## SYNTHESIS AND CHARACTERISATION OF VANADIUM PHOSPHOROUS OXIDE CATALYSTS

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FSAS 200419

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## DOCTOR OF PHILOSOPHY UNIVERSITI PUTRA MALAYSIA

## By

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

Specially dedicated to

## Husband, McCool, Anderson, Chawla, Clark, Ramon and Brown

the seven brave souls who perished on board the Columbia.

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

# SYNTHESIS AND CHARACTERISATION OF VANADIUM PHOSPHOROUS OXIDE CATALYSTS 

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February 2004

## Chairman: Taufiq Yap Yun Hin, Ph.D. <br> Faculty: Science and Environmental Studies

The V/P/O catalysts were prepared by using (a) organic method (VPO); (b) via dihydrate phase (VPD) and (c) aqueous method (VPA). The effect of calcination time, preparation method and addition of metal cations as dopants to the physico-chemical properties were studied using nitrogen physisorption measurements, scanning electron microscopy (SEM), X-ray diffraction, inductively coupled plasma (ICP) spectroscopy, redox titration, temperature programmed desorption (TPD) and temperature programmed reduction (TPR).

Surface areas of these mesoporous vanadium phosphorous oxides were apparently influenced by the length of calcination time, preparation method and incorporation of metal cations. The changes of surface areas were related to the changes of surface and bulk morphologies as evidenced by SEM.

X-ray diffraction revealed that while all of the V/P/O were consisted of predominantly $\mathrm{V}^{4+}$ phase of $(\mathrm{VO})_{2} \mathrm{P}_{2} \mathrm{O}_{7}$, minority $\mathrm{V}^{5+}$ phase which resumed many crystalline forms made up the remaining portion. Addition of metal cations to the basic matrix resulted
in slight loss of crystallinity for V/P/O by VPO method but a huge effect to V/P/O by VPD method which also accompanied by a marked increase in lattice strains.

Average oxidation state of vanadium (determined by redox titration) can be altered by (i) increase time of calcinations, (ii) predisposed by the preparation method and (iii) incorporation of metal cations.

The persistently lowering of the amount of oxygen atoms that were available thermally until stabilisation at around half a monolayer suggests that the catalytic activity, and hence the conversion of hydrocarbon is stabilised after 100 h . From the extra peak that appeared at higher temperature during TPR by $\mathrm{H}_{2}$ for V/P/O calcined for longer duration, it was postulated that the selective nature of equilibrated $\mathrm{V} / \mathrm{P} / \mathrm{O}$ is originated from these oxygen atoms.

Based on the above argument, it was suggested that the VPD type of preparation would result in V/P/O with more active and selective nature than VPO and VPA. The addition of metal cations to bulk VPO was shown to increase the activity in the order of $\mathrm{Zn}>\mathrm{VPO}$ (bulk) $>\mathrm{Cr}>\mathrm{Co}$ and selectivity in the order of $\mathrm{Co}>\mathrm{Cr}>\mathrm{Zn}>\mathrm{VPO}$ (bulk). While for VPD the activity and selectivity will be in the order of $\mathrm{Co}>$ VPD (bulk) $>\mathrm{Cr}>\mathrm{Zn}$ and $\mathrm{Zn}>\mathrm{Cr}>\mathrm{VPD}$ (bulk) $\approx$ Co, respectively.

# Abstrak thesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Doktor Falsafah <br> SINTESIS DAN PENCIRIAN MANGKIN VANADIUM FOSFORUS OKSIDA 

Oleh

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Februari 2004

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Mangkin V/P/O telah disintesis dengan menggunakan (a) kaedah organik (VPO); (b) melalui fasa dihidrat (VPD) dan (c) kaedah akuas (VPA). Kesan daripada tempoh pengkalsinan, keadah sintesis dan penambahan kation-kation logam sebagai penggalak kepada ciri-ciri fiziko-kimia telah dikaji dengan menggunakan kaedah fizijerapan nitrogen, mikroskop imbasan elektron (SEM), pembelauan sinar-X, spektroskopi plasma pasangan induktif (ICP), penitratan redoks, penyahjerapan suhu berprogram (TPD) dan penurunan suhu berprogram (TPR).

Luas permukaan oksida-oksida vanadium fosforus yang berciri liang meso ini dipengaruhi oleh tempoh pengkalsinan, cara sintesis dan juga penambahan kationkation logam. Perubahan luas permukaan ini boleh dikaitkan dengan perubahan morfologi permukaan dan pukal seperti yang dikesan oleh SEM.

