CATALYSIS for a Sustainable World

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31 JULY 2009

Dewan Taklimat
Bangunan Pentadbiran
Universiti Putra Malaysia

Universiti Putra Malaysia Press
Serdang • 2009
http://www.penerbit.upm.edu.my

First Print 2009

UPM Press is a member of the Malaysian Book Publishers Association (MABOPA)
Membership No.: 9802

Perpustakaan Negara Malaysia Cataloguing-in-Publication Data

Taufiq Yap Yun Hin
Catalysis for a sustainable world / Taufiq Yap Yun Hin.
(Inaugural lecture series)
Bibliography: p.53
ISBN 978-967-344-080-1
1. Catalysis--Environmental aspects. 2. Environmental chemistry.
3. Speeches, addresses, etc. I. Title. II. Series.
541.395

Design, layout and printed by
Penerbit Universiti Putra Malaysia
43400 UPM Serdang
Selangor Darul Ehsan
Tel: 03-8946 8855 / 8854
Fax: 03-8941 6172
http://www.penerbit.upm.edu.my

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ABSTRACT

Future global prosperity will depend on new or improved processes that are economically and environmentally sustainable. This is the paradigm shift of the early 21st century, driven by the threat of climate change and the increasing scarcity of raw materials. Catalysis has a leading role in many chemistry solutions, as the key enabling science in some cases, and as part of general technology in others.

Catalysts are used widely within chemical production, power production, refinery processes, conversion of natural gasses, chiral synthesis, agro chemistry, pharmaceutical processes, polymer and material production and biotechnology. The economic impact of catalysis is perhaps best illustrated by the fact that in the industrialized world heterogeneous catalysis is involved in 20-25% of the gross national products. Many of the major problems society is encountering, such as the need to create production in balance with the environment, better use of fuels, more economical energy production and the reduction of CO_2 and other green house gasses, will require solutions where catalysts play an important role.

Furthermore, the development of new catalysts and catalytic processes can open up new selective chemical processes which may lead to a considerable reduction of undesired by-products or waste products. Selective catalytic oxidation is one of the major areas in industrial chemical production. Vanadium phosphate catalyst is one of the most extensively used catalysts for several mild oxidation of hydrocarbons. Another example of catalytic technology development is the use of heterogeneous catalysts for promoting transesterification for the production of green biodiesel. Due to the high energy demand both in industrialized world and domestic sectors, and the pollution problems caused by the use of fossil fuels, it is necessary to develop a limitless duration with

smaller environmental impact of renewable energy sources. A lower cost of biodiesel can be obtained by using heterogeneous catalysts with higher quality of esters and glycerol.

INTRODUCTION

Catalysis plays a central role in the development of sustainable processes, which are of primary importance to allow present and future worldwide production and use of energy and chemicals while avoiding negative consequences for the environment. Future global prosperity will depend on new or improved processes that are economically and environmentally sustainable. This is the paradigm shift of the early 21st century, driven by the threat of climate change and the increasing scarcity of raw materials. Catalysts are used widely in several sectors including polymer production, agricultural production, and the petrochemicals, pharmaceutical and fine chemicals industries. The economic impact of catalysis is perhaps best illustrated by the fact that in the industrialized world heterogeneous catalysis is involved in 20-25% of gross national products. Many of the major problems society is encountering, such as the need to create production in balance with the environment, better use of fuels, more economical energy production and the reduction of CO_2 and other green house gasses, will require solutions where catalysts play an important role. Furthermore, the development of new catalysts and catalytic processes can open opportunities for new selective chemical processes which may lead to a considerable reduction of undesired by-products or waste products.

Basics of Catalysts and Catalysis

The term "catalysis" comes from two Greek words, "catal" and "lysein" which mean breaking down (Bond, 1987). It was first introduced by Berzelius in 1836. He defined catalysis as "the ability of substances to awaken affinities, which are asleep at a particular temperature, by their mere presence and not by their own affinity".

Ostwald proposed another definition in 1894 as it being a substance that accelerates the rate of chemical reaction without being consumed itself. The catalyst does not vary the thermodynamic equilibrium of reactions. Even before Berzelius coined the word ‘catalysis’ in its modern connotation in 1835, applied catalysis was already a reality. The writings of the Arabic alchemist, Jabir ibn Haiyan (Geber) in the 8th century reveal that mineral acid was used as a catalyst for the production of ether by the dehydration of alcohol even back then (Thomas, 1994).

Another definition is that a catalyst is a substrate which transforms reactants into products, through an uninterrupted and repeated cycle of elementary steps in which the catalyst participates while being regenerated to its original form at the end of each cycle during its lifetime (Boudart, 1991). A Catalyst influences not only the reaction rate, but also the distribution of products. Traditionally, catalytic systems are classified as either homogeneous or heterogeneous. Homogeneous catalysts are molecularly dispersed with the reactants in the same phase. This provides easy access to the catalytic site but can make the separation of catalyst and products difficult. Heterogeneous catalysts - usually solids - are in a different phase from the reactants, which reduces separation problems but provides more limited access to the catalytic site. Another type of reaction involves the enzymatic catalyst which is a subset of homogeneous catalysis where the reaction occurs by biological units.

The primary advantage of heterogeneous catalysts is that they are in a solid phase and can thus be easily be separated and recycled from the gas and/or liquid reactants and products. Thus the catalysts can be regenerated and last for several years before being replaced. In comparison, the homogeneous catalyst is difficult to recover and separate (Gates *et al.* 2008). Furthermore, most of homogeneous catalysts are normally highly acidic (*eg.* sulfuric acid) or base (*eg.* sodium hydroxide) and hence highly corrosive to the reactor unit

Heterogeneous catalysis plays an increasingly critical role in modern petrochemical industries as market demands for and specifications of petrochemical products are continuously changing (Lebedev, 1984). The petrochemical industry is an important sector in Malaysia with investments totalling RM 28 billion as at the end of 2004 (Razmahwata, 2005). The rapid growth of the industry is mainly attributed to the availability of oil and gas as feedstock and a well-developed infrastructure. Malaysia has the world's 13th largest natural gas reserves and 24th largest crude oil reserves. One of the major processes in the petrochemical sector is selective oxidation reactions. They have become of prime importance due to: (i) the great value of the compounds obtained by oxidation such as aldehydes, ketones, carboxylic acids and their anhydrides which are used as intermediates in orgarnic synthesis, solvent, monomers and as the feedstock for the production of polymeric, materials, plasticizers and so on; (ii) the wide range of various oxidation reactions in which many organic compounds, including all classes of hydrocarbons, can participate; and lastly (iii) the availability and low cost of most oxidising agents, the most important of which is air oxygen which makes the synthesis of some products by oxidation methods highly economical as compared with other possible methods of their manufacture (Centi *et al.*, 2001).

Catalysis: Sustainable and Green Chemistry

Catalysis is a necessary and critical tool for achieving social and economic objectives. Atom economy (introduced by Trost) is the first principle of green chemistry and is a parameter of synthetic efficiency. The concept of the *E* factor (environmental factor) proposed by Sheldon would be preferable. Defining waste as everything except the desired product, the *E* factor is the ratio (kg/kg) of by-products to products. Typical values are: oil refining (about 0.1), bulk chemicals (1–5 range) and pharmaceuticals (up to 100). By multiplying the *E* factor with an environmental quotient (*Q*) which depends on the nature of the waste, it is possible to obtain a weighted factor which allows the degree of "green chemistry" content of a chemical product to be classified. This concept is popular in the "green chemistry" community, but it is not very precise.

Industrial processes have now moved towards more efficient use of resources and improvement in selectivity, because both aspects correspond to an improvement in the process economics. An example of this process is the synthesis of maleic anhydride. The catalytic process starting from benzene was substituted with that using butane about 20 years ago for the following reasons:

- The loss of two carbon atoms (as starting from benzene) is avoided.
- The only by-products are carbon oxides and a minor amount of acetic acid. With benzene the selectivity is higher, but several by-products are formed requiring expensive separation.
- The toxicity aspects related to the use of benzene is avoided, reducing costs related to safety systems and benzene handling.

The butane process fully implements the principles of green chemistry *i.e.*:

(i) Use of non-toxic reactants.
(ii) Improved atom economy.
(iii) A complex multistep transformation (the reaction is a 14 e^- oxidation, with abstraction of eight H atoms from the butane

molecule and insertion of three O atoms) is realized in one single step, without using solvents.

(iv) Waste formation is minimized.

More than 95% of maleic anhydride plants use the butane process today. The reason, however, is not due to an early conversion of companies to the "green chemistry" philosophy. The use of the new process derives instead from the following economic reasons:

(i) Butane is cheaper than benzene and also requires less costly safety equipment.

(ii) The molar yield starting from butane instead of benzene is lower, but the weight yield (the relevant industrial parameter) is higher.

(iii) When a selective catalyst is available, reduction of process complexity means a reduction in both fixed costs and variable costs (utilities, labour, etc.).

(iv) Gas-phase reactions reduce the costs of separation.

(v) The formation of by-products and waste, besides a loss in selectivity, also implies higher costs of separation.

The butane process is now being adopted worldwide due to the better economics and the change is also in the direction of environmental protection. This is not an exception, but rather a common feature of most of the new chemical processes developed over the last two decades.

The process to obtain maleic anhydride from butane was possible only after the discovery of vanadyl pyrophosphate catalysts which possess unique characteristics of activity and selectivity unmatched in all other types of mixed oxides that have been studied for this reaction. Catalyst innovation is a key step in the development of new eco-efficient and also cost effective processes.

SELECTIVE OXIDATION OF LIGHT HYDROCARBONS

The possibility of developing new lower environmental impact and lower cost processes has recently generated interest in the transformation of light alkanes to valuable oxygenated compounds and alkenes by selective oxidation (Centi *et al.*, 2001). This is due to the abundance and low cost of the light alkanes such as ethane, propane and butane (Centi, 1993a). However, the possible utilisation of alkane feedstocks for selective oxidation reactions requires the discovery of a selective catalyst for the reaction, a difficult task due to alkanes being largely less reactive than most of the possible reaction products (Centi *et al.*, 2001). The selective oxidation of alkanes thus requires the development of novel concepts and catalytic systems to fulfil the strict requirements of controlled surface reactivity necessary for the selective behaviour (Centi, 1993a).

The production of maleic anhydride (MA) from *n*-butane over vanadium phosphorus oxide (VPO) catalysts is as yet the only industrial application of alkane selective oxidation (Centi, 1993b). This process typically achieves conversion of around 75% and selectivity near 67% (Hodnett, 2000). The vanadyl pyrophosphate, $(VO)_2P_2O_7$ which is obtained by activating the vanadyl phosphate hemihydrate, $VOHPO_4 \cdot \frac{1}{2}H_2O$ at temperatures of 673–723 K has been widely accepted as the most active phase of this reaction (Centi, 1993b). Another area with high potential for alkane oxidation commercialization is propane oxidation to acrolein and acrylic acid. Currently the feedstock is propene using two stage reactions with Bi-Mo as the active catalyst. Converting an abundant fuel like propane into a highly valuable chemical feedstock holds promise due to the lower cost of propane relative to propylene and propene. Provided that acrylic acid yields are close to those required for industrial applications, a single step process using propane as the feedstock would significantly reduce both costs and pollution. Direct synthesis of acrylic acid from propane results in not only cheaper feedstock, but also reduces process complexity.

Commercial Process for Maleic Anhydride Production from *n*-Butane

Maleic anhydride was originally produced almost exclusively by using benzene as the feedstock. However, beginning from 1974, *n*-butane was successfully used and replaced as the feed for MA production where the reaction is carried out at 673 K in gas phase and the catalyst is vanadium and phosphorus mixed oxide, used in bulk phase. In this reaction, eight hydrogen atoms are abstracted from *n*-butane, and three oxygen atoms are added to form maleic anhydride.

