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EFFECT OF DOPANTS AND MECHANOCHEMICAL TREATMENT ON VANADIUM PHOSPHATE CATALYSTS FOR PARTIAL OXIDATION OF *n*-BUTANE TO MALEIC ANHYDRIDE

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By

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Oxidation of *n*-butane to maleic anhydride catalyzed by vanadium phosphate catalyst is one of significant worldwide commercial interest since decades. Introductions of dopants and/or mechanochemical treatment are the most promising approach for the improvement of the catalytic performance of vanadium phosphate catalyst. Tellurium doped vanadium phosphate catalyst (VPDTe) was prepared via $VOPO_4 \cdot 2H_2O$ phase after calcinating the tellurium doped precursor, $VOHPO_4 \bullet 0.5H_2O$ at 733 K in a flowing of *n*-butane/air for 18 h. VPDTe catalyst gave very high for *n*-butane conversion, 80% compared to only 47% for the undoped catalytst. The crystallite size, morphology, surface reactivity and reducibility of the catalyst have been affected by the addition of tellurium.

VPDTe catalyst has result a higher existence of V^{5+} phase in the catalyst bulk with having nearly the optimum amount of V^{5+}/V^{4+} ratio, 0.23. The SEM micrographs showed that the tellurium altered the arrangement of the platelets from "rose-like" clusters to layer with irregular shape. The sizes of platelets are even thicker and

bigger which led to lower surface area compared to undoped VPD catalyst. An addition of 1% tellurium has markedly lowered the reduction activation energies of the vanadium phosphate catalyst as revealed by TPR profiles. The amount of oxygen species removed from the peak associated with V^{4+} phase for VPDTe catalyst significantly higher. These phenomenon suggested that the O=V bond of the VPDTe catalyst are weaker with higher mobility and more reactive of the oxygen as compared to the undoped counter part.

All mechanochemial treated VPD catalysts have shown an increased surface P/V ratio, reduced the crystallite size of the catalysts and displayed different degree of crystallinity. TPR results demonstrated that both reduction peaks for every mechanochemical treated catalyst shifted to lower temperature and improved the amount of oxygen removed from the catalysts. VPDM catalyst gave 57% of conversion, 10% higher from the untreated VPD catalyst. The presence of cobalt in mechanochemical treated vanadium phosphate catalyst has slightly lowered the *n*-butane conversion to 54%. Meanwhile, treating the tellurium doped catalyst through mechanochemical treatment *i.e.* milling in stainless steel (VPDTeM) or agate (VPDTeM-ag) with ethanol as solvent has reduced the conversion from 80% to 58% and 50%, respectively. The selectivity of all catalysts prepared was almost retained in all cases (~ 33%) except for VPDCoM catalyst (19%).

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

KESAN DOPAN DAN RAWATAN KIMIA-MEKANIKAL TERHADAP MANGKIN VANADIUM FOSFORUS OKSIDA UNTUK PENGOKSIDAAN SEPARA *n*-BUTANA KEPADA MALIK ANHIDRIDA

Oleh

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Pengoksidaan *n*-butana kepada malik anhidrida oleh vanadium fosfat merupakan salah satu antara cabang tindak balas komersial yang diberi perhatian di seluruh dunia. Penambahan pelbagai dopan dan/atau rawatan kimia-mekanikal adalah pendekatan yang biasanya dilihat akan meningkatkan kadar prestasi pemangkinan bagi mangkin vanadium fosfat. Mangkin yang ditambah dengan tellurium ini disintesis melalui fasa $VOPO_4 \cdot 2H_2O$ setelah prekursor yang telah ditambah dengan tellurium, $VOHPO_4 \bullet 0.5H_2O$ diaktifkan pada 733 K dalam aliran *n*-butana/udara selama 18 jam. Mangkin VPDTe memberikan kadar penukaran *n*-butana 80% berbanding hanya 47% bagi mangkin yang tidak ditambah dengan tellurium. Saiz kristal, morfologi, kereaktifan permukaan and ciri penurunan mangkin tersebut dipengaruhi olah penambahan tellurium.

