah menunjukkan bahawa V_2O_5 yang telah mengalami pancaran gelombang ultragema selama 30 min memberi penukaran *n*-butana yang tinggi (94%) disebabkan ia mempunyai morfologi

yang berbeza daripada struktur asalnya dan ia juga memiliki kinetik oksigen spesies yang reaktif. Tambahan pula, struktur nano mangkin VPO yang dihasilkan menggunakan V_2O_5 yang dirawat dengan sonokimia selama 30 min sebagai bahan pemulaan juga menunjukkan peningkatan yang drastik pada penukaran *n*-butana (9%) berbanding dengan mangkin rujukan yang telah disintesiskan melalui laluan organik. $VOPO_4 \cdot 2H_2O$ yang dihasilkan melalui cara sistesis sonokimia mengurangkan masa sistesis secara mendadak kepada 15 min berbanding dengan cara refluks secara konvensional yang memerlukan masa sebanyak 24 h. Mangkin VPO yang dihasilkan dengan cara sintesis sonokimia selama 120 min (VPDS120) menunjukkan peningkatan penukaran *n*-butana secara mendadak (36%) disebabkan diameter dan ketebalan kepingannya yang kecil yang secara langsungnya meningkatkan tapak aktif mangkin bagi pengoksidaan *n*-butana. Di samping itu, mangkin VPDS120 mempunyai lebihan peratus V^{4+} yang secara langsungnya mengakibatkan peningkatan jumlah kuantiti oksigen yang aktif dan bergerak yang terikat dengan fasa V^{4+} (pasangan O^{-}-V^{4+}). Mangkin VPO yang dihasilkan melalui kaedah interkelasi-exfoliasi-penurunan menggunakan campuran 2-butanol dan etanol sebagai agen penurunan disamping didop 1 % bismuth sebagai promoter, IERC(2Bu-Et)RBi1 memberi selektiviti maleik anhidrida yang tertinggi disebabkan spesies O^{2-} yang reaktif yang dibebaskan dari tambahan kristal V^{5+} yang terbentuk (pasangan O^{2-}-V^{5+}) pada suhu relatif yang lebih rendah. Mangkin VPO yang dirawat dengan mekanokimia, VPDM30 menunjukkan kedua-dua puncak penurunan wujud pada suhu yang lebih rendah berbanding mangkin rujukan dengan nisbah spesies oksigen dari V^{5+}/V^{4+} yang bersesuaian iaitu sekitar 0.25. Kikisi spesies oksigen dari fasa V^{5+} dan V^{4+} yang lebih reaktif dan mobil mampu dipindahkan dengan lebih senang menjadi sumbangan utama bagi VPDM30 untuk memperoleh penukaran *n*-butana

yang tinggi. Sejumlah oksigen aktif yang tinggi dibebaskan dari fasa V^{4+} (pasangan O^{-}-V^{4+}) menjadi sumbangan utama bagi mangkin VPO yang dirawat dengan mekanokimia dan didop dengan bismuth, VPDBiMill sebagai mangkin yang paling aktif untuk pengoksidaan *n*-butana.

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I certify that a Thesis Examination Committee has met on 25 August 2009 to conduct the final examination of Wong Yee Ching on his thesis entitled "Modification of Micro- and Nano-Structures of Vanadium Oxide-Based Catalyst for Partial Oxidation of *n*-Butane" 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 degree of Doctor of Philosophy.

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

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DECLARATION

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

WONG YEE CHING

Date: 4 September 2009

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BET	Brunauer Emmer Teller
FWHM	Full-Width at Half Maximum
GHSV	Glass Hourly Space Velocity
H_2-TPR	Temperature Programmed Reduction in Hydrogen
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standard
MA	Maleic Anhydride
MS	Mass Spectrometer
m/z	Mass to charge ratio
P/V	Phosphorus/Vanadium
rpm	Round per minute
SEM	Scanning Electron Microscope
T_{max}	Temperature at peak maximum
TEM	Transmission Electron Microscope
TCD	Thermal Conductivity Detector
TPRn	Temperature Programmed Reaction
VPO	Vanadium Phosphorus Oxide
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 General Introduction to Catalysis

Berzelius in 1836 introduced the term ‘catalysis’ (Bond, 1987), where he derived it from the Greek words *kata*, which stands for down and *lysein*, which means to split or break. Later in 1895, Ostwald was the first to write down a definition of a catalyst: “A catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products”. So, 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”. Catalysis is the phenomenon of a catalyst in action (Gates, 1992).

As befits a committee a longer, although more precise, description has been suggested by the UK Science Research Council (Hartley, 1985): A system is said to be “catalyzed” when the rate of change from state I to state II, is increased by contact with a specific material agent which is not a component of the system in either state and when the magnitude of the effect is such as to correspond to one or more of the following descriptions:

(i) Essentially, measurable change from state I to state II occurs only in the presence of the agent.

(ii) A similarly enhanced rate of change is found with the same sample of agent in repeated experiments using fresh reactants.

(iii) The quantity of matter changed is many times greater than that of the agent.

1.2 The Importance of Catalysis

Catalysts are among the most important technological materials, being used in the manufacture of chemicals, fuels, foods, clothing, pharmaceuticals, and materials such as organic polymers (Gates, 1992). The value of the goods manufactured in the United States in processes that at some stage involve catalysis is about $1 trillion annually; the catalysts used in these processes cost only a few tenths of a percent of the value of the products.

Today, almost 70% of all chemicals that are produced have been in contact with a catalyst somewhere in their synthesis process (Matthijs, 1999). This number stresses the importance of the role of catalysis in the chemical industry. Without a catalyst, processes are less clean and sometimes impossible to perform. In principal, catalysis can be used to abate environmental pollution in two ways:

(i) for cleaning of outgoing waste gases or water (end-of-pipe catalysis),

(ii) for improvement or replacement of existing processes in such a way that less harmful waste is produced (process-incorporated catalysis).

With regard to (i), two well known examples are the three-way catalyst, which is used to reduce the levels of CO, NO_x and VOC's in automotive exhaust gases, and the Claus catalyst utilised to convert sulphur (H_2S) from industrial exhaust gases.

The subject of this report is closely related to catalysis of type (ii), *i.e.* improvement of an existing process to achieve a higher product yield, and thus fewer byproducts. It is an important for the production of bulk and fine chemicals as well as minimise trace pollutants and contaminants (Hodnett, 2000).

1.3 Types of Catalysts

Generally, catalytic reactions can be divided into two major types, such as homogeneous and heterogeneous (Thomas and Thomas, 1997).

1.3.1 Homogeneous Catalyst

When the catalyst is of the same phase as the reactants and no phase boundary exists, we speak of homogeneous catalysis. This may take place either (Bond, 1987):

(i) In the gas phase, as, for example, when nitrogen oxide catalyses the oxidation of sulphur dioxide; or