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REFLUX SYNTHESIS AND PHYSICOCHEMICAL CHARACTERISATION OF MoVTeNbOx CATALYST FOR PROPANE OXIDATION INTO ACRYLIC ACID

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By

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REFLUX SYNTHESIS AND PHYSICOCHEMICAL CHARACTERISATION OF $MoVTeNbO_x$ CATALYST FOR PROPANE OXIDATION INTO ACRYLIC ACID

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Chairman: Assoc. Prof. Irmawati Ramli, PhD

Faculty: Science

The abundance of propane and its low price is one of the main factors that made selective oxidation of this light alkane to acrylic acid through heterogeneous catalytic pathway receives intensive research. $MoVTeNbO_x$ a quarternary metal oxide catalyst is reported to have shown the best performance for the direct oxidation of propane to acrylic acid to this date. In this work, $MoVTeNbO_x$ catalysts were prepared by reflux method. Synthesis parameters such as reflux time and drying method were found to have profound effect on the catalyst structure and chemical properties. Spray drying was found to give precursor which upon calcinations produced better formation of M1 and M2 phase $MoVTeNbO_x$ catalyst compared to samples dried by rotary evaporation method. This is proved by the X-ray diffragtogram of the samples as it shown peak at 2θ=6.6, 7.9, 9.0, 22.1 and 45° which correspond to orthorhombic (M1) phase and 2θ= 28.3, 36.2 and 50° of hexagonal (M2) phase. Longer reflux time gave better structural

formation and higher specific surface area (S_{BET}) thus led to a better catalyst performance of samples dried using spray dry method. Investigation on calcinations environment revealed that calcination in air followed by calcination in nitrogen flow gives better catalyst (catalyst B2). Catalyst B2 gave higher specific surface area (S_{BET}) and oxygen removed in H_2-TPR which is 5.3 m^2g^{-1} and $2.8x10^{21}$ $atomg^{-1}$ respectively. Thus indicates that sample B2 is an active catalyst. However calcination in air should not exceed 1 hour as longer calcination in air will impede the properties of the catalyst. Finally, washing the synthesized catalyst with hydrogen peroxide managed to eliminate the non-active M2 phase and improved the formation of the M1 phase. This is proved by a more significant X-ray diffraction patterns at 2θ = 6.6, 7.9, 9.0, 22.1, 27.0 and 45° with absences of diffraction peaks at 2θ = 28.3, 36.2 and 50° that related to the existence of M2 phase for after washing with H_2O_2 sample (B2W). Higher S_{BET} also observed for sample B2W which is 12.5 m^2g^{-1} compared to 5.3 m^2g^{-1} for sample before washing (B2). The catalytic tests were done at three different reaction temperatures which are 653, 673 and 693 K. Propane conversion was found to increase when the temperature was increased up to 693 K. Catalyst obtained from a longer reflux time (72 hours) and dried using a spray dry method give a better activity which is 6.53% at 693 K compared to the catalyst obtained from a shorter reflux time (24 hours) with 4.55% or the sample dried using rotary evaporator (3.76%) at the same temperature. The catalytic test of the catalyst after washing with H_2O_2 (B2W) showed very promising propane conversion (22.01 %) and higher reaction selectivity towards acrylic acid (24.21%).