(1)

The primary reasons for replacing benzene with *n*-butane are (Centi *et al.*, 2001):

i. Lower cost of the raw material: *n*-butane is present in natural gas and it is also produced by steam cracking of oil;

ii. Better yield by weight: starting from benzene two CO_2 molecules are co produced;

iii. Lower environmental impact: benzene is classified as a carcinogen and thus requires severe and costly process control for environment and safety monitoring, this is not the case with *n*-butane;

iv. Low costs of MA separation and purification: from benzene some heavy compounds (such as phthalic anhydride and benzoquinone) are also byproduced, whereas *n*-butane oxidation is a very clean reaction with minimal formation of by-products (apart from carbon oxides only acetic acid).

These advantages compensate the higher capital cost due to (i) the reduced productivity (a plant using *n*-butane is about 15% more expensive than one using benzene for similar production, due to the lower catalyst productivity and lower explosion limits of the hydrocarbon-oxygen reagent mixture); (ii) the lower production of steam (the heat of reaction for benzene is 1875 kJ/mol against 1260 kJ mol for benzene); and (iii) the lower selectivity.

MA is produced from *n*-butane by different technologies: (i) fixed bed and (ii) fluidized bed. The transported bed technology was applied by DuPont in the last 5 years, but recently this plant has been shut down (Cavani *et al.*, 2006).

Table 1 summarizes the possible process technologies, which are distinguished by:

a. Type of reactor (fixed or fluid bed);
b. Recovery method of crude MA (anhydrous or aqueous);
c. Gas phase composition (from 1.8% of *n*-butane in air in the case of fixed bed, to 5% in the fluidized bed);
d. Employed catalyst (synthesis, activation step, presence of promoters and regeneration).

Table 1 Industrial Technologies for Maleic Anhydride Production from *n*-Butane (Centi *et al.,* 2001)

Process	Type of reactor	Recovery method
ALMA (Lonzagroup, Lummus)	Fixed bed	Anhydrous
Lonzagroup	Fixed bed	Anhydrous or aqueous
Mitsubishi Chemicals	Fixed bed	Anhydrous
Monsanto	Fixed bed	Anhydrous
Denka Scientific Design	Fixed bed	Anhydrous
DuPont	Transported bed	Anhydrous
BP (Sohio)-UCB	Fixed bed	Anhydrous

Depending on the employed technologies (fixed or fluidized bed) the selectivity to maleic anhydride is around 65-70% under typical industrial conditions (less than 2 molar % *n*-butane in air, with conversion from 70 to 85% between 673 and 723 K (Centi *et al.*, 2000)). Only maleic anhydride (or acid), carbon oxides and a trace amount of acetic acid are detected under such conditions.

Catalyst System

The vanadium phosphorus oxide has a remarkable and complex catalytic system. Various distinct and well characterised compounds can be formed, for example, α-, β-, γ-$VOPO_4$, $VO(HPO_4)\cdot 4H_2O$, $VO(HPO_4)\cdot 0.5H_2O$, $VO(H_2PO_4)_2$, $VO(PO_3)_2$ and β-, γ- $(VO)_2P_2O_7$ (Bordes, 1987). In past academic literature, focus has been mainly on the vanadyl pyrophosphate, $(VO)_2P_2O_7$ phase, which is claimed as the most active and selective in *n*-butane oxidation to maleic anhydride, which has been applied in industry since 1960 (Centi, 1993b; Hutchings, 2004).

Vanadyl pyrophosphate, $(VO)_2P_2O_7$ (VPP) has a layered structure in which two octahedral pairs share edges (Hutchings, 1991). The octahedral pairs are connected by PO_4 tetrahedra which gives a layer structure in a (020) plane. Double vanadyl chains (perpendicular to the (020) plane) are present (Figure 1 and Figure 2) (Cavani *et al.*, 1985).

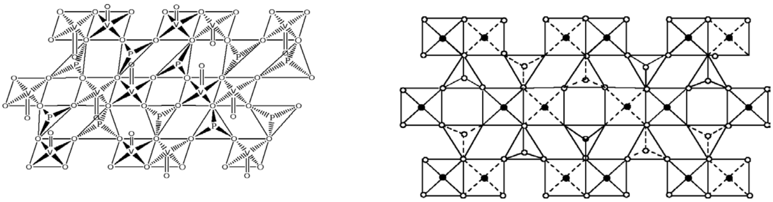


Figure 1 The Layered Structure of $(VO)_2P_2O_7$ (Cavani *et al.***,** 1985)

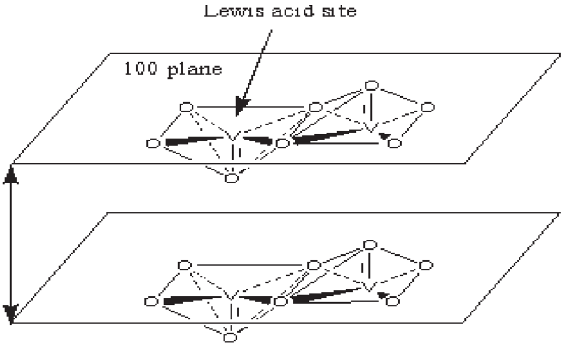


Figure 2 Idealized Vanadyl Pyrophosphate Structure (only vanadyl groups) in (020) plane (Cavani *et al.***,** 1985)

It has been widely accepted that the best performance of $(VO)_2P_2O_7$ is directly related to the presence and extent of exposed (020) facets, which is related to the (001) facet of $VOHPO_4•0.5H_2O$ (O'Mahony *et al.*, 2005). The $VOHPO_4•0.5H_2O$ and $(VO)_2P_2O_7$ phases possess similar crystal structures: the $[VOHPO_4]$ layers are hydrogen-bonded via HPO_4^{2-} groups in the precursor phase and become covalently bonded via pyrophosphate ($P_2O_7^{4-}$) groups during the thermal transformation to vanadyl pyrophosphate (Guliants *et al.*, 2001). The (020) basal plane of $(VO)_2P_2O_7$ where V–O–V pair sites are located and the side planes are non-selective is illustrated in Figs. 3 and 4 (Misono, 2002).

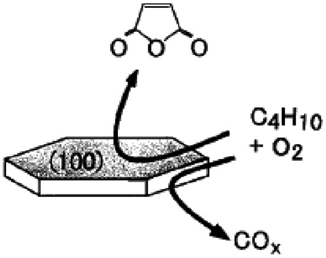


Figure 3 Catalytic oxidation of *n*-butane on the surface of $(VO)_2P_2O_7$ crystal. Selective moxidation to maleic anhydride takes place on the basal plane and deep oxidation on the (020) side planes (Misono, 2002).

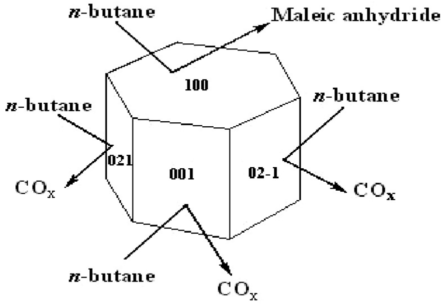


Figure 4 Selective and unselective oxidation site on crystal faces of $(VO)_2P_2O_7$ (Misono, 2002)

Modification of Vanadium Phosphate Catalysts

Due to the dissatisfaction of selectivity to maleic anhydride, several aspects of further improvement in the catalytic behaviour of VPP catalysts such as the chemistry of preparation, the nature of the active phase and active centres, the reaction mechanism, structure-activity relationship, reaction kinetics and the role of promoters have been shown over the past decade in a number of reviews (Hodnett, 1985; Hutchings, 1991; Centi, 1993b). Hodnett (1985) has extensively reviewed the role of the method of VPP catalyst preparation, such as the influence of method of active phase precursor preparation, P/V ratio, additives and activation conditions as well as some mechanistic aspects of the reaction. The role of promoters on VPP catalyst and reactant concentration for the selective oxidation has been expressed by Hutchings (1991). He has suggested that the roles of the promoters present in small amount could be: (i) to stabilise the average oxidation state of vanadium so that it would improve initial dehydrogenation of *n*-butane, and (ii) to control oxygen diffusion and adsorption and hence minimise the non-selective oxidation route. Centi (1993b) has examined the real nature of the active phase during the catalytic reaction such as the role of the V^{5+} species, the reaction mechanism, the relationship between reaction conditions, bulk and surface composition with catalytic behaviour, the reaction mechanism at a molecular level, the theoretical modelling behaviour and the surface mobility of adsorbed species. Recently, Hutchings (2004) looked into the new and optimal VPP catalysts preparation, the role of the promoters and the relative role of crystalline *versus* amorphous vanadium phosphate as active catalysts. However, even after all these investigations the nature of the active surface remains unclear. In this respect it is possible that the best or optimal vanadium phosphorus oxide materials are yet to be discovered and a number of preparation strategies can be envisaged to attempt to prepare improved catalytic materials. Therefore, there is still considerable space for further improvements in catalytic performance of the vanadium phosphorus oxide as oxidation catalysts. Several new techniques of preparation *i.e.* solvothermal (Taufiq-Yap and Rownaghi, 2007b) and microwave irradiation (Taufiq-Yap *et al.*, 2007b) methods will be discussed here.

Method of Preparation of Precursor

The methods for preparation of the catalyst precursor can be classified into four general methods *i.e.* aqueos, organic, dihydrate (Taufiq-Yap *et al.*, 2002; Hutchings, 2009) and hydrothermal (Taufiq-Yap and Mohd Hasbi, 2005; Taufiq-Yap *et al.*, 2006):

i) Aqueous method, VPA
The VPA method was used in early literature and uses water as the solvent. This was the original preparation method for VPO catalysts, which involved reducing V_2O_5 in an aqueous solution of hydrochloric acid, followed by addition of the phosphorus component, usually as 85 % *ortho*-H_3PO_4. The solid precursor was isolated by evaporation of the solvent. The presence of traces of chloride in the VPA method presents engineering difficulty, as it is corrosive to reactors. Significant amounts of an impurity $VO(H_2PO_4)_2$ was also obtained (Hutchings, 2004). This method produced catalysts with very low surface area (Taufiq-Yap *et al.*, 2002)

ii) Organic method, VPO
Due to the major disadvantage of the VPA method, a better method has been developed which substitutes both the acid and water needed in the aqueous method with organic solvents.

The precursor, $VOHPO_4.0.5H_2O$ is prepared by reduction of V_2O_5 by an alcohol to a partially soluble V^{4+} complex or suspensions, followed by addition of *ortho*-H_3PO_4, and isolation by precipitation (Hodnett, 2000). This organic method is found to be much better in terms of surface area, reducibility and mobility of oxygen species (Taufiq-Yap *et al.,* 2001d)

iii) Dihydrate method, VPD

This VPD method was first discovered by Johnson *et al.* (1984) and has continued to be investigated by Ellison *et al.* (1994) and Taufiq-Yap *et al.* (2003b, 2004b). In this method, an intermediate of V^{5+} dihydrate phase, $VOHPO_4.2H_2O$ is prepared by reacting V_2O_5 and H_3PO_4 using water as solvent before being further reduced (after dried) by isobutyl alcohol to $VOHPO_4.0.5H_2O$. By using primary alcohols, the material produced in the form of rosette clusters (Figure5) of thin hemihydrate can obtain a high surface area of 40 m^2g^{-1} (Sananes *et al.* 1996). TPR study of the VPD method prepared catalyst revealed a higher amount of lattice oxygen removed (Taufiq-Yap *et al.*, 2004b; Taufiq-Yap *et al.*, 2006b). This may explain the higher activity of this catalyst (*n*-butane conversion) due to the large amount of active oxygen species removed from the catalyst especially those linked to the V^{4+} phase (Taufiq-Yap *et al.*, 2009b).

