UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES OF NANOSIZED VANADIUM PHOSPHORUS OXIDE, AND ITS USE AS CATALYST IN SELECTIVE OXIDATION OF n-BUTANE TO MALEIC ANHYDRIDE

NURUL SUZIANA NAWI @ MOHAMED

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UNIVERSITI PUTRA MALAYSIA

2011

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By

NURUL SUZIANA NAWI @ MOHAMED

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

JANUARY 2011

Especially Dedicated To

My Dearest Mama & Abah	Nawi @ Mohamed b. Ismail Rohani bt. Mat Abd. Ghani
My Dear Brother	Jamsuri b. Nawi @ Mohamed
My Dear Sister-in-law	Salmah bt. Ismail
My Dear Fiancee	Izrul Azmi b. Md. Nasir

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 fulfillment of the requirement for the degree of Master of Science

SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES OF NANOSIZED VANADIUM PHOSPHORUS OXIDE, AND ITS USE AS CATALYST IN SELECTIVE OXIDATION OF *n*-BUTANE TO MALEIC ANHYDRIDE

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

Faculty: Science

In this study, nanosized vanadium phosphorus oxide (VPO) catalyst was synthesized via a new organic route. The synthesized nanosized VPO catalyst was compared with conventional VPO catalyst which was prepared via conventional organic route. Besides, various metal dopants *i.e* zirconium (Zr), zinc (Zn), nickel (Ni), molybdenum (Mo), manganese (Mn), niobium (Nb), iron (Fe), copper (Cu), chromium (Cr), cerium (Ce) and cobalt (Co) also used in this study in order to investigate the role of metal dopants on the nanosized VPO catalyst. The physico-chemical properties of the synthesized catalysts were characterized by using x-ray diffraction (XRD), BET surface area measurement, redox titration, inductively coupled plasma –atomic emission spectroscopy (ICP-AES), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) and temperature programmed reduction in H_2. The catalytic properties of the synthesized catalysts were carried out by using an on-line microreactor system. Results show that the nanosized VPO catalysts successfully synthesized via new organic route in far less duration *i.e.* 13 h compared to conventional organic route *i.e.* 109 h with good

properties of the VPO catalysts. XRD pattern of the synthesized VPO catalysts showed the major peak of pyrophosphate, $(VO)_2P_2O_7$ phase. However, the major peaks for nanosized VPO catalyst especially for (020), (204) and (221) phases are shown to be more prominent than those of conventional VPO catalyst. Besides, the new organic route also produced high surface area VPO catalysts with 5 times larger than conventional VPO catalyst. Formation of thin and increasing of platelets for nanosized VPO catalyst was also observed in SEM micrographs. Furthermore, particle size of this catalyst was found in nanoscale range (40-60 nm) as was proved by TEM. High amount of O^{2-} and O^{-} species removed for nanosized VPO was obtained by H_2-TPR directly lead to a significant improvement in *n*-butane conversion at 673 K and also at lower temperatures (643 and 623 K) with higher maleic anhydride (MA) selectivity for the respective temperatures. The introduction of various metal dopants into the lattices of VPO catalyst did not alter the phase of hemihydrate precursors and the final catalysts. There are small variations can be observed on the surface area, redox titration and average vanadium oxidation state for the nanosized doped VPO catalysts compared to the nanosized undoped VPO catalyst. On the other hand, the incorporation of 1% Nb, Ni, Ce, Zr, Zn, Cr and Fe successfully reduced the particle size below than 40 nm. Moreover, the certain metal dopants can induced the amount of oxygen O^{2-} and O^{-} species removed especially for Ce, Cr and Ni doped catalysts. These fascinating features gave drastic increment for *n*-butane conversion and maleic anhydride (MA) selectivity at higher and lower temperatures (673, 643 and 623 K). The selectivity of maleic anhydride (MA) of all the synthesized nanosized VPO catalysts at lower temperatures *i.e.* 643 and 623 K are comparable with the conventional VPO catalyst at higher temperature, 673 K.

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

SINTESIS DAN CIRI FIZIKO-KIMIA VANADIUM FOSFORUS OKSIDA BERSAIZ NANO, DAN PENGGUNAANYA SEBAGAI MANGKIN DALAM PENGOKSIDAAN TERPILIH *n*-BUTANA KEPADA MALIK ANHIDRIDA

Oleh

NURUL SUZIANA NAWI @ MOHAMED

JANUARI 2011

Pengerusi: Profesor Taufiq Yap Yun Hin, PhD, CChem, FRSC (UK)

