



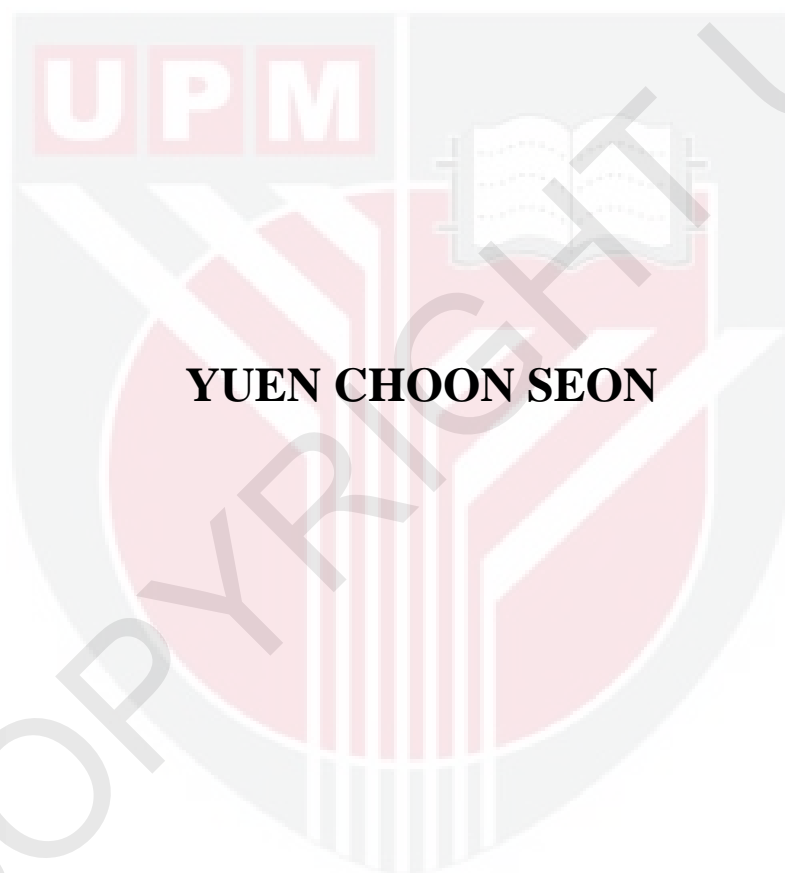
**UNIVERSITI PUTRA MALAYSIA**

**EFFECTS OF BISMUTH AND NICKEL ON PHYSICO-CHEMICAL AND  
CATALYTIC PROPERTIES OF VANADIUM PHOSPHORUS OXIDE  
CATALYST**

**YUEN CHOON SEON**

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**MASTER OF SCIENCE  
UNIVERSITI PUTRA MALAYSIA**

**2012**

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CATALYST**

**By**

**YUEN CHOON SEON**

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

**June 2012**

# ***Especially Dedicated To***

My Dearest Dad &  
Mum

Yuen Poo Haak  
Sam Guan Hah

My Beloved Wife &  
My Dearest Sons

Frennie Tang Pei Fun  
Matthew Yuen Kin Hou  
Ryan Yuen Kin Mun

My Dear Sisters

Yuen Mei Kean  
Yuen Mei Lian

My Dear Brother

Yuen Choon Wah

To my supervisor Prof. Dr. Taufiq Yap Yun Hin

For his valuable guidance, understanding and advices

To my co-supervisor Assoc. Prof. Dr. Irmawati Ramli

For her advices, encouragements and supports

To my seniors and lab mates

For their wonderful advices and supports

To my friends

For their moral supports and encouragement

With their spiritual support and encourages, make me feel new vigour and  
enthusiasms every day on the road to Master of Science.

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

**EFFECTS OF BISMUTH AND NICKEL ON THE PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF VANADIUM PHOSPHORUS OXIDE CATALYST**

By

**YUEN CHOON SEON**

**June 2012**

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

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Vanadium phosphorus oxide (VPO) catalysts in this study was synthesized by using dihydrate or VPD method which involved two steps of preparation. The first step is the preparation of dihydrate,  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  by using  $\text{V}_2\text{O}_5$  reacting with aqueous *o*- $\text{H}_3\text{PO}_4$  in distilled water. For the second step, the preparation of precursor, hemihydrate  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  is synthesized by reacting,  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  with isobutanol. For promoted VPO precursor, Bi or Ni salt were added in the mixture of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  and isobutanol. For milled unpromoted and promoted precursors, they were milled for 1 hour with ethanol as medium.

