UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF NEW METHODS FOR SYNTHESIZING REACTIVE NANOSTRUCTURED VANADIUM PHOSPHATE CATALYSTS FOR PARTIAL OXIDATION OF *N*-BUTANE TO MALEIC ANHYDRIDE

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ALI ASGHAR ROWNAGHI

DOCTOR OF PHILOSOPHY
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2007

Especially Dedicated To

My Mother, Who is the rarity of my life

The great soul of my father,
Which my knowledge is indebted to him

My beloved wife

My lovely sisters

and

My Dear brothers

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

DEVELOPMENT OF NEW METHODS FOR SYNTHESIZING REACTIVE NANOSTRUCTURED VANADIUM PHOSPHATE CATALYSTS FOR PARTIAL OXIDATION OF *N*-BUTANE TO MALEIC ANHYDRIDE

By

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Faculty : Science

Vanadium phosphate catalysts are well known as the active phase and are commercially used for the selective oxidation of *n*-butane to maleic anhydride. They represent the sole example of a commercialized material for the catalytic oxidation of an alkane. In this study, vanadium phosphate catalysts were synthesised via three methods including two new methods *i.e.* new organic and solvothermal method and via dihydrate method. These catalysts were modified by microwave irradiation, addition of dopants and reducing agent.

The effect of reducing agents (*i.e.* isobutyl alcohol, 1-butanol and ethylene glycol), distilled water, microwave irradiation and conventional heating were investigated. Both heating methods gave similar XRD patterns, however microwave irradiated sample showed higher crystallinity which indicated by the high intensity of the peaks. The microwave treated catalysts exhibit a more homogeneous distribution of the rosetteshape surface species and thin structure which consequently enhanced the specific surface area. However, microwave irradiation and the used of water treatment to enhance the crystalline phase, morphology and also increased the total amount of the oxygen species removed. The introduction of Nb, La and Ce as dopants to $(VO)_2P_2O_7$ catalysts prepared via reduction of $VOPO_4 \cdot 2H_2O$ gives significantly increased the surface area and subsequently improved the conversion efficiency of the catalyst.

A new organic route for preparation of high surface area (>50 m^2g^{-1}) of vanadium phosphate catalyst was developed, by reducing the time from 26 to only 8 h. This together with incorporation of dopants such as Nb, La, and Ce can increase the surface area by reducing the particle size to nanoparticle. The high surface area contributed to higher mobility and better activity of the lattice oxygen and enhanced the conversion and selectivity for achieve a significant yield of maleic anhydride. The new organic route also increased the amount of V^{5+} phase in the catalyst. An appropriate amount of V^{5+} phase presence significantly enhanced the activity of VPO catalysts.

A novel solvothermal method was also developed by using a number of primary alcohols (C_3-C_{10}) at various temperatures (<423 K, 72 h) via a mild solvothermal synthesis to prepare phase-pure crystalline $(VO)_2P_2O_7$ with specific surface area up to three fold higher than that can be achieved by hydrothermal method. Furthermore, $(VO)_2P_2O_7$ solid solution can be crystallized in alcohols at temperature lower than that required by hydrothermal conversion. The intensity of (020) phase of nanocrystalline VPO catalyst prepared by the solvothermal were remarkably higher than the hydrothermal method. Another advantage of this new method for the synthesis of the

solid solution of vanadium phosphate catalyst is the low consumption of organic media in a close autoclave system. This eliminates the usage of water and yielded higher *n*-butane conversion catalyst as compared to conventional organic VPO method.

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

PEMBANGUNAN KAEDAH BARU DALAM SINTESIS MANAKIN VANADIUM FOSFAT REAKTIF BERSTRUKTUR NANO UNTUK PENGOKSIDAAN SEPARA *N*-BUTANA KE MALEIK ANHIDRIDA

Oleh

ALI ASGHAR ROWNAGHI

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Mangkin vanadium fosfat terkenal sebagai fasa aktif dan digunakan secara komersil dalam pengoksidaan terpilih *n*-butana ke maleik anhidrida. Manglain ini merupakan satu-satunya bahan yang telah dikomersilkan sebagai mangkin dalam pengoksidaan alkana. Dalam kajian ini, mangkin vanadium fosfat telah disintesis melalui tiga kaedah termasuk dua kaedah baru iaitu kaedah organik dan solvoterma dan melalui kaedah dihidrat. Mangkin ini juga telah diubahsuai melalui pelbagai pra-rawatan iaitu,(i) pemancaran gelambang mikro (ii) penambahan dopan dan (iii) agen penurunan.