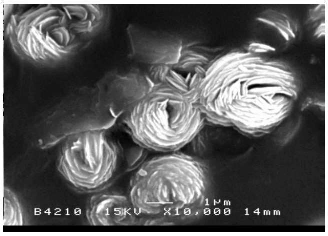


Figure 5 SEM micrograph of VPD catalyst (Taufiq-Yap *et al.*, 2006b)

iv) Hydrothermal method, VPH

Hydrothermal processing involves the chemistry of hot water under pressure to carry out precipitation reactions. The most recent method in preparing $VOHPO_4.0.5H_2O$ precursor is by reacting V_2O_5, *o*-H_3PO_4, water and oxalic acid in an autoclave at 383 K (Taufiq-Yap and Mohd Hasbi, (2005); Taufiq-Yap *et al.*, 2006a). The starting material and mineralizer were mixed uniformly before being discharged into a Teflon-lined cup with a filling capacity of 80 %, which was then sealed securely in a stainless steel container. The steel container was put into an oven at 423 K for 144 h. Subsequently, the autoclave was allowed to cool gently to room temperature. The powders obtained were centrifuged, washed with deionized water, and dried at ~373 K for 5 h. Taufiq-Yap *et al.* (2006a) synthesized two VPH catalysts via hydrothermal method with slight modification on the second one (VPH2). Both VPH catalysts exhibited only the highly crystalline pyrophosphate phase (Figure 6). SEM showed that the morphologies of these catalysts are in plate-like shape (Figure 7) and not in the normal rosette-type clusters. TPR in H_2 resulted in two reduction peaks at high temperature in the range of 600-1100 K (Figure 8). The second reduction peak appeared at 1074 K and occurred as a sharp peak indicating that the oxygen species originatiung from the V^{4+} phase are difficult to be removed and their nature less reactive compared to other methods of preparation. It is apparent that the hydrothermal synthesized catalysts have lower activity compared to VPO and VPD methods of preparation. However there is huge potential for improvement. In fact the modified VPH2 catalyst produces higher activity (35%), compared to only 7% for VPH1. Modified VPH2 gave better catalytic performance for *n*-butane oxidation to maleic anhydride contributing to a higher BET surface area, high mobility and reactivity of the lattice oxygen associated to the V^{4+} which is involved in the hydrocarbon's activation. A slight increase of the V^{5+} phase also enhanced the activity of the VPH2 catalyst. Modification of the VPH catalyst was also carried out with addition of dopants (Taufiq-Yap *et al,* 2009a) and mechanochemical treatment (Mohd. Hasbi and Taufiq-Yap, 2006). This will be discussed in the respective sections below.

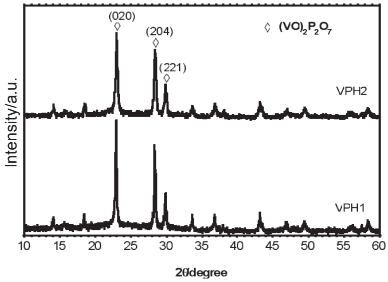


Figure 6 X-ray diffraction patterns of VPH1 and VPH2 catalysts

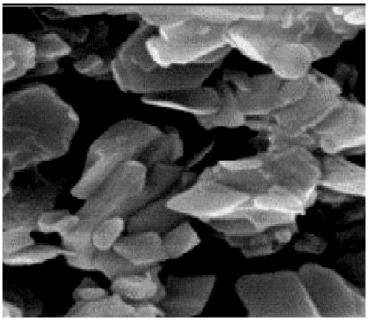


Figure 7 SEM micrographs for (a) VPH1 and (b) VPH2

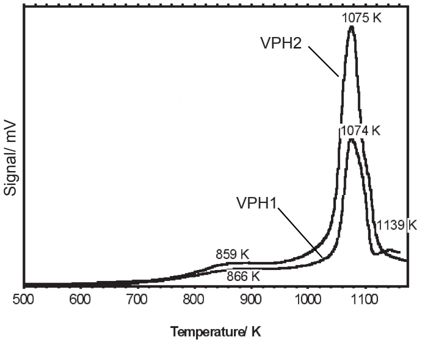


Figure 8 H_2 -TPR profiles of VPH1 and VPH2 Catalysts

An alternative precursor, vanadyl hydrogen phosphate sesquihydrate ($VOHPO_4 \cdot 1.5H_2O$) which was developed by Ishimura *et al.* (2000) was used to produce the VPP catalyst. It was prepared by the reduction of $VOPO_4 \cdot 2H_2O$ suspended in refluxed 1-butanol to give $(VO)_2P_2O_7$. Increasing the pretreatment duration of the sesquihydrate precursor in butane/air mixture at 673 K induced the formation of a new phase (V^{5+}) and a decrease of the surface area of the catalysts. The morphology of all the catalysts was shown to be in rosette-shape. However, significant changes were observed where the surface of the crystal platelet was getting cracked and rougher as the pretreatment duration increased. The consumption of H_2 in TPR showed that more lattice oxygen can be removed for the shortest period of pretreatment. This result is in contrast with the same catalyst prepared using the organic (VPO) method (Taufiq-Yap *et al.*, 2004a).

The phosphorus sources employed for the synthesis of $VOHPO_4 \cdot 0.5H_2O$ is normally H_3PO_4. This will have a strong influence on the synthesis of vanadium phosphate catalysts. $H_4P_2O_7$ was investigated as an alternative source (Taufiq-Yap *et al.*, 2004c). The catalyst was subjected to temperature programmed reactions in the *n*-butane/He environment. The most significant observation in the reaction study is that furan was observed as one of the intermediates found for this anaerobic partial oxidation of *n*-butane. This was not observed previously when using the same catalyst prepared using the 'classical' organic VPO method (Sakakini *et al.*, 2000).

Addition of Dopants

A wide range of cations have been added to vanadium phosphate catalysts and beneficial effects have been reported with: Co (Taufiq-Yap *et al.*, 2003; Taufiq-Yap, 2006; Sajip *et al.*, 2001; Abon *et al.*, 2001), Cr (Taufiq-Yap, 2006), Bi (Taufiq-Yap *et al.*, 2003b; Taufiq-Yap *et al.*, 2006), Fe (Taufiq-Yap *et al.*, 2005), Mo (Pierini and Lombardo, 2001), Ni (Taufiq-Yap and Abdul Ghani, 2007), K (Taufiq-Yap *et al.*, 2005b), Mn (Taufiq-Yap *et al.*, 2007c), Nb (Guliants *et al.*, 2000; Duarte de Farais *et al.*, 2002) and Ga (Sartoni *et al.*, 2004). The addition of the first row transition metals to vanadium phosphate catalysts is claimed to produce an improvement in the conversion of *n*-butane and maleic anhydride yield (Hutchings and Higgins, 1996). However, it appears that the way in which promoters are introduced is of crucial importance. A bimetallic promoter was also introduced to the VPP catalyst (Rownaghi *et al.,* 2009b) In general, the methods of preparing promoted catalysts are the same as those discussed for the unpromoted catalysts. Promoter compounds can be added either (a) together with the vanadium and phosphorus compounds prior to preparation of the catalyst precursor, or (b) by impregnation of the catalyst precursor prior to formation of the final catalyst by heat treatment (Hutchings, 1991).

In the course of reaction the activity of vanadium phosphate catalysts decreases as a result of the loss of phosphorus. One might expect that this process may be retarded by small additions of cations known to form stable phosphates. One of the possible cations which could give such an effect is cobalt (Zazhigalov *et al.*, 1993). Taufiq-Yap *et al.* (2006) revealed that cobalt lowered the temperature of the reduction peak associated with V^{5+} and increased the amount of oxygen species originated from the active phase, V^{4+} removed. Thus, it strongly improved the *n*-butane conversion without sacrificing the maleic anhydride selectivity. In another study, Co-promoted VPP catalyst (prepared via VPO method) also gave a higher conversion than the Cr-promoted catalyst. The enhancement of the catalytic performances of these promoted catalysts compared to unpromoted catalysts is attributed to the higher number of oxidants associated with the active V^{4+} phase as observed in the TPR experiments (Figure 9). A good correlation was observed between the oxygen species associated with V^{4+} and the *n*-butane conversion. The result shows that this specific oxygen species is highly active for partial oxidation of *n*-butane. A detailed discussion on the role of this active oxygen species is presented in following section..

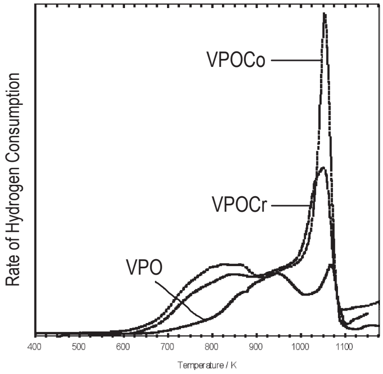


Figure 9 H_2 -TPR profiles of unpromoted, Co and Cr-promoted VPO catalysts

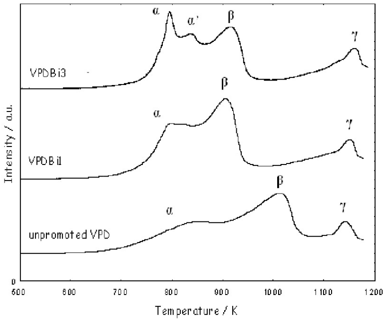


Figure 10 H_2 -TPR profiles of unpromoted and Bi promoted VPO Catalysts (1 and 3 %)

As reported earlier, selective oxidation of *n*-butane over the VPP catalyst was shown to proceed via a redox mechanism (Centi *et al.*, 1988). Hence the reduction behaviour of this catalyst is an indicator for the reaction performance. Addition of Bi significantly shifted the two major reduction peaks to a lower temperature region compared to the unpromoted catalyst (Figure 10). These two reduction peaks (α and β) which correspond to the removal of oxygen species linked to the V^{5+} and V^{4+} phases, respectively played a major role in the performance of the catalysts as shown in the increment of the conversion. A significant improvement in the oxygen's reactivity with an addition of Bi, by lowering the reduction activation energy, leads to enhanced catalytic performance for *n*-butane oxidation. Furthermore, the combination of these two types of oxygen species contributed to the hydrocarbon's activation. A correlation study of these oxygen species with the catalytic performance will also be discussed.

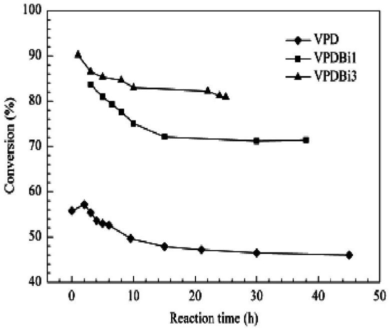


Figure 11 Time course changes of conversion oxidation of *n*-butane over unpromoted and promoted VPD catalysts (Taufiq-Yap *et al.*, 2006)

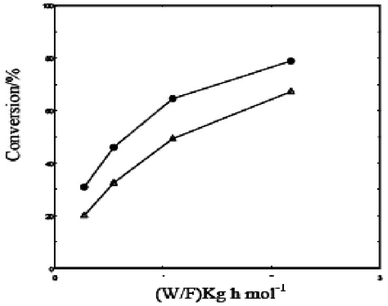


Figure 12 W/F dependence of conversion on *n*-Butane in : (•) undoped and (▲) Fe-doped (1%) Bi- vanadium phosphate catalysts prepared via VPD method (Taufiq-Yap *et al.*, 2005a)

Previous study (Hutchings *et al.*, 1996) has shown that Fe increases the specific activity up to a maximum level at ca. 2 mol% for vanadium phosphate catalysts prepared via VPO method. However, by using the VPD method, Fe reduced both the activity and selectivity (Figure 12). The main reason for this is that Fe^{3+} significantly lowered the amount of oxygen species removed which is linked to the V^{4+} and V^{5+} phases (Taufiq-Yap *et al.*, 2005a).

