HYDROTHERMAL SYNTHESIS OF VANADIUM PHOSPHORUS OXIDE CATALYSTS FOR SELECTIVE OXIDATION OF \textit{n}-BUTANE TO MALEIC ANHYDRIDE

By

MOHD HASBI BIN AB. RAHIM

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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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January 2006

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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, VOHPO$_4$·0.5H$_2$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 VOHPO$_4 \cdot 0.5$H$_2$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

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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 penyediakan 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 hidrotermawar 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 hidrotermawar 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 VOHPO$_4$·0.5H$_2$O dan juga perubahannya kepada mangkin VPO. Meninggikan 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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In The Name of ALLAH S.W.T., the Most Merciful, Most Compassionate

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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
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>ii</td>
<td>DEDICATION</td>
</tr>
<tr>
<td>iii</td>
<td>ABSTRACT</td>
</tr>
<tr>
<td>v</td>
<td>ABSTRAK</td>
</tr>
<tr>
<td>vii</td>
<td>ACKNOWLEDGEMENTS</td>
</tr>
<tr>
<td>viii</td>
<td>APPROVAL</td>
</tr>
<tr>
<td>x</td>
<td>DECLARATION</td>
</tr>
<tr>
<td>xiv</td>
<td>LIST OF TABLES</td>
</tr>
<tr>
<td>xv</td>
<td>LIST OF FIGURES</td>
</tr>
<tr>
<td>xvii</td>
<td>LIST OF ABBREVIATIONS</td>
</tr>
<tr>
<td>1</td>
<td>CHAPTER</td>
</tr>
<tr>
<td>1.1</td>
<td>INTRODUCTION</td>
</tr>
<tr>
<td>1.1.1</td>
<td>Catalysis in General</td>
</tr>
<tr>
<td>1.1.1.1</td>
<td>The Important of Catalysis in Chemical Industry</td>
</tr>
<tr>
<td>1.1.2</td>
<td>Heterogeneous Catalysis</td>
</tr>
<tr>
<td>1.1.3</td>
<td>Catalysts for Selective Oxidation of Light Alkanes</td>
</tr>
<tr>
<td>1.1.4</td>
<td>Selective Oxidation Catalysts: Special Requirement</td>
</tr>
<tr>
<td>6</td>
<td>1.2 Selective Oxidation Pathways at Oxide Surfaces</td>
</tr>
<tr>
<td>8</td>
<td>1.3 Catalysis and Sustainable (Green) Chemistry</td>
</tr>
<tr>
<td>11</td>
<td>1.4 Hydrothermal</td>
</tr>
<tr>
<td>11</td>
<td>1.4.1 Hydrothermal Synthesis</td>
</tr>
<tr>
<td>14</td>
<td>1.4.2 Advantages of Hydrothermal Synthesis</td>
</tr>
<tr>
<td>15</td>
<td>1.5 Objectives of Research</td>
</tr>
<tr>
<td>17</td>
<td>2 LITERATURE REVIEW</td>
</tr>
<tr>
<td>17</td>
<td>2.1 Vanadium Phosphorus Oxide Catalyst</td>
</tr>
<tr>
<td>21</td>
<td>2.2 Preparation Methods of Vanadium Phosphorus Oxide Catalyst</td>
</tr>
<tr>
<td>25</td>
<td>2.2.1 Hydrothermal Method</td>
</tr>
<tr>
<td>27</td>
<td>2.2.2 Mechanochemical Treatment</td>
</tr>
<tr>
<td>30</td>
<td>2.3 Role of Oxygen Species in VPO Catalyst</td>
</tr>
<tr>
<td>33</td>
<td>2.4 Factors Influencing the Catalyst Performances</td>
</tr>
<tr>
<td>33</td>
<td>2.4.1 Effect of the P/V Ratio</td>
</tr>
<tr>
<td>35</td>
<td>2.4.2 Activation of Catalyst Precursor</td>
</tr>
<tr>
<td>38</td>
<td>2.4.3 Influence of Vanadium Oxidation State Balances</td>
</tr>
<tr>
<td>40</td>
<td>2.5 Scope of Thesis</td>
</tr>
<tr>
<td>41</td>
<td>3 MATERIALS AND METHODS</td>
</tr>
<tr>
<td>41</td>
<td>3.1 Materials and Gases</td>
</tr>
<tr>
<td>42</td>
<td>3.2 Preparation of Vanadium Phosphorus Oxide Catalyst</td>
</tr>
<tr>
<td>42</td>
<td>3.2.1 Vanadium Phosphorus Oxide Catalyst Prepared Using Method A</td>
</tr>
<tr>
<td></td>
<td>3.2.1.1 Methodology</td>
</tr>
</tbody>
</table>
3.2.2 Vanadium Phosphorus Oxide Catalyst Prepared Using Method B
   3.2.2.1 Methodology 43
   3.2.3 Mechanochemical Treatment 44
      3.2.3.1 Methodology 45
3.3 Catalysts Characterization 45
   3.3.1 X-Ray Diffraction Analysis 45
   3.3.2 BET Surface Area Measurement 46
   3.3.3 Volumetric Titration 47
   3.3.4 Chemical Analysis 48
   3.3.5 Scanning Electron Microscopy 48
   3.3.6 Temperature Programmed Analysis 49
      3.3.6.1 Temperature Programmed Desorption (TPD) 49
      3.3.6.2 Temperature Programmed Reduction (TPR) 50
3.4 Catalytic Test

4 PHYSICO-CHEMICALS CHARACTERIZATION AND CATALYTIC TEST
4.1 Vanadium Phosphorus Oxide Catalyst Prepared Using Method A 51
   4.1.1 Crystalline Structure 51
   4.1.2 BET Surface Area 55
   4.1.3 P/V Ratio and V Oxidation State 55
   4.1.4 Surface Morphology 56
   4.1.5 Oxygen Desorption 57
   4.1.6 Reducibility of the Catalyst 59
   4.1.7 n-Butane Oxidation 63
4.2 Vanadium phosphorus Oxide Catalyst Prepared Using Method B 63
   4.2.1 Crystalline Structure 63
   4.2.2 BET Surface Area 67
   4.2.3 P/V Ratio and V Oxidation State 68
   4.2.4 Surface Morphology 69
   4.2.5 Oxygen Desorption 71
   4.2.6 Reducibility of the Catalyst 73
   4.2.7 n-Butane Oxidation 77
4.3 Effects of Mechanochemical Treatment 79
   4.3.1 Crystalline Structure 79
   4.3.2 BET Surface Area 82
   4.3.3 P/V Ratio and V Oxidation State 83
   4.3.4 Surface Morphology 84
   4.3.5 Oxygen Desorption 85
   4.3.6 Reducibility of the Catalyst 87
   4.3.7 n-Butane Oxidation 90
5 CONCLUSION 92
RECOMMENDATION AND SUGGESTION 95
REFERENCES 96
BIODATA OF THE AUTHOR 110