MODIFICATION AND CHARACTERIZATION OF VANADIUM PHOPHOSRUS OXIDE CATALYSTS FOR SELECTIVE OXIDATION OF PROPANE TO ACRYLIC ACID

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By

SAW CHAING SHEN

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February 2006

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Faculty : Science

Vanadium phosphate catalysts synthesized via $VOPO_4 \cdot 2H_2O$ were further reduced in isobutanol to produce $VOHPO_4 \cdot 0.5H_2O$ precursor. Calcination of this precursor in propane/air environment (1% propane in air) transformed into activated $(VO)_2P_2O_7$ catalysts. The morphology, structure, oxidant's nature and catalytic performance for propane oxidation to acrylic acid over this catalyst strongly depended on the duration of calcination. The catalyst calcined for 36 h (VPD36P) exhibits low surface area. However, prolonged calcination promoted a higher surface area with better crystallization. V^{III} and V^{V} phases are detected in all catalysts. The SEM micrographs showed that all propane/air catalysts gave rosebud type agglomerates with various sizes but in a uniform shape.

A comparison of effect of calcinations environments on the vanadium phosphate catalyst in flow of both propane/air and butane/air, the latter calcinations environment produced catalyst with more platelet and higher surface area. Chemical analysis also shows that VPDB catalyst consist of higher amount of V^{V} (26%) and 74% of V^{IV}

phase whereas VPDP only contains 76 and 9.8% of V^{IV} and V^{V} phases, respectively. Interestingly, VPDP also showed 14.2% of V^{III} phase. For n-butane oxidation at 673 K, VPDB gave 83% of conversion and 63% of MA selectivity whereas VPDP gave 75% of conversion and 64% of MA selectivity. The *n*-butane/air calcined catalyst, VPDB showed better activity (14.1%) in propane oxidation than the propne/air calcined catalyst, VPDP (7.9%).

The addition of 1, 2 and 5 mol % of Zr into $(VO)_2P_2O_7$ catalysts produced a single vanadyl pyrophosphate phase in $VOPO_4{\cdot}2H_2O$ method with different degree of crystallinity. The presence of lower percentage of Zr (1 and 2%) improved the surface area of the catalysts; however, the surface area of the catalyst with 5% of Zr added is decreased. The SEM micrograph for all Zr modified catalysts gave roughed rosebud agglomerates as compared to the unpromoted catalyst. VPDZr1 catalyst was found to be the most selective catalyst among all the Zr doped catalysts in propane oxidation.

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

MODIFIKASI DAN PENCIRIAN MANGKIN VANADIUM FOSFORUS OKSIDA UNTUK PENGOKSIDAAN TERPILIH PROPANA KEPADA ACID AKRILIK

Oleh

SAW CHAING SHEN

Februari 2006

Pengerusi: Profesor Madya Taufiq Yap Yun Hin, PhD

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Mangkin vanadil fosfat telah disintesis melalui vanadil fosforus dihidrida, $VOPO_4{\cdot}2H_2O$ dan kemudian diturunkan kepada vanadil hidrogen hemihidrida, $VOHPO_4{\cdot}0.5H_2O$ dengan menggunakan isobutanol. Pengkalsinan prekursor dalam persekitaran 1% propana/udara akan menukar kepada mangkin $(VO)_2P_2O_7$ yang aktif. Morfologi, struktur, sifat pengoksidaan dan kecekapan permangkinan mangkin VPO dalam proses pengoksidaan propana kepada acid akrilik amat bergantung kepada jangka masa pengkalsinan. Mangkin yang dikalsin selama 36 jam (VPD36P) menunjukkan luas permukaan yang rendah. Tetapi, pengkalsinan yang lebih lama akan meningkatkan luas permukaan dan tahap penghabluran. Fasa-fasa V^{III} dan V^{V} berjaya dikesan dalam kesemua mangkin. Mikrograf-micrograf SEM menunjukkan kesemua mangkin yang diklasin dalam keadaan propana/udara mempunyai struktur hablur yang berbentuk bunga ros dengan saiz yang berbeza.

Perbandingan antara kesan persekitaran perkalsinan dalam propane/udara dan butane/udara terhadap mangkin vanadil fosfat menunjukkan bahawa persekitaran

butana/udara dapat menghasilkan mangkin yang mempunyai bilangan plat yang lebih banyak dan luas permukaan yang lebih besar. Analisis kimia turut menunjukkan mangkin VPDB mempunyai jumlah V^{V} (26%) yang tinggi dengan 74% fasa $V^{IV.}$ Sementara VPDP pula mengandungi 76% dan 9.8% fasa V^{IV} dan V^{V}. Yang menariknya, VPDP menunjukkan kehadiran fasa V^{III} sebenyak 14.2%. Dalam pengoksidaan butana pada suhu 673 K, VPDB menunjukkan 83% kadar penukaran dengan 63% pemilihan terhadap maleik anhidrida, MA. Manakala, VPDP hanya menunjukkan 75% kadar penukaran dan 64% pemilihan terhadap MA. Mangkin yang dikasin dalam butana/udara mampu menunjukkan aktiviti yang lebih baik (14.1%) daripada mangkin yang dikalsin dalam propana/air, VPDP (7.9%).

Penambahan 1, 2 dan 5 mol % kation Zr kedalam sebatian $(VO)_2P_2O_7$ telah menghasilkan fasa tunggal vanadil pirofosfat dengan darjah prnghabluran yang berbeza melalui kaedah $VOPO_4 \cdot 2H_2O$. Kehadiran Zr dalam peratusan yang lebih rendah (1 dan 2%) dapat meningkatkan luas permukaan mangkin. Manakala, luas permukaan mangkin didapati menyusut apabila 5% Zr ditambah. Mikrogaf-mikrograf SEM untuk kesemua mangkin yang dimodifikasi dengan Zr menujukkan hablur berbentuk bunga ros tetapi dengan keadaan permukaan yang lebih kasar apabila dibandingkan dengan mangkin tanpa dop. Di antara mangkin-mangkin yang didop dengan Zr, VPDZr1 merupakan mangkin yang paling memilih dalam proses pengoksidaan propana.

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I certify that an Examination Committee has met on 24th February 2006 to conduct the final examination of Saw Chaing Shen on his Master of Science thesis entitled "Modification and Characterization of Vanadium Phophosrus Oxide Catalysts for Selective Oxidation of Propane to Acrylic Acid" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination are as follows:

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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.

SAW CHAING SHEN

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