Mechanochemical Treatment

The mechanochemical method has been employed in the modification of the morphology and textural characteristics of the catalyst precursor to improve the catalytic performance of the vanadium phosphate catalyst. The most efficient mechanochemical treatment of the solids can be achieved by using the planetary ball mill. Zazhigalov *et al.* (1997) reported that the mechanochemical treatment could cause repeated fracture of the solids, reducing its particle size and corresponding increase of the specific area. In another study, the precursor, $VOHPO_4 \cdot 0.5H_2O$ was prepared by reduction of $VOPO_4 \cdot 2H_2O$ by isobutyl alcohol and subjected to a high energy planetary ball mill (1400 rpm) for 30, 60 and 120 mins in ethanol (Taufiq-Yap *et al.*, 2006). The ball milling process reduced the crystallite size of the catalysts and consequently increased their surface area. The morphologies of the milled catalysts are dependent on milling time. The highest reactivity and mobility of the lattice oxygen species has been achieved by the catalyst milled for 60 mins (Figure 13) with lower reduction peak temperature and higher amount of oxygen atoms removed. The oxygen species removed from the active V^{4+} phase was shown to be correlated with the rate of reaction. A good relationship was also found between the oxygen species associated with V^{5+} and MA selectivity. However, a larger amount of this oxygen species will have a deleterious effect on the conversion rate. This study also demonstrated that the mechanochemical method (with an appropriate duration) effectively enhanced catalytic activity by increasing the surface area and controlling the reactivity, and that the amount of oxygen species contributed to the partial oxidation of *n*-butane to MA.

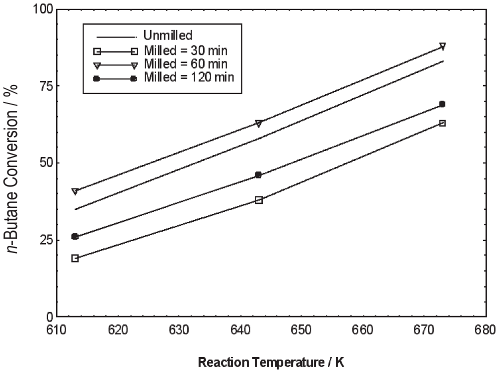


Figure 13 *n*-Butane conversion as a function of the reaction temperatures (Taufiq-Yap *et al.*, 2006)

Mechanochemical treatment was also subjected to Mn (Taufiq-Yap and Goh, 2005), Bi (Taufiq-Yap *et al.*, 2008), Cr-doped (Taufiq-Yap and Yeoh, 2008) and hydrothermal (VPH) prepared (Mohd. Hasbi and Taufiq-Yap, 2006) vanadium phosphate catalysts.

Organic method prepared Cr-promoted precursor, $VOHPO_4 \cdot 0.5H_2O$ was mechanochemical treated in cyclohexane for 2 h by using a high energy planetary ball miller followed by calcination in a flow of *n*-butane/air mixture at 673 K (Taufiq-Yap and Yeoh, 2008). The BET surface area of the milled catalyst showed that it possesses higher surface area (13 m^2g^{-1}) compared to the unmilled catalyst (6 m^2g^{-1}). Milling also caused a slight increment in the average oxidation state of vanadium as well as the percentage of V^{5+} oxidation state. The major diffraction peaks were broadened indicating a reduction of particle size. SEM micrographs showed the loss in the blossom morphology and the formation of layer packages, with more circular particles in the milled catalyst. The amount of active lattice oxygen species being removed from V^{4+}-O^- pairs increased significantly for mechanochemical treated

Cr-doped VPO catalyst leading to the enhancement of the catalytic activity for *n*-butane oxidation to maleic anhydride.

Similar to the Cr-doped VPO, the mechanochemical treatment also significantly increased the surface area of the hydrothermally prepared vanadium phosphate catalyst from 9.5 m^2g^{-1} for unmilled to 16 m^2 g^{-1} (Mohd. Hasbi and Taufiq-Yap, 2006). Milled VPH catalyst was also shown to have higher amount of V^{5+} phases and the *n*-butane conversion was improved (58% compared to 36% at 673 K and GHSV : 2400 h^{-1}). In conclusion, the presence of the $VOPO_4$ (V^{5+}) phase is important in controlling the catalytic activity for *n*-butane oxidation to MA. A higher amount of reactive and labile lattice oxygen and high development of (100) $(VO)_2P_2O_7$ face also contribute to the higher activity of milled catalysts.

Effect of Calcination Duration/Condition

Activation conditions and duration play an important role in obtaining the active site of VPP catalysts for *n*-butane oxidation to MA. The activation can be carried out either in air or hydrocarbon-air mixture atmosphere. In an earlier study on the calcination effect on VPP catalysts, three catalysts had been prepared by calcining vanadium hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) which was prepared in an organic medium, for different lengths of time (40, 100 and 132 h) in a *n*-butane (0.75%)/air mixture at 673 K (Taufiq-Yap *et al.*, 2000b; Taufiq-Yap *et al.*, 2001b; Waugh and Taufiq-Yap, 2003). The catalysts were designated VPO40, VPO100 and VPO132. Increasing the duration of reaction with *n*-butane/air mixture led to an increase in the total surface area from 21.3 (VPO40) to 24.9 m^2 g^{-1} (VPO100) and 27 m^2 g^{-1} (VPO132). It also led to the complete removal of the $VOPO_4$ phase from catalysts VPO100 and VPO132 and this $VOPO_4$ phase being seen as a minor component of catalyst VPO40. SEM showed that longer periods of pretreatment in the *n*-butane/air mixture produced catalysts with increasing amounts of a characteristic rosette-type of agglomerate (Figure 14). Increasing the duration of the butane/air pretreatment at 673 K resulted in a lowering in the amount of oxygen desorbed on temperature programming, indicating that the butane/air pretreatment was effectively reducing. However, and apparently paradoxically, increasing the duration of the butane/air pretreatment resulted in an increase in the amount of oxygen removed from the catalysts by temperature programmed reduction in H_2, rising from 11 monolayers for VPO40 to 14 monolayers for VPO100 and to 15 monolayers for VPO132. All three catalysts showed a reduction peak with a maximum temperature of $\sim$1000 K for the removal of 11 monolayers of oxygen, while catalysts VPO100 and VPO132 showed a second reduction peak at $\sim$1100 K for the removal of an additional three (VPO100) and four monolayers (VPO132) of oxygen.

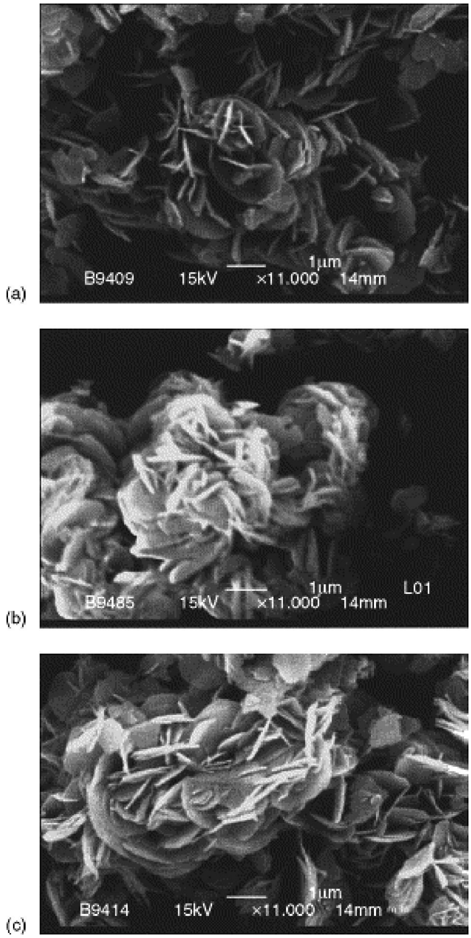


Figure 14 SEM micrographs of (a) VPO40, (b) VPO100 and (c) VPO132

The effect of different environments for calcination was also investigated. Vanadium phosphate catalysts synthesized via $VOPO_4{\cdot}2H_2O$ were calcined in two different hydrocarbon air mixture environments, *i.e.* *n*-butane/air and propane/air (Taufiq-

Yap and Saw, 2008). Both catalysts, denoted VPDB and VPDP respectively, exhibited a good crystalline with characteristic peaks of pyrophosphate phase. However, the peaks for VPDP were more prominent than those of VPDB (Figure 15). BET surface area showed that VPDB gave a higher surface area (23 $m^2 g^{-1}$) compared to VPDP (18 $m^2 g^{-1}$). The average V valence state for VPDP was 4.08 and the higher V valence state for VPDB was 4.26 due to the higher amount of V^{5+} for VPDB. Furthermore 14.2% of V^{3+} was found for VPDP but none for VPDB. SEM micrographs clearly revealed that the morphologies of both catalysts were composed of plate-like crystallite that was arranged in the characteristic rosette cluster. However, the catalyst calcined in *n*-butane/air environment (VPDB) resulted in an increment of the amount of plate-like crystal formed in the rosette rosebud agglomerates. TPR in H_2 profiles (Figure 16) of both catalysts gave two reduction peaks corresponding to two kinetically different oxygen species which were associated with the V^{5+} and V^{4+} phases, respectively. VPDB removed a larger amount of the active oxygen species linked to the V^{4+} phase which eventually caused a higher conversion rate in the selective oxidation of *n*-butane and propane to MA and acrylic acid, respectively.

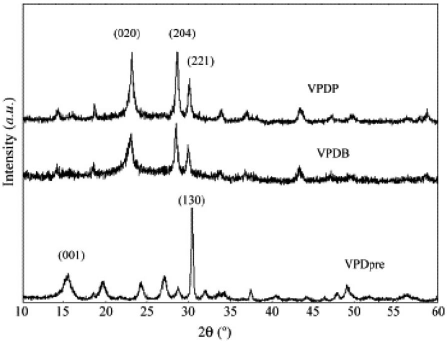


Figure 15 XRD patterns of VPDpre, VPDB and VPDP

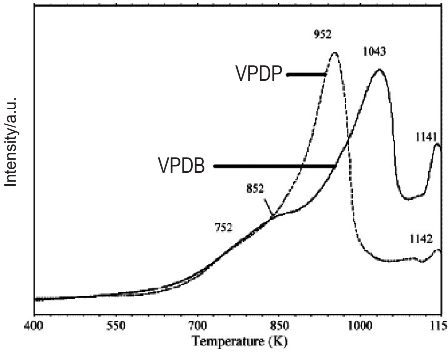


Figure 16 TPR profiles for VPDP and VPDB catalysts

Both catalysts (VPDP and VPDB) were tested for propane oxidation to acrylic acid at 673 K, this temperature being a typical operating temperature for VPO catalysts (Table 2). It is clear that propane/air calcined VPO catalyst, VPDP generally favoured the higher selectivity of AA. VPDB was found to be more active with 14.1% of propane conversion, while only 7.9% propane conversion rate was obtained by VPDP. This is in good agreement with the reduction behaviour of both catalysts as discussed earlier. Further, many papers have reported that the VPO catalysts containing discrete amounts of V^{5+} sites have in general a better catalytic performance in the oxidation of *n*-butane than the catalysts which exclusively contain V^{4+} sites (Volta, 2000). Han *et al.* (1992) also reported that the presence of a minor $VOPO_4$ (V^{5+}) phase in $(VO)_2P_2O_7$ was shown to be effective for propane oxidation. Our data clearly indicate that with the combination of minor V^{5+} sites in the bulk of the vanadyl pyrophosphate, the activity of the catalyst was enhanced. The selectivity towards acrylic acid (AA) of VPDP (81.5%) at 673 K was found to be significantly higher than for VPDB (57.7%). This indicates that the catalysts that calcined in the propane/air stream are more selective than the *n*-butane calcined catalysts. The difference may be due to the presence of V^{3+} in the propane/air calcined catalyst, VPDP. The selectivity towards AA and percentage of V^{3+} species for both catalysts showed a good relationship, clearly showing a trend of increasing percentage of selectivity towards AA with an increase of V^{3+} species percentage. This behaviour confirms the role of the V^{3+} species, which particularly improves selectivity towards AA in propane oxidation, and is in good agreement with our previous observation (Taufiq-Yap *et al.*, 2005c). The increase in selectivity lowers the contribution of the consecutive reaction of acrylic acid combustion. The enhancement of acrylic acid (AA) selectivity is balanced by the decrease of CO_x selectivity.

