UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF VANADIUM PHOSPHATE CATALYST USING MICROWAVE TECHNIQUE TO OXIDIZE n-BUTANE INTO MALEIC ANHYDRIDE

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By

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DEVELOPMENT OF VANADIUM PHOSPHATE CATALYST USING MICROWAVE TECHNIQUE TO OXIDIZE *n*-BUTANE INTO MALEIC ANHYDRIDE

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Chairman: Professor Taufiq Yap Yun Hin, PhD

Faculty: Science

New VPO catalysts were prepared via microwave method. Comparison of these catalysts with those from conventional reflux method on the microstructure, morphology, oxygen nature and catalytic performance for *n*-butane oxidation to maleic anhydride are described and discussed. The catalyst's precursor, $VOHPO\cdot0.5H_20$ prepared by reduction of $VOPO_4\cdot2H_2O$ by isobutyl alcohol under microwave irradiation exhibited similar pattern with conventional catalysts and more crystalline, which was indicated by high intensity of the peaks in XRD. It is interesting that the use of the microwave had significantly shorten the duration (<1 h) in the preparation of the precursor compared to 22 h normally used in the conventional method. Temperature-programmed reduction (TPR) in H_2 resulted two reduction peaks which were observed in the range of 600-1100 K. The present work demonstrated that the influence of microwave irradiation on vanadium phosphate catalysts effectively enhanced the catalytic activity and selectivity for the oxidation of *n*-butane to maleic anhydride which contributed by the higher BET surface area and the higher amount of active and selective oxygen species removed from V^{4+} and V^{5+} phases, respectively. Mechanochemical treatment applied on vanadium phosphate (VPO) catalyst's precursor, $VOHPO_4 \cdot 0.5H_2O$ prepared by the reduction of $VOPO_4 \cdot 2H_2O$ with isobutanol under microwave irradiation, was subjected to a high energy ball mill for 60 min in ethanol as solvent. The treatment increased the average oxidation number of catalysts without changing the phase composition. The particle sizes of catalysts decreased after the ball milling process. The morphologies of milled catalysts are dependent on milling time. The surface area of milled catalysts decreased due to the time applied of ball milling on precursor was longer. High mobility of the lattice oxygen species has been achieved for milled catalysts with higher amount of oxygen atoms removed. A good correlation was shown between the oxygen (O^-) species associated with V^{4+} and *n*-butane conversion. A good correlation between *n*-butane conversion and V^{4+} phase can be observed. The reactive pairing of V^{4+}-O^- was suggested to be the center for *n*-butane activation. However, a large amount of oxygen species removed from V^{5+} would give a deleterious effect on the conversion rate. The present study showed that the mechanochemical method has effectively enhanced the microwave synthesized catalysts on the catalytic activity by increasing *n*-butane conversion and maintaining the MA selectivity. Nd-doped (1, 3, and 5 %) vanadium phosphate (VPO) catalysts were prepared by including an introduction of microwave irradiation in the synthesis of $VOPO_4 \cdot 2H_2O$. The dopant, Nd (in nitrate form) was added during the refluxing of $VOPO_4 \cdot 2H_2O$ with isobutanol. The precursors and catalysts were characterized using XRD, BET, redox titration, SEM and H_2-TPR to obtain the linkage information of catalytic behavior of the solids with their physicochemical properties.