Kesan agen penurunan (iaitu isobutil alkohol, 1-butanol dan etilena glikol), air suling, pemancaran gelombang mikro dan kaedah pemanasan konvensional telah dikaji. Kedua-dua bahan memberikan corak perghabluran yang sama, bagaimanapun sampel yang telah disinarkan dengan gelombang mikro menunjukkan struktur keamatan kehabluran yang tinggi yang ditunjukkan melalui keamatan puncak yang tinggi. Mangkin yang dihasilkan melalui kaedah gelombang mikro menunjukkan taburan permukaan bercorak ros yang

lebih homogen, berstruktur nipis dan seterusnya meningkatkan luas permukaan spesifik. Walaubagaimanapun, mangkin yang disinarkan oleh gelombang mikro dengan menggunakan air sebagai pelarut telah meningkatkan fasa kehabluran, morfologi dan juga meningkatkan jumlah keseluruhan spesies oksigen yang dibebaskan. Penambahan Nb, La dan Ce sebagai dopan ke atas mangkin $(VO)_2P_2O_7$ yang dihasilkan melalui penurunan $VOPO_4{\cdot}2H_2O$ telah meningkatkan luas permukaan yang ketara dan seterusnya meningkatkan penukaran mangkin.

Mangkin vanadium fosfat yang mempunyai luas permukaan yaug tinggi (> 50 m^2g^{-1}) telah dibangunkan dengan menggunakan medium organik memerlukan masa penyediaan yang singkat (8 jam) berbanding kaedah organik konvensional (26 jam). Pengurangan masa tindakbalas kepada 8 jam dan penggunaan dopan seperti Nb, La dan Ce dapat meningkatkan luas permukaan melalui pengurangan saiz partikel mangkin kepada berskala nano. Luas permukaan yang tinggi menyumbang ke arah mobiliti dan aktiviti oksigen kekisi yang meningkatkan penukaran dan keterpilihan untuk pengoksidaan *n*-butana. Kaedah organik baru ini juga meningkatkan bilangan fasa V^{5+} mangkin. Dengan nisbah V^{5+}/V^{4+} yang bersesuaian sebenarnya dapat meninakatkan aktiviti mangkin ini dengan ketara.

Kaedah baru solvoterma juga telah dibangunkan dengan menggunakan beberapa jenis alkohol primer (C_3-C_{10}) dalam pelbagai suhu melalui sintesis solvoterma lembut (< 423 K, 72 jam) telah digunakan untuk menyediakan fasa hablur $(VO)_2P_2O_7$ yang tulen dengan peningkatan luas permukaan spesifik dua kali ganda berbanding penukaran yang diperlukan dalam hidroterma. Keamatan fasa (020) mangkin hablur nano VPO yang disediakan melalui solvoterma menunjukkan peningkatan berbanding kaedah hidroterma. Kebaikan kaedah baru ini dapat diguakan untak mensintesis larutan pepejal mangkin vanadium fosfat disamping penggunaan media organik yang kurang di dalam sistem tertutup”autoclove”. Kaedah ini juga dapat mengurangkan sisa air dan meningkatkan penukaran berbanding dengan mangkin yang disediakan melalui kaedah organik VPO konvensional.

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I certify that an Examination Committee has met on 12th November 2007 to conduct the final examination of Ali Asghar Rownaghi on his Doctor of Philosophy thesis entitled "Development of New Methods for Synthesizing Reactive Nanostructured Vanadium Phosphate Catalysts for Partial Oxidation of *N*-Butane to 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 Doctor of Philosophy.

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Date: 22 January 2008

DECLARATION

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

ALI ASGHAR ROWNAGHI

Date: 27 November 2007

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