Table 2 The catalytic performance of VPDP and VPDB in propane oxidation

Catalyst	**Conversion of propane (%)**	**Product selectivity (%)**		
		AA	**CO**	**CO_2**
VPDP	7.9	81.5	0	2.2
VPDB	14.1	57.5	17.9	9.6

The catalytic performance of the VPDP and VPDB catalysts for *n*-butane oxidation to MA was also been tested at 613, 643 and 673 K, the latter being a typical operating temperature for VPO catalysts. Figure 17 shows the catalytic performance of VPO as a function of the reaction operating temperature. At 673 K, the *n*-butane conversion for VPDB and VPDP was excellent at 75% and 83%, respectively. As expected, the conversion of *n*-butane decreased with decreasing reaction temperature. The selectivity towards MA increased with decreasing operating temperature. However, it was also noted that there was a decrease in *n*-butane conversion with an increase of MA selectivity for both catalysts tested. Higher activity of VPDB compared to VPDP was also contributed by the higher amount of oxygen species removed associated with V^{4+} (~ 30% more). The role of the active oxygen species (O^-) is clearer now as this oxygen is the main factor for hydrocarbon activation which is the main determining step in light hydrocarbon oxidation.

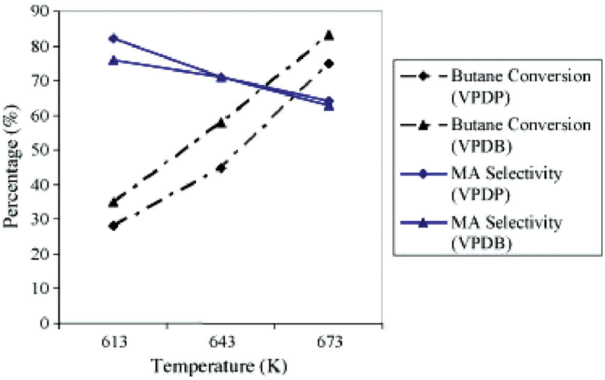


Figure 17 The catalytic performance of VPO catalysts (VPDP and VPDB) as a function of the reaction operating temperature in *n*-butane oxidation

Effect of Microwave Irradiation

Microwave heating has been shown to be a promising technique for catalyst preparation because of its heating characteristic (Dagani, 1997; Roussy *et al.*, 1994). The XRD patterns of VPP catalysts prepared via $VOPO_4 \cdot 2H_2O$ with microwave irradiation method appears to be different from that of the conventionally prepared ones (Taufiq-Yap *et al.*, 2007b; Rownaghi *et al.,* 2009c). The particle thickness at (020) plane for the microwave irradiated catalyst is generally smaller compared with the catalyst prepared via conventional heating. Furthermore, the particle thickness of (204) planes for all catalysts prepared by microwave heating is also smaller compared to the catalysts prepared by conventional heating. A smaller particle size at (020) plane may enhance the selectivity of the catalyst. The exposure of (020) plane would be of great significance in the improvement of the catalytic performance of vanadium phosphate catalysts.

Detailed investigation of the influence of microwave irradiation on undoped and doped VPP using TPR has shown that the total amount of the oxygen species removed from the microwave-heated catalyst is much higher than the conventional heated catalyst. A significant improvement of the catalytic performance (1.5% *n*-butane/air, 673 K, GHSV = 2400 h^{-1}) was obtained for the *n*-butane conversion (χ_{C4} = 74%) and for the selectivity of MA (S_{MA} = 60%) when the VPO catalyst was irradiated with microwave compared to the conventional heated catalyst (χ_{C4} = 25% and S_{MA} = 56%). This effect can be correlated with the increase of the BET area which is connected to the development of the (020) plane of $(VO)_2P_2O_7$. Higher amount of active site (V^{4+}) and its associated oxygen species which is responsible for activation of *n*-butane also contributed to enhancement of the activity. Furthermore, the smaller particle size at (020) plane obtained for the microwave irradiated catalyst, also strongly contributed to improvement of MA selectivity.

The Origin of the Selectivity of Maleic Anhydride

The oxidation of butane to maleic anhydride involves 7 O atoms and is a 14 electron process. The stoichiometry of the reaction is shown in Scheme 1. Aerobically, the oxidation of butane to maleic anhydride over a $(VO)_2P_2O_7$ catalyst occurs with a selectivity of ~65%. Anaerobically, the selectivity increases to ~80%. We have studied this reaction in some detail (Taufiq-Yap *et al.*, 1997a; Taufiq-Yap *et al.*, 1997b; Sakakini *et al.*, 2000). In a classic paper, Mars and van Krevelen (1954) postulated that the oxidizing species in hydrocarbon oxidation was the lattice O atoms of the oxide. Figure 18 shows the schematic representation of the reaction mechanism.

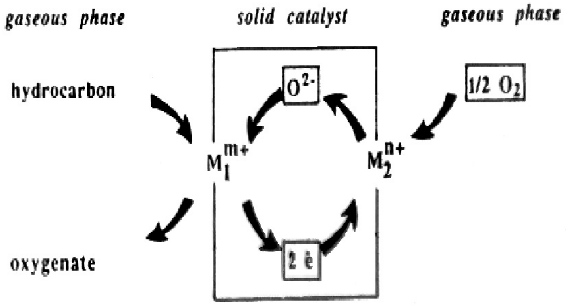


Figure 18 Schematic Representation of the Mars and van Krevelen Mechanism.

Apparent verification of this mechanism is to be found in the new process patented by DuPont (Lerou and Millsin, 1993). It is called a ‘Recirculating Solids Reactor’ and in it a butane/nitrogen mixture is passed over the catalyst in one wing of the reactor. The maleic anhydride, which is formed using the lattice O atoms of the catalyst, is removed from the catalyst, which is then moved to a regenerating reactor where it is re-oxidised. The re-oxidised reactor is then transferred back to the original tube. A schematic diagram of the reactor system is shown in Figure 19.

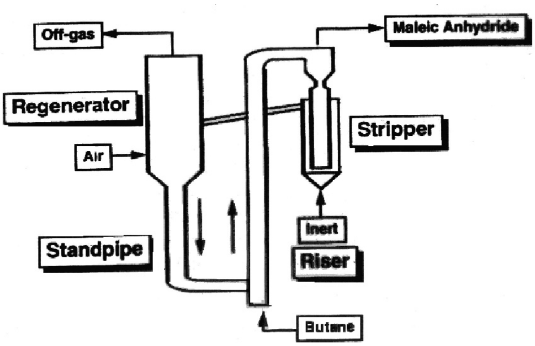
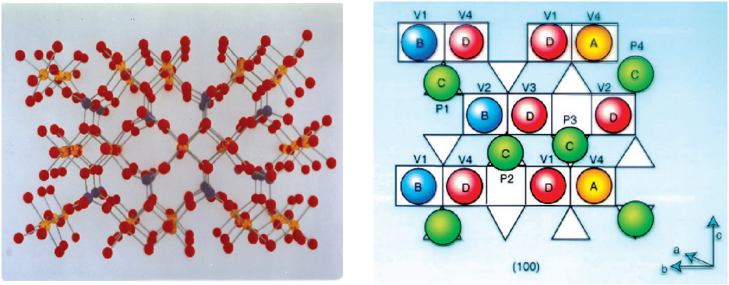


Figure 19 Recirculating Solids Reactor for MA Production

There is a plentiful supply of O atoms in the VPO lattice as can be seen by inspection of the crystallographic model of the (100) face of $(VO)_2P_2O_7$ shown in Figure 20(a). In the figure the red balls are O atoms, the orange balls are vanadium atoms and the blue balls are phosphorus atoms. A second representation of the arrangement of the O atoms on the (100) face of $(VO)_2P_2O_7$ is shown in Figure 20(b). The O atoms A, B and D are bonded to vanadium and the C atom is bonded to phosphorus. They are of increasing electronegativity.



(a) (b)

Figure 20 The arrangement of the O atoms on the (100) face of $(VO)_2P_2O_7$

Figure 21 is the O_2 desorption spectrum obtained by dosing pure O_2 at 673K for 1 h and cooling to 77K under the O_2. Two peaks are observed: (i) at a peak maximum temperature of 91 K corresponding to a desorption activation energy of 25 kJ mol^{-1} (This is physisorbed O_2) and (ii) at 1023K with a shoulder at 998 K. The total number of O atoms desorbed at these temperatures is 9.4 x 10^{14} atom cm^2. This is more than a monolayer coverage and so the O atoms are from the surface and subsurface regions of the $(VO)_2P_2O_7$ catalyst.

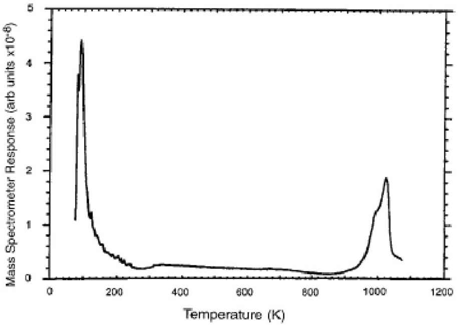


Figure 21 O_2 – TPD spectrum of VPP catalyst

It is possible to calculate the selectivity for each O atom reaction with butane. If x is the selectivity for O atom reaction, for an overall selectivity of 80% involving 7 O atom reactions, then

$$x^7 = 0.8$$

$$7 \log (x) = \log(0.8)$$

From this x = 0.97.

In other words, each O atom reaction must be 97% selective. The O atom reactions cannot, therefore, be random and the reaction must, therefore, be concerted. Recognising this fact, Bordes (1993), proposed the 'Crystallographic Model of Active Centres' (CMAS) in which the crystallographic arrangement of the O atoms on the (100) surface of $(VO)_2P_2O_7$ catalyst predisposed the structure of the adsorbed butane to produce maleic anhydride on reaction with the O atoms of that face. A schematic diagram of the CMAS model is shown in Figure 22.

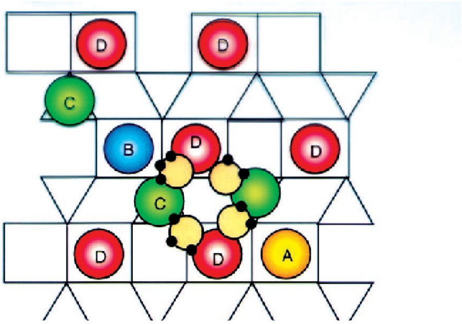


Figure 22 Crystallographic Model of Active Centres (CMAS) for (100) face of VPP Catalyst (Bordes, 1993)

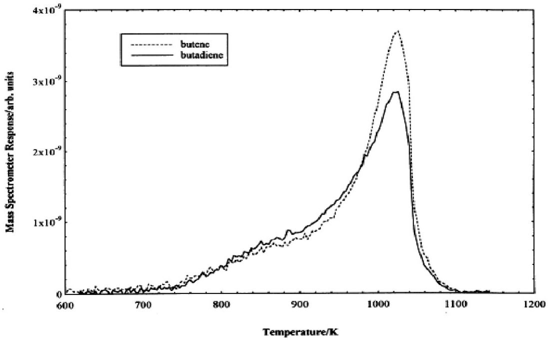


Figure 23 The reaction profile of the anaerobic temperature programmed oxidation of *n*-butane over the $(VO)_2P_2O_7$ catalyst. The dotted line is the butene curve and the solid line is the butadiene curve.

It can be seen from Figure 23 that but-1-ene and but-1-diene are formed simultaneously with the same kinetics. The mechanism of the reaction is, therefore, that it is not sequential whereby the butadiene is formed after the butene has been formed. Since the butene and butadiene are formed with the same temperature dependence as that of the appearance of O_2 from the lattice, the rate determining step in the reaction is the appearance of lattice O at the surface.

It can be seen from Figure 24 that the products butadiene, dihydrofuran and furan are all formed simultaneously. Again, the reaction is not sequential on the dihydrofuran and furan being formed successively. Here, also, the temperature dependence of all of the products follows that of the evolution of O_2 from the catalyst.