Fakulti: Sains

Dalam kajian ini, mangkin vanadium fosforus oksida (VPO) bersaiz nano disintesis melalui satu kaedah organik yang baru. Mangkin VPO bersaiz nano telah dibandingkan dengan mangkin VPO konvensional yang mana telah disediakan melalui kaedah organik yang konvensional. Selain itu, pelbagai logam penggalak *i.e* zirkonium (Zr), zink (Zn), nikel (Ni), molibdenum (Mo), mangan (Mn), niobium (Nb), ferum (Fe), kuprum (Cu), kromium (Cr), cerium (Ce) dan kobalt (Co) juga digunakan dalam kajian ini bertujuan untuk mengkaji peranan bahan penggalak terhadap magkin VPO bersaiz nano. Sifat-sifat fizikal-kimia mangkin yang disintesis telah dicirikan dengan menggunakan pembelauan sinar-X (XRD), pengukuran luas permukaan BET, penitratan redok, plasma gandingan teraruh-spektroskop 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 yang disintesis telah dijalankan dengan menggunakan sistem reaktor mikro dalam talian. Keputusan menunjukkan mangkin VPO bersaiz nano berjaya disintesis melalui kaedah organik yang baru dalam masa jauh berkurang *i.e.* 13 jam berbanding dengan kaedah organik konvensional *i.e.* 109 jam dengan

mangkin VPO menunjukkan sifat-sifat yang baik. Corak XRD bagi mangkin VPO yang disintesis menunjukkan puncak utama fasa pirofosfat, $(VO)_2P_2O_7$. Walaubagaimanapun, puncak-puncak utama mangkin VPO bersaiz nano terutama untuk fasa (020), (204) dan (221) lebih jelas kelihatan berbanding mangkin VPO konvensional. Selain itu, kaedah organik yang baru juga menghasilkan luas permukaan mangkin VPO 5 kali lebih besar berbanding mangkin VPO konvensional. Pembentukan dan penambahan platlet untuk mangkin VPO bersaiz nano juga diperhatikan dalam mikrograf SEM. Tambahan pula, saiz partikel mangkin ini berada di dalam julat berskala nano (40-60 nm) seperti yang dibuktikan melalui TEM. Jumlah pembebasan spesis O^{2-} dan O^{-} yang tinggi untuk mangkin VPO bersaiz nano diperolehi melalui H_2-TPR secara langsung membawa kepada penambahbaikan yang ketara dalam penukaran *n*-butana pada 673 K dan juga pada suhu terendah (643 dan 623 K) dengan pemilihan terhadap malik anhidrida yang tinggi untuk suhu-suhu berkaitan. Pengenalan pelbagai logam penggalak ke dalam kekisi mangkin VPO tidak mengubah fasa prekursor-prekursor hemihidrat dan mangkin-mangkin akhir. Terdapat perbezaan yang kecil dapat dilihat terhadap luas permukaan, penitratan redok dan keadaan purata vanadium untuk mangkin penggalak bersaiz nano berbanding kepada mangkin VPO tanpa bahan penggalak bersaiz nano. Sebaliknya, kemasukan 1% Nb, Ni, Ce, Zr, Zn, Cr dan Fe berjaya mengurangkan saiz partikel di bawah 40 nm. Tambahan pula, sesetengah logam penggalak boleh meningkatkan pembebasan jumlah spesis-spesis oksigen O^{2-} dan O^{-} spesis terutama kepada mangkin penggalak Ce, Cr dan Ni. Sifat-sifat menarik ini memberikan penigkatan drastik kepada penukaran *n*-butana dan pemilihan terhadap malik anhidrida (MA) pada suhu tertinggi dan terendah (673, 643 dan 623 K). Pemilihan terhadap malik anhidrida (MA) untuk semua mangkin VPO bersaiz nano yang disintesis pada suhu terendah

i.e. 643 and 623 K boleh dibandingkan dengan mangkin VPO konvensional pada suhu tertinggi, 673 K.

ACKNOWLEDGEMENTS

I would like to express my appreciation to Professor Dr. Taufiq Yap Yun Hin for all his generous guidance, dedicated supervision and precious suggestion throughout my Master degree journey. Without the help from Professor Taufiq-Yap, I will not be able to complete my Master research. It has been a wonderful experience to work under a professional researcher. This has enabled me to gather enough experience and knowledge about the research that I have been handling during master's time. My pleasure thanks also to my co-supervisor Professor Dr. Mohd Zobir Hussein for his supervision and in valuable advice throughout this study.

My sincere thanks also extended to all Science Officers in the Department of Chemistry, Faculty of Science for their assistance in the characterisation works. Not to forget officers in Electron Microscopy Unit, Institute Bioscience especially Puan Nooraini Mohd. Ain and En. Rafi for their help and advices in running SEM and TEM analysis.

I also need to appreciate Dr. Wong Yee Ching, colleagues and friends for their help, support and discussion during my stay in the PutraCat Laboratory, Centre of Excellence for Catalysis Science and Technology, Universiti Putra Malaysia.

Most especially, I wish to thank my parents, family and best friend forever, Sir Izrul Azmi Md. Nasir for their love, never ending support and encouragement throughout these years. Financial support from Universiti Putra Malaysia through Graduate Research Fellowship (GRF) is gratefully acknowledged.

I certify that an Examination Committee has met on 19th of January 2011 to conduct the final examination of Nurul Suziana Nawi @ Mohamed on her Master of Science thesis entitled "Synthesis and Physico-chemical Study of Nanosized Vanadium Phosphorus Oxide Catalysts for Selective Oxidation of *n*-Butane towards Maleic Anhydride" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the degree of Master of Science.

Members of the Examination Committee were as follows:

Tan Yen Ping, PhD
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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 Master of Science. The members of Supervisory Committee were as follows:

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Mohd. Zobir bin Hussein, PhD
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HASANAH MOHD GHAZALI, PhD
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Date:

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.

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NURUL SUZIANA NAWI @ MOHAMED

Date: 19 JANUARY 2011

TABLE OF CONTENTS