The catalytic test was carried out at 673 K (2400 h^{-1}) in a microreactor by flowing a mixture of *n*-butane/air. The present work demonstrated that the addition of Nd dopants to VPO catalysts increased the catalytic performance significantly compared to the undoped VPO catalysts. TPR analysis showed that the reduction behaviour of Nd-doped catalysts was dominated by reduction of V^{4+} and V^{5+} species. An excess of the oxygen species (O^{2-}) associated with V^{5+} in Nd-doped catalysts improved the maleic anhydride selectivity but reduced the conversion rate of *n*-butane. Good correlation obtained on the *n*-butane conversion versus the amount of oxygen (O^{-}) removed associated with V^{4+} and amount of V^{4+} phase. The reactive pairing of V^{4+}-O^{-} was shown to be a centre for *n*-butane activation in agreement to earliest findings. Among the catalysts tested, an addition of 3 % Nd (VPDNd3) in VPO catalyst gave the highest *n*-butane conversion (75 %) and MA selectivity (46 %) as compared to only 58 % and 32 % for undoped catalyst. The advantages on Nd^{3+} insertion is to enable the formation of required V-P-O compounds and increase the average oxidation number of the catalysts from 4.02 to 4.13. High catalytic performance of VPO was attributed to the large number of actual V^{4+} phase and high oxygen mobility of the catalysts.

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

PEMBANGUNAN MANGKIN VANADIUM FOSFAT GUNA TEKNIK GELOMBANG MIKRO UNTUK PENGOKSIDAAN *n*-BUTANA KEPADA MALEIK ANHIDRIDA

Oleh

TANG LOK HING

Oktober 2010

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Mangkin VPO baru telah disediakan melalui kaedah gelombang mikro. Perbandingan mangkin ini dengan kaedah konvensional refluks atas mikrostruktur, morfologi, sifat dasar oksigen dan prestasi pengoksidaan *n*-butana kepada maleik anhidrida telah dijelaskan dan dibincangkan. Prekursor mangkin, $VOHPO\ 0.5H_20$ disediakan oleh penurunan $VOPO_4 \cdot 2H_2O$ dengan menggunakan alkohol isobutil bawah penyinaran gelombang mikro menunjukkan pola yang sama dengan mangkin konvensional dan lebih kristal, yang ditandai dengan keamatan tinggi di XRD puncak. Lebih menarik adalah bahawa penggunaan gelombang mikro adalah penting secara memendekkan tempoh (<1 jam) dalam penyediaan prekursor berbanding kepada 22 jam biasanya digunakan dalam kaedah konvensional. Suhu-pengurangan diprogram (TPR) atas H_2 menghasilkan dua penurunan puncak yang diamati dalam kisaran 600-1100 K. Pada kajian ini menunjukkan bahawa pengaruh penyinaran gelombang mikro kepada mangkin

vanadium fosfat adalah berkesan dalam meningkatkan aktiviti mangkin dan selektiviti pengoksidaan *n*-butana kepada maleik anhidrida yang telah disokong oleh luas permukaan BET lebih tinggi dan amaun yang aktif dan pilihan spesies oksigen lebih tinggi masing-masing dilepaskan dari V^{4+} dan V^{5+} fasa. Rawatan mekanokimia telah dilaksanakan pada prekursor mangkin vanadium fosfat (VPO), $VOHPO_4{\cdot}0.5H_2O$ disediakan melalui penurunan $VOPO_4{\cdot}2H_2O$ menggunakan isobutanol bawah penyinaran gelombang mikro, tertakluk dalam tenaga tinggi kisaran bebola selama 60 minit dalam etanol sebagai pelarut. Rawatan ini meningkatkan jumlah purata nombor pengoksidaan mangkin tanpa mengubah komposisi fasanya. Saiz zarah mangkin menurun selepas proses kisaran bola. Morfologi bagi pengisaran mangkin adalah tergantung kepada masa pengisaran. Luas permukaan bagi pengisaran mangkin menurun kerana masa kisaran bebola yang dilaksanakan atas prekursor adalah terlalu lama. Mobiliti yang tinggi bagi spesies kekisi oksigen telah tercapai bagi mangkin yang dikisarkan dengan amaun atom oksigen yang lebih tinggi dilepaskan. Hubungan yang baik ditunjukkan antara oksigen (O^-) spesies yang berkait dengan V^{4+} dan penukaran *n*-butana. Hubungan lain yang baik antara penukaran *n*-butana dan fasa V^{4+} fasa dapat diamati. Pasangan reaktif dari V^{4+}-O^- dicadangkan sebagai pusat bagi pengaktifan *n*-butana. Namun, amaun spesies oksigen yang besar dilepaskan dari V^{5+} akan memberikan kesan yang merugikan pada peringkat penukaran. Kajian ini menunjukkan bahawa kaedah mekanokimia berkesan meningkatkan mangkin yang disintesis oleh gelombang mikro atas aktiviti mangkin dengan meningkatkan penukaran *n*-butana dan mengekalkan selektiviti kepada MA. Nd-dop (1, 3, dan 5%) fosfat vanadium (VPO) mangkin telah disediakan yang mana termasuk pengenalan sinaran gelombang mikro