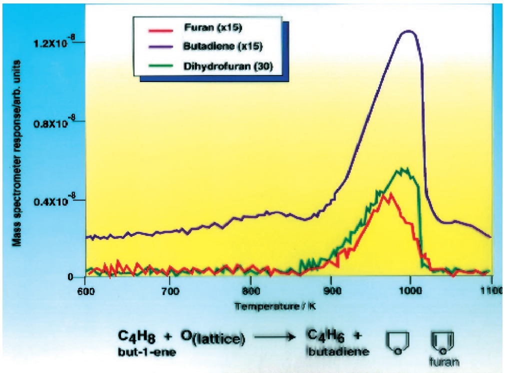


Figure 24 Anaerobic temperature programmed reaction profiles of but-1-ene over the $(VO)_2P_2O_7$ catalyst.

Figure 25 shows the anaerobic temperature programmed reaction profiles of but-1,3-diene over the $(VO)_2P_2O_7$ catalyst. In this figure it can be seen that furan and dihydrofuran are formed simultaneously at a peak maximum temperature of 990K. Maleic anhydride forms at a peak maximum temperature of ~1150K. All of these products follow the temperature dependence of the evolution of lattice O atoms at the surface.

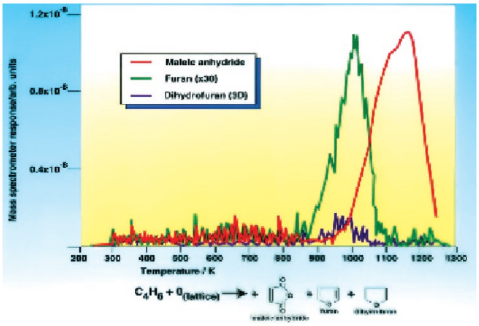


Figure 25 TPRn of but-1,3-diene over $(VO)_2P_2O_7$ catalyst.

In all cases the amounts of O atoms required for the quantities of products formed (3×10^{20} atom g^{-1}) is roughly the same as the amount of lattice O atoms which are desorbed. Hence, these desorbing O atoms appear to be 100% selective in both dehydrogenation reactions and O atom insertion reactions.

The source of the O atoms is the atoms which are found in the (201) direction in the $(VO)_2P_2O_7$ lattice. This direction in the lattice is indicated by the arrow in Figure 26 (Gai, 1999).

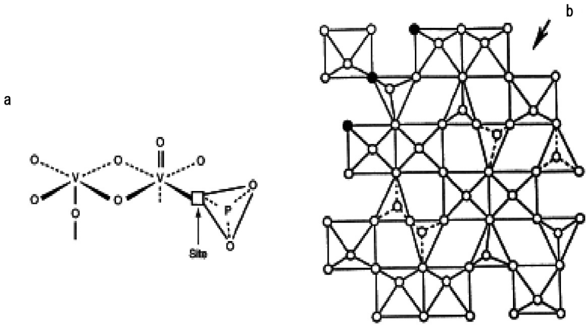


Figure 26 The position of Oxygen atom found in the (201) direction of $(VO)_2P_2O_7$ lattice.

Synthesis of High Surface Area Nanostructured Vanadium Phosphate Catalysts

Nanotechnology has gained substantial popularity recently due to the rapidly developing techniques both to synthesize and characterize materials and devices at the nano scale, as well as the promises that such technology offers to substantially expand the achievable limits in many different fields including medicine, electronics, chemistry and engineering. Nano size noble metal particles have occupied a central place in heterogeneous catalysis for many years, long before recognition of nanotechnology (Kung and Kung, 2004). The invention of a new method for preparation of the VPP catalyst precursor increased the full width at half maximum (FWHM) and reduced the particle size of the catalysts and consequently increased their surface area without affecting the principal phase structures of $VOHPO_4 \cdot 0.5H_2O$ and $(VO)_2P_2O_7$ (Taufiq-Yap and Rownaghi, 2007 and 2008). This new method of preparation promoted a significantly high surface area (>50 m^2g^{-1}) for the VPP catalyst which provides a high active site for reaction to occur. The active VPP catalyst has linear relationship between light alkane conversions with the catalyst surface area (Hutchings, 2004). The increase in the surface area may be associated with the morphologies of the catalysts by increasing the pore volume. To a greater extent the surface area may be increased by decreasing the mean pore width value of the catalyst. Nanostructured VPP promoted a significant increment in *n*-butane conversion and MA selectivity. The development of this method also reduced the preparation duration of vanadium phosphate catalyst from 26 h to only 6 h.

In another study, nanostructured VPP catalysts were also prepared via nanostructured V_2O_5 (Figure 27) obtained through sonochemical treatment (Taufiq-Yap *et al.*, 2009c) using a different type of mineralizer (Taufiq-Yap *et al.*, 2009d). However, the catalytic performance of this nanostructured VPP is considered low as compared to the one prepared using nanostructured vanadium triisopropoxide oxide (40% selectivity at 50% conversion) as starting material (Salazar *et al.*, 2007). In conclusion, the shape and the starting vanadium source are the main factors affecting the properties of the catalyst synthesized.

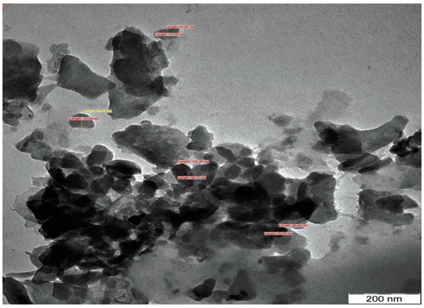


Figure 27 TEM Micrograph of Nanostructured VPP Catalysts Prepared Via Sonichemicated bulk V_2O_5 in KCl.

Significant role of V^{5+} and V^{4+} with their Associated Oxygen Species

The main active component of the effective VPO catalysts comprises of the V^{4+} phase known as $(VO)_2P_2O_7$. However, the presence of certain amounts of V^{5+} phase also contributed to better performance of the catalyst. Generally, redox mechanism or Mars & van Krevelen mechanism is well accepted for selective oxidation of alkanes with the participation of lattice oxygen. However, different oxygen species associated with a unique oxidation state of active metal presence in the oxide catalyst also play a significant role in the partial oxidation (Taufiq-Yap *et al.*, 2006b). Since a mixture of V^{4+} and V^{5+} are necessary in order to provide a highly reactive and selective catalyst then this will also affect the number of different oxygen species.

A good correlation of *n*-butane conversion and V^{4+} phase was observed as shown in Figure 28. This suggested that the V^{4+} species *i.e.* pyrophosphate phase is highly active for *n*-butane conversion. A minimum of ~ 10% of V^{4+} is necessary to activate the *n*-butane. MA selectivity is shown to be proportionate with the V^{5+} phase at lower percentage (< 30%). However, when the amount of V^{5+} exceeds ~ 43%, the MA selectivity was found to drop drastically (Figure 29). High amount of V^{5+} phase also deteriorated the conversion of *n*-butane (Figure 30). Having excess of V^{5+} phase with low amount of V^{4+} clearly inhibits the activity of the catalyst. Several V^{5+} phases (α_{II}-$VOPO_4$, β-$VOPO_4$ and γ-$VOPO_4$) were observed on the VPO catalysts. Only α_{II}-$VOPO_4$ was shown to be beneficial for *n*-butane oxidation. However, presence of a small amount of V^{5+} can also enhance the catalytic activity.

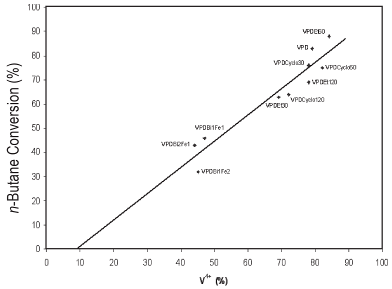


Figure 28 *n*-Butane conversion as a function to the percentage of V^{4+}

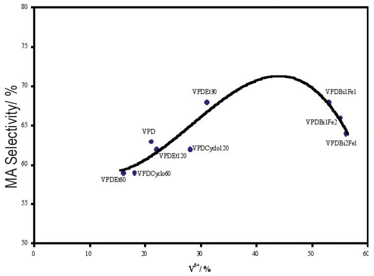


Figure 29 MA selectivity as a function to the percentage of V^{5+} phase

TPR in H_2 shows two reduction peaks which correspond to the removal of two kinetically different oxygen species *i.e.* O^{2-} and O^{-} which are associated with V^{5+} and V^{4+} phases, respectively. Electrical conductivity used by Herrmann *et al.* (1997) shows that the O^{-} and O^{2-} species are associated with V^{4+} and V^{5+}, respectively. The availability and behaviour of these oxygen species play an important role in determining the catalytic performance.

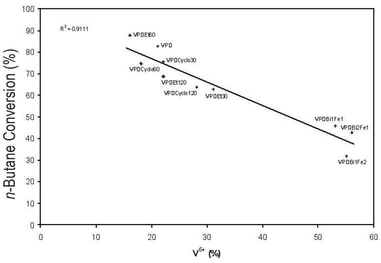


Figure 30 Correlation between *n*-butane conversion and with V^{5+} phase

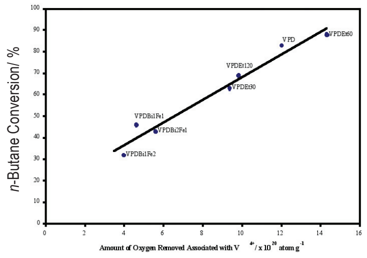


Figure 31 Correlation between *n*-Butane conversion and oxygen Species Associated with V^{4+}

There is a direct relationship between the amounts of oxygen removed from V^{4+} with the reaction rate of *n*-butane (Figure 31). The role of this oxygen species assigned to O^- highly contributed to the conversion of the *n*-butane. A low amount of oxygen species associated with V^{4+} removed from BiFe-doped catalysts clearly showed poor activity of these catalysts. Correlation between the percentage of V^{4+} and oxygen species removed associated with V^{4+} showed that at least 30% of V^{4+} is necessary to provide an active site for *n*-butane activation. The dependence of the *n*-butane conversion on the highly reactive oxygen species suggested that the release of the O^- anion from the surface of the VPO catalyst is the rate determining step for activation of *n*-butane. V^{4+} contributed to the abstraction and scission of C-H bonding of *n*-butane and this was shown to be a major role (Taufiq-Yap *et al.*, 2009e). The oxygen species associated with V^{5+} also showed good correlation with MA selectivity (Figure 32). However, an excess of this type of oxygen species significantly reduced catalytic activity (Figure 33). The catalytic performance of the catalysts also revealed that the oxygen species ratio of O^{2-} to O^- is important to provide high activity for the catalyst. Figure 34 shows that an optimal value of a ratio of O^{2-} to O^- is shown to be 0.23 in order to provide high activity.

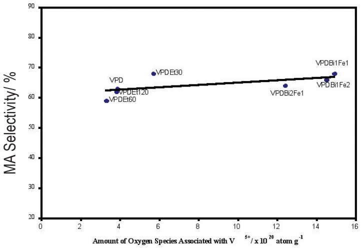


Figure 32 Correlation between MA selectivity and oxygen Species associated with V^{5+}

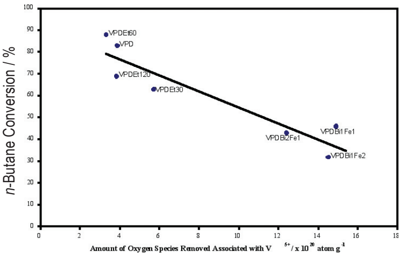


Figure 33 *n*-Butane conversion as a function of to the amount of oxygen species associated with V^{5+}

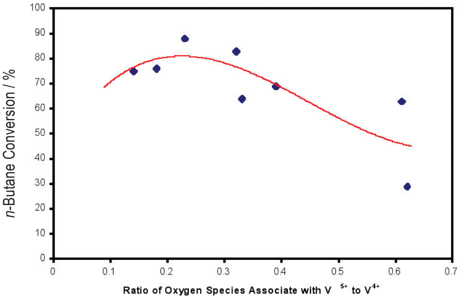


Figure 34 Relationship between *n*-Butane Conversion and the Oxygen Species ratio Associate with V^{5+} to V^{4+}

Propane Oxidation to Acrylic Acid over Vanadium Phosphate Catalyst

In the present economic circumstances, the high cost of propylene production prompted the development of research on production of aldehydes and acids from propane through selective oxidation. The saturated hydrocarbon is three or four times cheaper and also much less chemically active due to π-electrons and no empty orbital. Converting an abundant fuel like propane into a highly valuable chemical feedstock holds promise due to the lower cost of propane relative to propylene and propene. Provided that acrylic acid yields are close to those required for industrial applications a single step process using propane as feedstock would significantly reduce both costs and pollution. Direct synthesis of acrylic acid from propane provides not only cheaper feedstock, but also reduces process complexity.