The precursors produced were calcined in a flow of *n*-butane/air mixture. The catalysts obtained were confirmed as  $(\text{VO})_2\text{P}_2\text{O}_7$  phase by X-ray Diffraction (XRD). The catalysts were characterized by Brunauer-Emmett-Teller (BET) surface area measurement, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), scanning electron microscopy (SEM) and temperature programmed reduction in  $\text{H}_2$  ( $\text{H}_2$ -TPR) techniques. The catalytic properties of the synthesized catalysts were

carried out by using an fixed bed microreactor. All catalysts gave main peaks at  $2\theta=22.9^\circ$ ,  $28.5^\circ$  and  $30.0^\circ$  which correspond to (020), (204) and (221) reflections of pyrophosphate phase respectively. The incorporation of Bi and Ni promoters (in mole ratio) into the VPO catalyst enhanced the surface area of the synthesized catalysts. SEM micrographs clearly revealed that the formation of more isolated platelets and more prominent plate-like crystallite that was arranged into the characteristic of rosette cluster. On the other hand, the reactivity of the oxygen species linked to  $V^{5+}$  and  $V^{4+}$  was investigated in the unpromoted and promoted catalysts by using  $H_2$ -TPR, which also affected the catalytic performance of the catalyst. The results showed that promoted VPO catalysts remarkably lowered the temperature of the reduction peak associated with  $V^{5+}$ . This  $V^{5+}$  led to the enhancement of the *n*-butane activation and improvement of the selectivity to the maleic anhydride. Moreover, the TPR profile also showed that promoted VPO catalysts possesses higher amount of active oxygen species associated with  $V^{4+}$ . It meant that promoted VPO catalysts possesses higher amount of  $V^{4+}-O^-$  pair, which eventually caused a higher conversion rate in the selective oxidation of *n*-butane to maleic anhydride. Besides, the mechanochemical treatment successfully reduced the crystallite size of the catalysts and consequently increased their surface area, especially promoted milled catalysts. TPR results demonstrated that both reduction peaks for each mechanochemical treatment catalyst shifted from the maxima reduction peak to lower temperature. It then improved the amount of oxygen species removed from the catalysts.

Furthermore, the milled catalysts have shown better catalytic performance than unmilled catalysts. Addition of promoters for milled catalysts were shown to enhance the activity and the selectivity of *n*-butane. CatBi1Ni1M has the highest *n*-butane

conversion (60%) and selectivity to maleic anhydride (42%), while CatUnpromotedM has only 41% conversion and 29% selectivity to maleic anhydride. Besides, promoted unmilled catalysts were also shown to increase the activity and selectivity of *n*-butane. CatBi1Ni1 gave an *n*-butane conversion of 52% and selectivity of 39%, while CatUnpromoted gave *n*-butane conversion 38% and selectivity of 28%.



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

**KESAN-KESAN BISMUT DAN NIKEL TERHADAP FIZIKAL-KIMIA DAN  
SIFAT-SIFAT PEMANGKINAN  
PADA MANGKIN VANADIUM FOSFORUS OKSIDA**

Oleh

**YUEN CHOON SEON**

**Jun 2012**

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

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Penyediaan mangkin vanadium fosforus oksida (VPO) disintesis melalui dua langkah. Langkah pertama ialah penyediaan dihidrat,  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ , dengan menggunakan  $\text{V}_2\text{O}_5$  bertindak balas dengan asid *o*-fosforik akueus di dalam air suling. Untuk prekursor VPO tanpa penggalak,  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  telah ditindak balas dengan isobutanol. Langkah kedua, penyediaan prekursor, hemihidrat  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  disintesis dengan tindak balas antara  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  dengan isobutanol. Untuk VPO dengan penggalak, garam Bi atau Ni telah ditambah ke dalam campuran  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  dan isobutanol. Untuk prekursor VPO tanpa penggalak dan dengan penggalak yang dikisar, prekursor tersebut telah dikisar selama 1 jam dengan etanol sebagai medium.

Prekursor yang dihasilkan kemudiannya dikalsikan dalam aliran campuran *n*-butana/udara. Mangkin yang dihasilkan telah disahkan merupakan fasa  $(\text{VO})_2\text{P}_2\text{O}_7$  melalui pembelauan sinar-X (XRD). Seterusnya, mangkin tersebut dicirikan dengan pengukuran luas permukaan Brunauer Emmett Teller (BET), plasma gandingan



teraruh-spektroskopi pancaran atom (ICP-AES), mikroskop elektron imbasan (SEM) dan teknik penurunan suhu terprogram dalam aliran H<sub>2</sub> (H<sub>2</sub>-TPR). Sifat pemangkinan untuk mangkin yang disintesis telah dijalankan dengan menggunakan katil tetap reaktor mikro. Semua mangkin memberi puncak utama pada  $2\theta=22.9^\circ$ ,  $28.5^\circ$  dan  $30.0^\circ$  di mana masing-masing berpadanan dengan pantulan (020), (204) dan (221) pada fasa pirofosfat. Penambahan penggalak Bi dan Ni (dalam nisbah mol) ke dalam mangkin VPO telah menambah luas permukaan mangkin yang disintesis. Mikrograf SEM jelas menunjukkan pembentukan kepingan yang terencil dan lebih kristal yang menyerupai kepingan di mana ianya diatur dalam ciri-ciri gugusan mawar. Selain itu, kereaktifan spesies oksigen yang berkaitan dengan V<sup>5+</sup> and V<sup>4+</sup> untuk mangkin tanpa penggalak dan dengan penggalak telah dikaji dengan penggunaan H<sub>2</sub>-TPR, di mana ia juga mempengaruhi prestasi mangkin. Keputusan menunjukkan mangkin VPO dengan penggalak telah merendahkan suhu puncak penurunan yang berkaitan dengan V<sup>5+</sup>. V<sup>5+</sup> ini menyebabkan peningkatan pengaktifan *n*-butana dan peningkatan keterpilihan malik anhidrida.