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

SINTESIS REFLUKS DAN PENCIRIAN FIZIKOKIMIA MANGKIN $MoVTeNbO_x$ UNTUK PENGOKSIDAAN PROPANA KEPADA ASID AKRILIK

Oleh

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November 2011

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Banyaknya sumber dan kos yang lebih murah gas asli propana adalah salah satu faktor utama yang menjadikan pengoksidaan terpilih alkana kepada asid akrilik dengan mangkin heterogen menjadi tumpuan penyelidikan secara intensif. Mangkin $MoVTeNbO_x$ oksida logam kuarternari dilaporkan telah menunjukkan prestasi yang terbaik untuk pengoksidaan langsung propana ke asid akrilik. Sintesis $MoVTeNbO_x$ dilakukan melalui kaedah refluks. Sintesis parameter seperti masa reflux dan kaedah pengeringan didapati mempunyai kesan yang mendalam kepada struktur dan sifat-sifat kimia mangkin. Pengeringan secara semburan didapati memberikan prekursor yang menghasilkan pembentukan yang lebih baik fasa M1 dan M2 $MoVTeNbO_x$ berbanding sampel yang dikeringkan dengan kaedah penyejatan. Ini dibuktikan oleh diffragtogram sinar-X sampel yang menunjukkan puncak pada 2θ = 6.6, 7.9, 9.0, 22.1 dan 45 ° untuk fasa ortorombik (M1) dan 2θ = 28.3, 36.2 dan 50 ° untuk fasa heksagonal (M2). Masa

refluks yang lebih lama mambantu dalam pembentukan struktur yang lebih baik dan luas permukaan spesifik yang lebih tinggi (S_{BET}). Ini membawa kepada prestasi mangkin yang lebih baik untuk sampel yang dikeringkan menggunakan kaedah semburan. Persekitaran pengkalsinan mangkin secara pemanasan pada suhu yang tinggi juga mempengaruhi sifat mangkin. Pemanasan dalam persekitaran udara bebas diikuti pemanasan dalam persekitaran N2 menghasilkan mangkin yang lebih baik (mangkin B2). Mangkin B2 memberikan luas permukaan spesifik yang lebih tinggi (S_{BET}) dan oksigen yang dikeluarkan H_2-TPR yang 5.3 m^2g^{-1} dan $2.8x10^{21}$ atom g^{-1}. Ini menunjukkan bahawa mangkin B2 merupakan mangkin yang aktif. Walau bagaimanapun proses pengkalsinan dalam udara tidak boleh melebihi 1 jam. Pembasuhan dengan hidrogen peroksida berjaya menghapuskan fasa tidak-aktif M2 dan meningkatkan pembentukan fasa M1. Ini dibuktikan oleh corak pembelauan sinar-X yang lebih jelas di 2θ = 6.6, 7.9, 9.0, 22.1, 27.0 dan 45 ° dan ketiadaan puncak pembelauan pada 2θ = 28.3, 36.2 dan 50 ° yang berkaitan dengan kewujudan fasa M2 untuk mangkin selepas dibasuh dengan H_2O_2 (B2W). S_{BET} yang lebih tinggi untuk mangkin B2W juga boleh dilihat iaitu 12.5 m^2g^{-1} berbanding dengan 5.3 m^2g^{-1} untuk mangkin sebelum dibasuh (B2). Ujian pemangkinan untuk tindak balas propana telah dilakukan pada tiga suhu tindak balas yang berbeza yang 653, 673 dan 693 K. Aktiviti mangkin didapati meningkat apabila suhu telah meningkat sehingga 693 K. Mangkin diperolehi dari masa refluks yang lebih lama (72 jam) dan dikeringkan menggunakan kaedah semburan memberikan aktiviti yang lebih baik iaitu 6.53% pada suhu 693 K berbanding dengan mangkin yang diperolehi dari masa refluks yang lebih singkat (24 jam) dengan aktiviti 4.55% atau sampel yang dikeringkan menggunakan kaedah

penyejatan (3.76%) pada suhu yang sama. Ujian pemangkinan selepas dibasuh dengan H_2O_2 (B2W) menunjukkan aktiviti penukaran propane yang lebih cekap (22.01%) dan kepilihan tindak balas yang lebih tinggi ke arah pembentukan asid akrilik (24.21%).

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I certify that an Examination Committee has met on ……..to conduct the final examination of Ahmad Zaidi Ismail on his Master of Science thesis entitled "Reflux Synthesis And Physicochemical Characterisation Of $MoVTeNbO_x$ Catalyst Used Propane Oxidation To Acrylic Acid" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the student be awarded the……

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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 quotation and citation which have been duly acknowledged. I also declare that if it has not been previously and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

AHMAD ZAIDI ISMAIL

Date: 29th November 2011

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