dalam sintesis $VOPO_4 \cdot 2H_2O$. Dopan Nd (bentuk nitrat) telah ditambah semasa refluks $VOPO_4 \cdot 2H_2O$ dengan isobutanol. Untuk mendapatkan maklumat perkaitan pertautan perangai kemangkinan pepejal dengan cirri-ciri fisikokimia, prekursor dan mangkin telah dicirikan melaui XRD, BET, titratan redox, SEM dan H_2-TPR. Uji kaji ciri-ciri kemangkinan telah dilakukan pada 673 K (2400 h^{-1}) dalam microreaktor dengan aliran campuran *n*-butane/air. Pada kajian ini telah menunjukkan bahawa penambahan dopan Nd pada VPO mangkin adalah penting dalam meningkatkan prestasi kemangkinan berbanding dengan mangkin VPO yang tidak ada dop. TPR analisis menunjukkan bahawa perangai penurunan mangkin dop Nd telah dikuasai oleh puncak penurunan yang ditugaskan sebagai penurunan V^{4+} dan V^{5+} spesies. Kelebihan oksigen (O^{2-}) species yang berkait dengan V^{5+} dalam mangkin Nd-doped meningkatkan selektiviti maleik anhidrida tetapi mengurangkan kadar penukaran *n*-butana. Korelasi yang baik diperolehi atas penukaran *n*-butana versus amaun oksigen (O^-) dilepaskan berkait dengan V^{4+} dan amaun V^{4+} fasa. Pasangan reaktif dari V^{4+}-O^- ditunjukkan sebagai pusat untuk pengaktifan *n*-butana dalam persetujuan dengan penemuan awal. Antara mangkin yang diuji, penambahan 3% Nd (VPDNd3) dalam mangkin VPO memberi penukaran *n*-butana tertinggi (75%) dan selektiviti MA(46%) berbanding dengan hanya 58% dan 32% bagi mangkin yang tidak ada dopant. Kelebihan pada penyisipan Nd^{3+} adalah untuk membolehkan pembentukan sebatian V-P-O diperlukan dan membuat mangkin peningkatan dalam purata nombor pengoksidaan dari 4.02 kepada 4.13. Sifat kemangkinan VPO ini dicirikan kepada jumlah nombor sebenar V^{4+} fasa dan mobiliti oksigen mangkin yang tinggi.

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I certify that an Examination Committee has met on 26th October 2010 to conduct the final examination of Tang Lok Hing on his thesis entitled “Development of Vanadium Phosphate Catalyst using Microwave Technique to Oxidize *n*-Butane Into Maleic Anhydride” in accordance 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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DECLARATION

I declare that the thesis is my original work except for 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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LIST OF ABBREVIATIONS

B.E.T.	Brunauer, Emmet, and Teller
FHWM	Full width at half maximum
GSHV	Gas hour space velocity
ICP-AES	Inductively coupled plasma atomic emission spectrometer
I_{020}/I_{204}	Intensity ratios of (020) and (204) reflection planes
JCPDS	Joint Committee on Powder Diffraction Standards
MA	Maleic anhydride
Nd/V	Neodymium/Vanadium
SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
T_{max}	Temperature at peak maximum
TPR	Temperature-programmed reduction
XRD	X-ray diffraction

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