The one-step oxidation of propane in gas phase with molecular oxygen to acrylic acid follows the equation below:

$$C_3H_8 + 2O_2 \rightarrow CH_2{=}CH\text{-}COOH\,(g) + 2H_2O \qquad \Delta H = -171\ \text{kcalmol}^{-1} \qquad (2)$$

This catalyzed reaction, which involves the transfer of eight electrons, most likely requires the coordinated efforts of several active sites, as well as balanced reduction-oxidation properties of the catalyst to complete the catalytic cycle. Compared to the propylene oxidative dehydrogenation, this reaction requires the transfer of more electrons or oxygen atoms. In terms of product stability, acrylic acid, the desired product in propane oxidation, is less stable and more prone to further oxidation than acrylonitrile and maleic anhydride, the desired products in propane ammoxidation and *n*-butane oxidation, respectively. Part of the instability of acrylic acid is likely to be related to the additional adsorptive ability of its acid functional group onto the catalyst surface, which renders it susceptible to further oxidation.

The excellent performance of the VPP catalyst in *n*-butane selective oxidation has stimulated great interest in propane selective oxidation to acrolein and acrylic acid (AA). Ai (1986) reported that the VPO catalyst is one of the catalysts with the best performance among those proposed for propane oxidation although acrylic acid selectivity and the yields are still low. The yield of acrylic acid reached 7.5 mol% at propane conversion of 46% and the selectivity is about 15 mol%. These days, acrylic acid is produced through a double step process starting from propylene (Lin, 2001). A single step process using propane as feedstock would significantly reduce both cost and pollution (Landi *et al.*, 2003). $(VO)_2P_2O_7$ was found to be the major crystal phase in VPO catalysts active in *n*-butane oxidation (Cavani and Trifiro, 1994) and propane oxidation (Han *et al.*, 1992).

Effect of Calcination Duration and Environments

The effect of varying the duration of the propane/air pretreatment at 673K on the structural, morphological and catalytic performances of the $(VO)_2P_2O_7$ catalysts produced for propane oxidation to AA are reported as follow (Taufiq-Yap *et al.*, 2005c). $VOHPO_4{\cdot}0.5H_2O$ synthesized by $VOPO_4{\cdot}2H_2O$ and isobutanol was activated in a flow of propane/air mixture (1% propane in air) at 673 K for 36, 75 and 132 h. The three vanadyl pyrophosphate catalysts obtained were denoted as VPD36P, VPD75P and VPD132P. The crystallinity of all the propane/air pretreated catalysts as shown in XRD increased with the duration of calcination. SEM micrographs showed the formation of more isolated platelets and more prominent rosebud-shape agglomerate when the pre-treatment was longer. Four reduction peaks maxima at 752, 920, 1026 and 1140K were observed in the rate of hydrogen consumption for VPD36P (Figure 35).

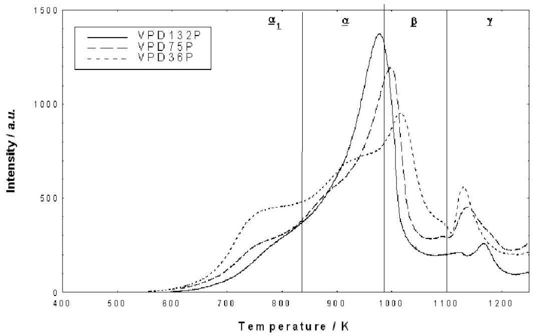


Figure 35 H_2-TPR profiles for VPD36P, VPD75P and VPD132P catalysts

As the calcination duration increased to 75 h, the H_2 reduction peaks shifted to lower temperatures at 750, 882, 1004 and 1140 K. When the calcination duration was further increased to 132 h, only three reduction peaks were observed at 752, 952 and 1142 K. Despite the progressive shift of the major reduction peak maximum as the duration of calcination increased from 36 to 132 h, the lattice oxygen from VPD36P was found to be the most reactive.

The catalytic performance for propane oxidation to acrylic acid showed that VPD36P had the highest activity (9.6 %) with 83.0 % of selectivity to acrylic acid.

Effect of Dopants

Great efforts have been made to modify the VPO catalyst formulation and the preparation method to improve the catalytic performance. Some interest has been directed at the chemical modification of VPO catalysts. The first report using the VPO catalyst for selective oxidation of propane was carried out by Ai (1986) using Te-promoted VPO catalysts. He observed that a small addition of TeO_2 further increased the selectivity and yield to acrylic acid. Han *et al*. (1992) found that the addition of Zr significantly enhanced acrylic acid selectivity. Ieda and co-workers (2005) investigated the effect of several promoters and reported that $(VO)_2P_2O_7$ catalysts promoted with Sb, Ti and Zr increased the selectivity to acrylic acid significantly.

The addition of 1, 2 and 5 mol % of Zr dopant into vanadium phosphate (VPO) catalysts produced a single pyrophosphate phase synthesized via $VOPO_4{\cdot}2H_2O$ method with different degrees of crystallinity (Taufiq-Yap and Saw, 2008). 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 was significantly low. The SEM micrographs for all the Zr modified catalysts gave rough rosebud agglomerates as compared to the undoped catalyst. The VPDZr1 catalyst was found to be the most selective catalyst among all the Zr doped catalysts in propane oxidation to acrylic acid.

SOLID HETEROGENEOUS CATALYSTS FOR HIGHER GRADE BIODIESEL

The search for alternative and sustainable fuels has gained more importance due to several current situations *i.e.* (i) gradual depletion of world petroleum reserves, (ii) increase in the price of petroleum and (iii) environmental concerns about air pollution caused by the combustion of fossil fuels. Biodiesel is a renewable fuel which consists of fatty acid methyl esters (FAME) derived through transesterification of vegetable oils, animal fat and also recycling of oil from the food industry with methanol. Biodiesel is recognized as "green fuel" with several advantages, *i.e.* safe, non-toxic and biodegradable compared to petroleum diesel. It is oxygenated and essentially free of sulfur and aromatics making it a cleaner burning fuel with reduced emission of SO_x, CO, unburnt hydrocarbons and particulate matter. Moreover, using biodiesel as a fuel in a car can give many advantages *eg*. it is not harmful to the environment, does not require engine modification, it is cheap, makes the vehicle perform better, the car last longer, reduces the environmental effect of waste products and is energy efficient. However, when compared to the cost of diesel obtained from petroleum, the high cost is the main drawback in biodiesel production. However, the cost of biodiesel could certainly be lowered by improving the production process. The first step in this direction could be represented by the use of heterogeneous catalysts instead of homogeneous ones.

Current technology processes for biodiesel manufacturing employ transesterification of triglycerides with methanol using homogeneous acid or base catalysts. The homogeneous acid-catalyzed process often uses hydrochloric acid and sulfonic acid as a catalyst. The problem with this process is the costly separation of the catalyst which is also corrosive to equipment and toxic (Chai *et al.*, 2007). Moreover, the reaction time is very long and a high molar ratio of methanol to oil is needed (30-150:1 mol %) (Xie *et al.*, 2006a; 2006b). Potassium hydroxide and sodium hydroxide are usually used as a homogeneous base-catalyst. These base catalysts show better performance in obtaining biodiesel but, they also react with free fatty acids (FFA) to form unwanted soap by-products in which an expensive separation is required (Kiss *et al.,* 2006). Since the homogeneous catalysts can cause many problems and increase the production cost, they can be replaced by environmentally friendly heterogeneous catalysts because of environmental constraints and simplifications in the existing processes. Moreover, heterogeneous catalysts can be more easily separated and produces higher quality of ester products and glycerol by-products. In this case, pure high grade glycerol can be obtained without expensive refining operations (Serio *et al.*, 2007). Most heterogeneous catalysts employed for transesterification are solid bases. Solid base catalysts have higher activity and faster reaction rates as compared to solid acid catalysts. However solid base catalysts are very sensitive to the presence of FFA and water (He *et al.*, 2007). In contrast to solid bases, solid acid catalysts can be applied to feedstock with high FFA and water. Furthermore, by using solid acid catalysts no polluting by-products are formed and the catalysts do not have to be removed since they do not mix with the product. When compared to liquid acids that possess well-defined acid properties, solid acids may contain a variety of acid sites. However, transesterification using solid acids is not yet well established in industry, as it is more difficult to find a suitable solid acid catalyst for long-chain acids compared to shorter acids such as acetic acid.

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water. The reaction is represented by the general equation below:

$$\underset{\text{Ester}}{RCOOR^1} + \underset{\text{Alcohol}}{R^2OH} \longleftrightarrow \underset{\text{Ester}}{RCOOR^2} + \underset{\text{Alcohol}}{R^1OH} \qquad (3)$$

Transesterification is a reversible reaction and proceeds essentially by mixing the reactants. However, the presence of a catalyst accelerates the conversion (Meher *et al.*, 2004). The transesterification process is affected by the mode of reaction condition, molar ratio of alcohol to oil, type and amount of catalysts, reaction time and temperature and purity of reactants.

The advantage of using heterogeneous catalysts for making biodiesel via FAME is now well understood. The main problem is finding a suitable catalyst which is active, selective and stable under process conditions. Based on this, our laboratory is progressively working on the search for the right material as the heterogeneous catalyst for transesterification reaction (Taufiq-Yap *et al.*, 2008b). However, recently biofuel has been blamed as one of the causes for the worldwide rapid increase in food prices. A big market for biofuels has created a new and significant source of demand for some agricultural commodities such as sugar, corn, cassava, oilseeds and palm oil. This increase in demand, according to a report prepared by the UN's Food and Agriculture Organization (FAO, 2008) "*has been one of the leading factors behind the increase in their prices in world markets which, in turn, has led to higher food prices.*" Due to this reason, we are working mainly on waste cooking oil and non-edible oils such as Jatropha oil. Jatropha oil is a non-edible oil obtained from the *Jatropha curcas* plant. *Jatropha curcas*, an agro-forestry crop is a genus comprising 70 species growing in topical and sub-tropical countries. Jatropha's natural habitat spans across sub-Saharan Africa, India, South East Asia and China. *Jatropha curcas* is a low-growing tree, generally planted as a hedge to protect crops from animals. It can be grown on barren land under harsh conditions and can be cultivated as part of the strategy for reclaiming degraded lands (Rathore and Madras, 2007). It grows rapidly, takes approximately 2–3 years to reach maturity and generate economic yields. It has a productive lifespan in excess of 30 years. The seed kernel contains 40–60% (w/w) oil. Saturated fatty acids constitute 20% of this, with the remaining being unsaturated ones. Oleic acid is the most abundant (44.8%) followed by linoleic acid (34%), palmitic acid (12.8%) and stearic acid (7.3%). The fatty acid composition of Jatropha oil is similar to other edible oils but the presence of some anti-nutritional factors such as toxic phorbol esters renders this oil unsuitable for cooking purposes. Jatropha oil is thus a promising candidate for biodiesel fuel production in terms of availability and cost. Jatropha oil makes the biodiesel fuel production more feasible for industrial applications compared to other edible vegetable oils (Shah and Gupta, 2007).

