UNIVERSITI PUTRA MALAYSIA

VANADIUM PHOSPHATE CATALYST SYNTHESIZED BY ORGANIC METHOD USING SONICATED V2O5 FOR SELECTIVE OXIDATION OF n-BUTANE TO MALEIC ANHYDRIDE

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By

SUHAIZAM SHAHRUL AFFENDY BIN SUHAIMI

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

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Abstract of thesis to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

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Chairman: Prof. Taufiq Yap Yun Hin, PhD

Faculty: Science

Selective oxidation of alkanes by heterogeneous catalytic reaction has been one of the most active areas in the field of catalysis. The selective oxidation of *n*-butane to maleic anhydride (MA) over vanadium phosphate catalyst (VPO) was recognized as one of the most studied reaction for the past few decades. A number of new methods were suggested in the preparation of VPO catalyst to increase the performance of the catalyst in terms of activity and selectivity. In this study, VPO catalysts were synthesized using sonicated V_2O_5. V_2O_5 obtained from the commercial sources was treated using ultrasound pretreatment with two different mineralizers (NaCl and $NaNO_3$) in several durations (30-120 min). XRD patterns of the sonicated V_2O_5 gave similar structure like the pure V_2O_5 phase and prolonged the duration of sonication had led to an increase in the intensity of the diffraction peaks, which indicated the high crystallinity of the sonicated V_2O_5. SEM micrographs showed that longer

periods of sonication pretreatment produced sonicated V_2O_5 with higher amount of plate-like crystals. TEM micrographs showed that due to the sonication pretreatment, V_2O_5 with nano scale size and in the form of wires was successfully synthesized. Prolonged duration of sonication up to 120 min also had reduced the diameter of the sonicated V_2O_5 to below than ~20 nm. Further study on the effect of sonication pretreatment to the physical and chemical properties of vanadium phosphate catalyst (VPO) was performed by using the sonicated V_2O_5 for the synthesis of $VOHPO_4{\cdot}0.5H_2O$ precursor. Comparative study between the sonicated VPO catalysts and VPO synthesized using conventional method (organic route) was done by using XRD, BET, bulk composition analysis, volumetric titration method analysis, SEM and H_2-TPR. Results showed that the application of sonicated V_2O_5 had reduced the crystallite size of the final VPO catalyst and increased the total surface area of the catalyst. TPR analysis also showed that the reactivity and reducibility of oxygen species for VPO catalyst synthesized by sonicated V_2O_5 was slightly improved, where the reduction peaks which correlated to the V^{5+} and V^{4+} phases were shifted to much lower temperatures. High amount of oxygen species at lower temperature will increase the availability of oxygen for the breaking of C-H bond during the partial oxidation of *n*-butane. As evident, the MA selectivity for VPO60 tremendously increased up to 52% while the *n*-butane conversion of VPO90 had greatly increased up to 43% during the selective oxidation of *n*-butane to MA.

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

PENGHASILAN MANGKIN VANADIUM FOSFAT SECARA ORGANIK MENGGUNAKAN V_2O_5 YANG DIRAWAT DENGAN ULTRABUNYI UNTUK PENGOKSIDAAN *n*-BUTANA KEPADA MALEIK ANHIDRIDA

Oleh

SUHAIZAM SHAHRUL AFFENDY BIN SUHAIMI

Mei 2012

Pengerusi: Prof. Taufiq Yap Yun Hin, PhD

Fakulti: Sains

Pengoksidaan terpilih alkana melalui tindak balas pemangkin merupakan salah satu daripada cabang yang aktif di dalam bidang pemangkinan. Pengoksidaan butana kepada malik anhidrida (MA) melalui mangkin vanadium fosfat (VPO) telah dikenal pasti sebagai salah satu tindak balas yang sering dikaji untuk beberapa dekad yang lepas. Pelbagai kaedah baru telah dicadangkan untuk penyediaan mangkin VPO bagi meningkatkan prestasi mangkin dari segi aktiviti dan keterpilihan. Dalam kajian ini, mangkin VPO dihasilkan melalui V_2O_5 yang telah dirawat. V_2O_5 dari sumber komersial dirawat menggunakan rawatan ultrabunyi bersama dengan dua mineral yang berbeza (NaCl dan $NaNO_3$) pada masa tertentu (30-120 min). XRD menunjukkan bahawa V_2O_5 yang telah diolah masih mempunyai pola yang sama seperti V_2O_5 yang tulen dan masa rawatan ultrabunyi yang semakin panjang akan meningkatkan keamatan bagi setiap puncak yang merujuk kepada pembentukan

hablur V_2O_5 yang semakin tinggi disebabkan oleh rawatan ultrabunyi yang telah dilakukan. Mikrograf SEM menunjukkan bahawa apabila masa untuk rawatan ultrabunyi dipertingkatkan, kuantiti hablur berbentuk kepingan yang terhasil juga menjadi semakin banyak. Mikrograf TEM menunjukkan bahawa kesan daripada proses rawatan ultrabunyi, V_2O_5 bersaiz nano dan berbentuk wayar telah terbentuk. Apabila masa rawatan ditingkatkan ke 120 minit, diameter V_2O_5 juga akan turut berkurangan kepada ~20 nm. Lanjutan tentang kesan rawatan ultrabunyi terhadap sifat fizikal dan kimia mangkin VPO telah dikaji dengan menggunakan V_2O_5 yang telah diolah untuk menghasilkan prekursor, $VOHPO_4{\cdot}0.5H_2O$. Perbandingan di antara mangkin VPO yang dihasilkan dengan menggunakan V_2O_5 yang telah diolah dan mangkin VPO yang dihasilkan secara konvensional (secara organik) dilakukan dengan menggunakan XRD, BET, kaedah analisis komposisi, kaedah pentitratan isipadu, SEM dan H_2-TPR. Data yang diperolehi menunjukkan bahawa aplikasi V_2O_5 yang diolah telah mengurangkan saiz purata hablur dan mangkin VPO yang dihasilkan turut mempunyai luas permukaan yang lebih tinggi. Analisis H_2-TPR juga menunjukkan bahawa kadar keaktifan spesis oksigen bagi mangkin VPO yang menggunakan V_2O_5 yang dirawat menjadi semakin baik kerana puncak penurunan yang berkaitan dengan fasa V^{5+} dan V^{4+} di dalam mangkin VPO telah beralih kepada suhu yang lebih rendah. Peningkatan jumlah spesis oksigen pada suhu yang rendah akan mempengaruhi sifat mudah-alih oksigen yang terdapat di permukaan mangkin untuk proses pemutusan ikatan C-H semasa pengoksidaan *n*-butana. Hal ini jelas dibuktikan melalui kadar penghasilan MA bagi VPO60 yang telah meningkat kepada 52% dan juga kadar penukaran *n*-butana bagi VPO90 yang telah meningkat kepada 43%.

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I certify that a Thesis Examination Committee has met on 30th May 2012 to conduct the final examination of Suhaizam Shahrul Affendy Bin Suhaimi on his thesis entitled "Vanadium Phosphate Catalyst Synthesized by Organic Method using Sonicated V_2O_5 for Selective Oxidation of *n*-Butane to Maleic Anhydride" 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.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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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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SUHAIZAM SHAHRUL AFFENDY BIN SUHAIMI

Date: 30/May/2012

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