Mangkin VPDTe menunjukkan kewujudan fasa V^{5+} yang lebih tinggi dengan hampir mencapai nisbah optimum V^{5+}/V^{4+}, 0.23. Mikrograf-mikrograf SEM menunjukkan tellurium telah mengubah susunan platlet-platlet dari gugusan seperti ros kepada lapisan dengan bentuk tidak tetap. Saiz platlet-platlet juga semakin tebal and besar

yang mana telah membawa kepada penurunan luas permukaan jika dibandingkan dengan mangkin VPD yang tidak ditambah dengan tellurium. Penambahan 1% tellurium telah menyebabkan penurunan ketara terhadap tenaga pengaktifan penurunan bagi mangkin vanadium fosfat seperti yang dinyatakan melalui profil TPR. Jumlah spesis oksigen yang disingkirkan dari puncak yang mewakili fasa V^{4+} bagi mangkin VPDTe adalah jauh lebih tinggi. Fenomena ini mencadangkan ikatan O=V bagi mangkin VPDTe adalah lebih lemah dengan pergerakan oksigen untuk mengaktifkan butana adalah lebih tinggi dan lebih reaktif berbanding mangkin yang tidak ditambah tellurium.

Semua mangkin VPD yang dirawat dengan kimia-mekanikal telah menunjukkan peningkatan nisbah permukaan P/V, penurunan saiz kristal dan kepelbagaian darjah penghabluran. Keputusan TPR menunjukkan kedua-dua puncak penurunan bagi setiap mangkin yang dirawat dengan kimia-mekanikal bergerak ke arah suhu yang lebih rendah dengan jumlah oksigen yang disingkirkan dari mangkin turut meningkat. Mangkin VPDM menunjukkan kadar penukaran *n*-butana 57% iaitu 10% lebih tinggi berbanding mangkin VPD yang tidak ditambah dengan tellurium. Kehadiran kobalt dalam mangkin yang dirawat dengan kimia-mekanikal telah mengakibatkan sedikit penurunan kadar penukaran *n*-butana kepada 54%. Dalam pada itu, rawatan kimia-mekanikal yang dilakukan terhadap mangkin yang ditambah dengan tellurium sama ada di dalam peralatan besi tahan karat atau silika dengan etanol sebagai pelarut telah menyebabkan kadar penukaran butana menurun dari 80% kepada 58% dan 50%. Kadar pemilihan bagi malik anhidrida kesemua mangkin

hampir dikekalkan pada kadar yang sama (~ 33%) bagi semua kes kecuali bagi mangkin VPDCoM (19%).

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I certify that an Examination Committee met on 5th June 2007 to conduct the final examination of Nor Asrina binti Sairi on her Master of Science thesis entitled "Effect of Dopants and Mechanochemical Treatment on Vanadium Phosphate Catalysts for Partial 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.

_____

NOR ASRINA BINTI SAIRI

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmer-Teller
EPA	Environmental Protection Energy
FWHM	Full Width of Half Maximum
GHSV	Gas Hourly Space Velocity
ICP-AES	Inductive Couple Plasma – Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
JEOL	Japan Electron Optics Laboratory
LRS	Low Resolution Spectroscopy
OSHA	Occupational Safety and Health Organization
PTMEG	Polytetramethylene Ether Glyol
SEM	Scanning Electron Microscopy
T_{max}	Temperature at Peak Maximum
TCD	Thermal Conductivity Detector
TPD/R/O	Temperature Programmed Desorption/Reduction/Oxidation
TPR	Temperature Programmed Reduction
VPA	Aqueous Method
VPD	Dihydride Method
VPH	Hydrothermal Method
VPO	Organic Method
XPS	X-ray Photoelectron

XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 An Outlook in Catalytic Oxidation Process

Oxidation reaction has vastly contributed to the science of catalysis and also to the development of modern society (Taufiq-Yap, 1997). More than 60% of the chemicals and intermediates synthesized via catalytic processes are products of oxidation. Today, catalytic oxidation is the basis for the synthesis of a large percentage of the monomers or modifier used for the production of synthetic fibers and plastics and include large volume products such as ethylene oxides, acrylonitrile, vinyl chloride, maleic and phthalic anhydride (Centi *et al*., 2000).