Pembelauan sinar-X menunjukkan bahawa semua V/P/O terdiri daripada fasa $\mathrm{V}^{4+}$ dalam bentuk $(\mathrm{VO})_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ sebagai fasa majority dan fasa minoriti $\mathrm{V}^{5+}$ yang menpunyai pelbagai bentuk kristal. Sel unit untuk prekursor dan mangkin telah ditentukan sebagai ortorombik dengan pemalar-pemalar kekisi yang menyerupai bahan piawai.

Penambahan kation-kation logam kepada matriks asas menyebabkan sedikit pengurangan dalam kekristalan untuk V/P/O yang disintesis melalui kaedah VPO. Kesan yang nyata kepada sifat kekristalan dan panambahan regangan kekisi V/P/O dengan kaedah VPD telah diperhatikan.

Keadaan pengoksidaan purata untuk vanadium (dengan penitratan redoks) boleh diubah dengan (i) menambahkan tempoh pengkalsinan, (ii) kaedah sintesis dan (iii) penambahan kation-kation logam.

Atom-atom oksigen yang diperolehi secara terma sentiasa berkurangan sehingga tahap stabil pada lebih kurang setengah mono-lapisan mencadangakan bahawa aktiviti mangkin dan seterusnya penukaran hidrokarbon akan stabil selepas 100 j . Daripada puncak tambahan yang muncul pada suhu yang lebih tinggi semasa TPR dengan hydrogen untuk V/P/O yang dikalsinkan dalam masa yang lebih panjang, cadangan bahawa sifat pemilihan V/P/O dalam keadaan keseimbangan berasal daripada atomatom oksigen ini telah dibuat.

Berasaskan kepada perbincangan di atas, kaedah VPD akan menghasilkan V/P/O yang bersifat lebih aktif dan pemilih daripada kaedah VPO dan VPA. Penambahan kation-kation logam kepada pukal VPO akan meningkatkan aktiviti dalam susunan Zn $>$ VPO $($ pukal $)>\mathrm{Cr}>\mathrm{Co}$ dan pemilihan dalam susunan $\mathrm{Co}>\mathrm{Cr}>\mathrm{Zn}>\mathrm{VPO}$ (pukal). Semetara untuk VPD pula, aktiviti dan pemilihan akan berada dalam susunan $\mathrm{Co}>$ VPD (pukal) $>\mathrm{Cr}>\mathrm{Zn}$ dan $\mathrm{Zn}>\mathrm{Cr}>\mathrm{VPD}$ (pukal) $\approx$ Co masing-masing.

## ACKNOWLEDGEMENTS

First of all, I would like to thank my loving parents for their unconditional love, care and support throughout the years. I also owe my thanks to my sisters and brother who always stand by me.

I would like to acknowledge gratefully my principle supervisor Associate Professor Dr. Taufiq Yap Yun Hin for his excellent guidance, invaluable suggestions and help rendered throughout this research work. I would also like to thank my co-supervisors Professor Dr. Mohd. Zobir bin Hussein and Associate Professor Dr. Zulkarnain bin Zainal for their patience, help and advice all along.

My high appreciation to the cooperation from all the administrative staff and all the technicians in the laboratories in the Department of Chemistry and the Faculty of Science and Environmental Studies who are always there to help. The School of Graduate Studies which has provided assistance for the postgraduate program is also acknowledged.

The financial support by the Ministry of Science, Technology and Environment, Malaysia under IRPA grant is acknowledged. Scholarship in the form of PASCA Postgraduate Fellowship Scheme is also gratefully acknowledged.

My gratitude is also extended to Dr. Luca Lucarelli of Thermo Finnigan, Milan, Italy for his assistance in running the temperature-programmed desorption (TPD) of oxygen and reduction (TPR) by hydrogen analysis. I would also like to thank Mr

Guee Eng Hwa and Madam Rafizah binti Budin of O'Connor's Engineering Sdn. Bhd. for facilitating the correspondence with Dr. Lucarelli. My acknowledgement is also due to Mr. Zaimi bin Naim and Ms. Shamsina binti Sabdin of Petronas Research \& Scientific Services Sdn. Bhd. for completing part of the TPD and TPR analysis.

Last but not least, I would like to thank all my friends, particularly Vee Min, Kia Chet and Pooi Wooi, and colleagues of Catalysis Laboratory (Lab 1) and Material Science Laboratory (Lab 2) for their help, advice and moral support.

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