

**HYDROTHERMAL SYNTHESIS OF VANADIUM PHOSPHORUS OXIDE
CATALYSTS FOR SELECTIVE OXIDATION OF *n*-BUTANE TO MALEIC
ANHYDRIDE**

By

MOHD HASBI BIN AB. RAHIM

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia
in Fulfilment of the Requirements for the Degree of Master of Science
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Special Appreciation to.....my family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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Vanadium phosphorus oxide (VPO) catalyst is commercially used in industry for the selective oxidation of *n*-butane to maleic anhydride. A number of new methods have been suggested by researchers worldwide in the preparation of precursor compound, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ which is subsequently transformed under suitable reaction condition to give the better catalysts in terms of selectivity to maleic anhydride and the *n*-butane activity. In this study, VPO catalysts were synthesized using a new hydrothermal method. Roughly, this study can be divided into three sections based on three groups of VPO catalysts prepared. The first catalyst was prepared following the procedure in the literature. The second group of VPO catalyst were prepared by the modification of this procedure which focused on different reaction time in autoclave. Lastly, the effect of mechanochemical treatment on the hydrothermal prepared sample was studied.

The results show that VPO catalysts were successfully prepared by hydrothermal method. The morphology, structure, oxidant's nature and catalytic performance for butane oxidation to maleic anhydride over these catalysts strongly depended on the

preparation procedure of the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ precursor and also the transformation into the VPO catalyst. Increasing the length of reaction time in autoclave at 423 K does not affect the surface area and bulk morphology of the catalyst. However, amounts of O_2 removed and desorbed from the lattice are directly proportional with reaction time in autoclave.

Interestingly, there are trends of results were observed for the milled material. This mechanochemical treatment contributed to a higher surface area with high mobility and reactivity of the lattice oxygen. The pretreatment also induced the amount of V^{5+} phase of the catalyst. An appropriate amount of V^{5+} phase present in VPO catalyst is significantly increased the activity of these catalysts.

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

**PENYEDIAAN MANGKIN VANADIUM FOSFORUS OKSIDA UNTUK
PENGOKSIDAAN TERPILIH *n*-BUTANA KEPADA MALEIK ANHIDRIDA
DENGAN MENGGUNAKAN KAEDAH HIDROTERMA**

Oleh

MOHD HASBI BIN AB. RAHIM

Januari 2006

Pengerusi: Profesor Madya Taufiq Yap Yun Hin, PhD

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Vanadium fosforus oksida (VPO), adalah mangkin komersial untuk pengoksidaan terpilih butana kepada maleik anhidrida. Pelbagai kaedah terbaru telah dicadangkan dan diperkenalkan oleh penyelidik-penyelidik seluruh dunia bagi menyediakan sebatian prekursor, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ yang mana akan bertukar kepada mangkin, $(\text{VO})_2\text{P}_2\text{O}_7$ di bawah keadaan tindak balas seterusnya memberikan mangkin yang lebih baik dari segi keterpilihan kepada maleik anhidrida dan aktiviti kepada butana. Di dalam kajian ini, mangkin-mangkin VPO telah disediakan dengan menggunakan kaedah hidroterma yang baru. Secara amnya, kajian ini boleh dibahagikan kepada 3 kumpulan mangkin VPO. Dalam kumpulan pertama, mangkin disediakan dengan mengikut prosedur dari sorotan literatur. Seterusnya, modifikasi telah dibuat ke atas prosedur ini yang mana kajian telah difokuskan kepada perbezaan masa penyediaan prekursor, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ di dalam autoklaf. Akhir sekali, kajian kesan rawatan kimia-mekanik ke atas sampel yang disediakan melalui kaedah hidroterma telah dijalankan.

Semua keputusan menunjukkan mangkin-mangkin VPO telah berjaya disediakan dengan menggunakan kaedah hidroterma. Struktur, morfologi, sifat pengoksidaan dan pelaksanaan mangkin ke atas pengoksidaan butana kepada maleik anhidrida bergantung kuat kepada kaedah penyediaan $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ dan juga perubahannya kepada mangkin VPO. Meningkatkan masa tindak balas dalam autoklaf pada suhu 423 K tidak memberi kesan yang ketara ke atas luas permukaan dan saiz morfologi mangkin. Bagaimanapun, jumlah O_2 yang disingkirkan dan diyahjerapkan daripada kekisi adalah berkadar terus dengan masa tindak balas dalam autoklaf.

Menariknya, wujudnya tren keputusan-keputusan yang dapat diperhatikan pada sampel yang dikisarkan. Rawatan kimia-mekanik ini telah menyumbang kepada luas permukaan yang tinggi disertai dengan penambahan mobiliti dan reaktiviti oksigen kekisi. Rawatan ini juga telah menggalakkan kuantiti fasa V^{5+} ke atas mangkin VPO ini. Kuantiti fasa V^{5+} yang sesuai dalam mangkin VPO ini telah memberikan peningkatan yang penting ke atas aktiviti mangkin-mangkin ini.

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I certify that an Examination Committee met on 27 January 2006 to conduct the final examination of Mohd Hasbi Bin Ab. Rahim on his Master of Science thesis entitled “Hydrothermal Synthesis of Vanadium Phosphorus Oxide Catalysts For Selective 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 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.

MOHD HASBI BIN AB. RAHIM

Date: 20 March 2006

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