In organic chemistry and technology, oxidation processes are defined as conversions of compounds under the influence of various oxidizing agent. A distinction is made between complete and partial oxidation. Complete oxidation is an undesirable side process in organic synthesis which leads to the formation of CO, CO_2 and H_2O. It is partial oxidation which is important. This reaction leads to a special product in which the rate of production of the desired product is being formed over others (Taufiq-Yap, 1997).

Partial oxidation processes using air or oxygen are used to manufacture a variety of chemicals, and complete catalytic oxidation is a practicable method for elimination of organic pollutants in gaseous streams. In the manufacture of chemicals, oxygen may be incorporated into the final products, as in the oxidation propylene to acrolein or *o*-xylene to pthalic anhydride: or the reaction may be an oxidative dehydrogenation in which oxygen does not appear in the desired product, as in the conversion of butene to butadiene. The desired reaction may or may not involve C-C bond scission (Taufiq-Yap, 1997). The role of oxidation catalysis in industry in which examples are given of its application in different branches of industry is illustrated in Table 1.1.

Table 1.1: Oxidation catalysis in industry (Taufiq-Yap, 1997).

	Industrial	Catalyst(s)
1.	**Inorganic Industry**	
	Nitric acid oxidation of ammonia	Pt, Rh
	Sulphuric acid by oxidation of SO_2	V_2O_5
2.	**Synthetic Rubber**	
	Butadiene by oxydehydrogenation of C_4	$(Co, Ni)_3(PO_4)_2$
	Styrene by oxydehydrogenation of ethylbenzene	Fe_2O_3
3.	**Plastics**	
	Formaldehyde by oxidation of methanol	$Fe_2(MoO_4)_3$
	Phthalic anhydride from *o*-xylene	V_2O_5/TiO_2
4.	**Synthetic Fibers**	
	Ethylene oxide	Ag/Al_2O_3
	Acrylonitrile by ammoxidation of propene	$Bi_2(MoO_4)_3$
	Maleic anhydride from C_4	$(VO)_2P_2O_7$
5.	**Pollution Control and Environmental Protection**	
	Catalytic car mufflers	Pt/Al_2O_3
	Combustion of hydrocarbons in flue gases	$CuCo_2O_4$

Although rough estimates place the worth of the world products that have undergone a catalytic oxidation step at $ 20 to $ 40 billion, there are some important limitations in catalytic oxidation, which can be summarized as follows (Centi *et al*., 2000):

i) Because of the formation of undesired by-products, none of the reactions runs at maximum selectivity, and few reactions attain total or close-to-total conversion

ii) Processes can generate co-products that are not always of economic interest

iii) Some raw materials and products are suspected or proven carcinogens

iv) Some processes require expensive oxidizing agents.

1.2 General Requirements of the Catalysts for Industrial Processes

The criteria for industrially successful catalysts are very stringent. First, the catalyst must be able to affect the desired reaction at an acceptable rate under conditions of temperature and pressure that are practicable (Taufiq-Yap, 1997). Chemical technology has advanced to the point where temperatures as high as 1600 K and pressure up to 350 atm. If however good yields can be obtained at low temperatures and pressures, then there is every incentive to find a catalyst that will operate under the mildest possible conditions, since the use of extreme conditions is very costly. It is concurrently

important that side-reactions are minimal, especially those leading to poisoning or deactivation through carbon deposition on catalyst.

Second, the catalyst must be able to sustain the desired reaction over prolonged periods: in some processes, a catalyst life of several years is not uncommon, and is economically necessary. Clearly the longer it lasts, the smaller will be the contribution that its initial cost makes the overall cost of the process. Initial cost is rarely of over-riding importance: it is usually cheaper in the long run to use an expensive catalyst that will last a long time than a cheap one that has to be replaced frequently.

1.3 Catalytic Selective Oxidation Process

A large segment of the modern chemical industry is based on catalytic selective oxidation processes. Therefore, research in the area of selective oxidation is rapidly changing. In fact, the economic potential of any improvements in this area is enormous. It may be recalled, for example, that the economic impact deriving from the expected selectivity improvements in the largest scale petrochemical oxidation processes, is about US$ 1.4 billion, worldwide (Centi *et al*., 2000).

In brief, selectivity is the key aspect in the industrial development of oxidation processes, usually more than activity itself. The selectivity of a reaction is the fraction of the starting material that is converted to the desired product. It facilitates maximum