Dalam pada itu, profil TPR juga menunjukkan mangkin VPO dengan penggalak mempunyai spesies oksigen kekisi aktif tertinggi dengan fasa V<sup>4+</sup>. Ini bermakna mangkin yang sangat aktif ini mempunyai jumlah pasangan V<sup>4+</sup>-O<sup>-</sup> yang tertinggi, di mana akhirnya menyebabkan kadar penukaran terpilih yang lebih tinggi dalam pengoksidaan *n*-butana ke malik anhidrida. Selain itu, mangkin VPO yang dirawat dengan kimia-mekanikal telah berjaya menunjukkan penurunan saiz kristal dan seterusnya meningkatkan luas permukaannya, terutamanya mangkin kisar yang berpenggalak. Keputusan TPR menunjukkan kedua-dua puncak penurunana bagi setiap mangkin yang dirawat dengan kimia-mekanikal berpindah dari puncak

penurunan maksimum ke arah suhu yang lebih rendah. Kemudian, jumlah spesies oksigen yang disingkirkan dari mangkin turut meningkat.

Di samping itu, mangkin kisar telah menunjukkan prestasi mangkin yang lebih baik berbanding dengan mangkin tanpa kisar. Penambahan penggalak untuk mangkin kisar telah meningkatkan pengaktifan dan keterpilihan *n*-butana. CatBi1Ni1M mempunyai penukaran *n*-butana (60%) dan keterpilihan malik anhidrida (42%) yang tertinggi, manakala CatUnpromotedM hanya mempunyai 41% penukaran dan 29% keterpilihan malik anhidrida. Selain itu, mangkin kisar tanpa penggalak juga menunjukkan peningkatan aktiviti dan keterpilihan untuk *n*-butana. CatBi1Ni1 memberi 52% penukaran *n*-butana dan 39% keterpilihan, manakala CatUnpromoted memberi 38% penukaran dan 28% keterpilihan.

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To my beloved parents and family, I would like to express my deepest affection for their consistent support, endless love, encouragement and understanding towards the completion of this study.

I certify that a Thesis Examination Committee has met on 27 June 2012 to conduct the final examination of Yuen Choon Seon on his thesis entitled “Effects of Bismuth and Nickel on the Physico-Chemical and Catalytic Properties of Vanadium Phosphorus Oxide Catalyst” 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 Master of Science.

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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 type of degree. The members of the Supervisory Committee were as follows:

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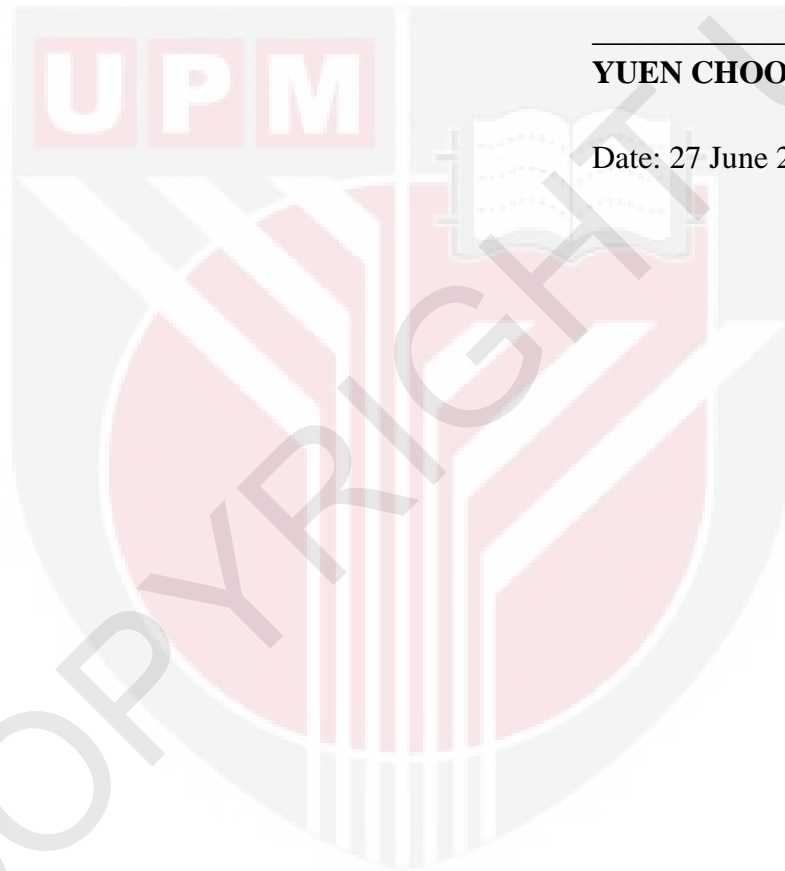
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## DECLARATION

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.



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**YUEN CHOON SEON**

Date: 27 June 2012

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