Transesterification of Jatropha Oil with Methanol to Biodiesel using Ca-based Mixed Oxide Catalysts

Transesterification of Jatropha oil (JCO) with methanol over calcium-based mixed oxides catalysts (CaO-MgO and CaO-ZnO) have been investigated batchwise at 338 K and 1 atm, in order to evaluate their potential as heterogeneous catalysts for biodiesel production (Taufiq-Yap and Lee, 2009). CaMg oxide and CaZn oxide catalysts were prepared via a conventional coprecipitation of the corresponding mixed metal nitrate solution in the presence of a soluble carbonate salt at ~ pH 8-9. The catalysts were characterized by X-ray diffraction (XRD), temperature programmed desorption using CO_2 (CO_2-TPD) and N_2 adsorption (BET). The conversion of JCO by CaO-MgO and CaO-ZnO were studied and compared with the calcium oxide (CaO) catalyst. Both CaO-MgO and CaO-ZnO catalysts showed high activity similar to pure CaO and were easily separated from the product. CaO-MgO mixed oxide was found to be more active than CaO-ZnO mixed oxide in the transesterification of JCO with methanol. Under suitable transesterification conditions at 338 K (catalyst amount = 3 wt. %, methanol/oil molar ratio = 15, reaction time = 6 h), ME content of >90% can be achieved over CaO-MgO and CaO-ZnO catalysts with the Ca/M ratio of 0.25. Even though CaO gave the highest activity, the conversion of JCO decreased significantly after the forth run whereas the conversion was only slightly lowered for the CaO-MgO and CaO-ZnO catalysts even after the sixth run (Figure 36).

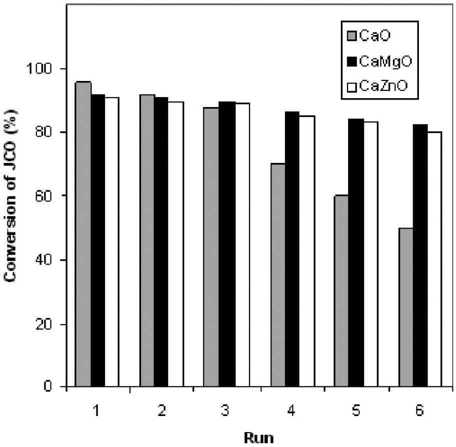


Figure 36 Reusability study of CaO, CaO-MgO and CaO-ZnO catalysts. Reaction condition: Jatropha oil 10 g, catalyst amount 3%, reaction temperature 338 K, reaction time 6 h, methanol/oil ratio 15:1.

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BIOGRAPHY

Professor Dr. Taufiq Yap Yun Hin was born in Kota Kinabalu, Sabah. His primary education began at SRJK St Agnes in 1974 and he then continued his secondary education at SMJK All Saints, Kota Kinabalu, Sabah from 1980 to 1986. He then pursued the Diploma in Agriculture in 1987 at Universiti Pertanian Malaysia (now known as Universiti Putra Malaysia, UPM) at the Bintulu, Sarawak Campus. One year later, he was promoted to pursue the Bachelor of Science degree majoring in Chemistry in the same university at the Serdang, Selangor Campus. He graduated with a Bachelor of Science (Hons) degree majoring Chemistry in 1992 and later a MSc degree in April 1994 in the area of Natural Products Chemistry, both from UPM.

His career in UPM began in July 1993 as a tutor. In April 1994, he embarked on his PhD studies in the area of heterogeneous catalysis at University of Manchester Institute of Science and Technology (UMIST), United Kingdom, which he graduated in June 1997. Upon return from his studies he was appointed as a lecturer in the Department of Chemistry, UPM in 1997 and was later promoted to Associate Professor in May 2002. He was promoted to Full Professor in October 2007.

Professor Taufiq Yap is involved in the teaching of several chemistry courses at degree level. This includes organic chemistry, petroleum refining processes, petrochemicals, catalysis and industrial chemistry. At postgraduate level, he is responsible for teaching Research Methodology in Chemistry and Spectroscopy. He is also involved with a number of administrative duties such as as Principal/College Master of Pendeta Zaaba College (2000-2003), Chairman of Committee for Management of Integrity in Administration (2004-2006), Coordinator for Industrial Training for

Chemistry (2001-2003), Member of Curriculum Committee (1997 – now), Member of Research Committee (2009-2010) and several others. He was appointed as the founding Coordinator for the Centre of Excellence for Catalysis Science and Technology (PutraCAT) in September 2008, the first such Centre of Excellence in the Faculty of Science, UPM. He has also been supervising 1 post-doctoral, 15 PhD students (including 7 students as main supervisor), 33 MSc students and more than 100 final year student projects. To date, 11 PhD (including 6 students as main supervisor) and 21 MSc students have graduated.

Professor Taufiq Yap's research interests encompass a broad area involving heterogeneous catalysis, advanced materials and natural products chemistry. He has received 13 research grants including those from the Malaysian Ministry of Science, Technology and Innovation and private company. Professor Taufiq Yap's research interest in catalysis lies in determining the nature of adsorbed hydrocarbons and oxygen species which ultimately leads to the high selectivity and activity observed in the partial oxidation reaction on metal oxide catalysts, development of heterogeneous catalysts for biodiesel production, dry reforming of methane and biomass conversion to syngas and bio-oil. He developed the first catalysis Laboratory in the university (since 1997) and led the Putra Laboratory for Catalysis Science and Technology before it was upgraded to a Centre of Excellence in September 2008. His research interest in advanced materials is on synthesis and application of activated carbon and photodegradation of dyes and chemicals using photocatalyst, TiO_2 whereas his research interest in natural products chemistry lies in the isolation and structural determination of bioactive compounds from Rutaceae and Anonaceae.

He has received several awards at Invention and Research Exhibitions at university, national as well as international levels.

He has also organized a few international and national congresses including playing the role as Secretary for the 16th National Seminar on Natural Products (2000), Secretary for the 7th Annual Seminar on Industrial Chemistry (2000), Chairman for the 1st (2000) and 2nd (2006) Malaysian Conference on Catalysis, Committee Member for 13th (2000) and Chairman for International and 19th (2006) Malaysian Symposium on Analytical Chemistry, Herbal Symposium (2003), 4th Malaysian International Conference on Essential Oils and Fragrance and Flavour Materials (2005), International Conference and Exhibition on Green Chemistry (2006) and National Committee Member for the 12th Asian Chemical Congress (2007). Professor Taufiq Yap has also been appointed a member of the International Advisory Board for the 5th Asia Pacific Conference on Catalysis (APCAT5) which will be held in Sapporo, Hokkaido, Japan in 2010.

Professor Taufiq Yap has authored and co-authored a total of 123 articles in various international and national refereed journals including those with high impact factor. He has also successfully filed three patents *i.e.* two in the Malaysian Patent Office (MyIPO) and one in PCT. In addition, over hundreds of papers have been presented by him at local and international conferences. This includes being Plenary Speaker at the Indonesian Chemistry Seminar (2006) and Keynote Speaker at the 12th Asian Chemical Congress (2007) and 10th Asian Conference on Analytical Sciences (ASIANALYSIS X) (2009). He was also an Invited Speaker at the International Conference and Exhibition on Green Chemistry (2006), 8th Eurasia Conference on Chemical Sciences (2006), Annual Fundamental Science Seminar (2006) and Regional Annual Fundamental Science Seminar (2007).

He has also been invited to be a reviewer/referee for several international high impact factor journals. He is currently a member of the Editorial Board for Catalysis Survey from Asia and Bulletin of Catalysis Society of India, and the International Advisory Board for the Bulletin of Chemical Reaction and Catalysis.

Professor Taufiq Yap has received several awards from the faculty and university such as the Potential Researcher Award (2001), Excellent Researcher Award (2002 and 2005), Eminent Scientist Award (2003) and Excellent Service Award (2005). At the national level, he has been awarded the prestigious Young National Scientist Award by the Malaysian Ministry of Science, Technology and Innovation for his outstanding research performance in 2002. Recently, Professor Taufiq Yap received the Outstanding Young Malaysian Award 2008 for the Science and Technology Development category from the Junior Chamber International Malaysia and MASS Young Researcher Award 2008 from the Malaysian Solid State Science and Technology Society (2008). He received the Overseas Advanced Research Fellowship twice from the Malaysian Ministry of Science, Technology and Innovation to undertake research in the area of heterogeneous catalysis from Oct-Dec 2004 and Jun-July 2007 at the School of Chemistry, Cardiff University, United Kingdom. This research was in collaboration with the well-known Professor G. J. Hutchings.

Professor Taufiq Yap has been a Chartered Chemist and Professional Member (CChem., MRSC) of the Royal Society of Chemistry, U.K. since 1997. In September 2008, he was awarded as a Fellow (FRSC) of The Royal Society of Chemistry, United Kingdom. He was also elected as an Associate Member of the Malaysian Institute of Chemistry (since 2004). He is currently a committee member of the Asia Pacific Association of Catalysis Societies (APACS) and member of the Malaysian Natural Products Society. He was elected as an Honorary Treasurer (2004) and Executive Council member (2005) of the Academic Staff

Association of Universiti Putra Malaysia and Executive Board Member of the Malaysian Analytical Sciences Association (2006-2009).

ACKNOWLEDGEMENTS

First of all, I would like to express my gratitude to all my colleagues (and teachers) and collaborators in the Department of Chemistry, Faculty of Science, UPM, all members and staff of the Centre of Excellence for Catalysis Science and Technology, Faculty of Science, UPM, all my dedicated postgraduate and undergraduate students working in my research groups as well as other individuals for being together with me for knowledge advancement.

I also gratefully acknowledge Universiti Putra Malaysia, Ministry of Science, Technology and Innovation and Centre of Excellence for Catalysis Science and Technology for their financial support.

My special appreciation and thanks also go to the former Head of Department of Chemistry *i.e.* Prof. Dr. Karen Badri, Prof. Dr. Mawardi Rahmani, Prof. Dr. Md Jelas Haron and Prof. Dr. Zulkarnain Zainal; my former supervisors, Emeritus Prof. KC Waugh (UMIST now known as The University of Manchester) and Prof. G. Hutchings (Cardiff Catalysis Institute, Cardiff University); my collaborators, Prof. Mohd. Zobir Hussein (UPM), Dr. Nicholas Dummer, Dr. Jonathan Bartley (Cardiff University), Prof. Dr. Mohd. Ambar Yarmo (UKM), Assoc. Prof. Dr. Irmawati Ramli (UPM), Assoc. Prof. Dr. Yuichi Kamiya (Hokkaido University) and Prof. J. M. Lopez Nieto (ITQ, Spain). Special thanks also go to my collaborators in Natural Products Chemistry *i.e.* Prof. Dr. Gwendoline Ee, Prof. Dr. Mawardi Rahmani, Prof. Dr. Mohd. Aspollah Sukari, Prof. Dr. Faujan Hj Ahmad, Prof. Dr. Abdul Manaf Ali and Prof. Dr. Asmah Rahmat.

Last but not least, my loving thanks to all my family members - my beloved wife, Amalina Abdullah, daughter – Farah Hannani Yap, sons – Danial Anas Yap, Adam Anas Yap and Danish Anas Yap, dad - Allahyarham Abdullah Lim Heng Fui and mum - Aishah Chin Szi Kiaw; for all their love, endless support and understanding. May God Bless you all.

LIST OF INAUGURAL LECTURES

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3. Prof. Dr. Abdul Rahman Abdul Razak
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4. Prof. Dr. Mohamed Suleiman
   Numerical Solution of Ordinary Differential Equations: A Historical Perspective
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5. Prof. Dr. Mohd. Ariff Hussein
   Changing Roles of Agricultural Economics
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6. Prof. Dr. Mohd. Ismail Ahmad
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   6 April 1994

7. Prof. Dr. Mohamed Mahyuddin Mohd. Dahan
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   20 April 1994

8. Prof. Dr. Ruth Kiew
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9. Prof. Ir. Dr. Mohd. Zohadie Bardaie
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10. Prof. Dr. Shamsuddin Jusop
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11. Prof. Dr. Abdul Salam Abdullah
    Natural Toxicants Affecting Animal Health and Production
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12. Prof. Dr. Mohd. Yusof Hussein
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    9 July 1994

13. Prof. Dr. Kapt. Mohd. Ibrahim Haji Mohamed
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14. Prof. Dr. Hj. Amat Juhari Moain
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    6 Ogos 1994

15. Prof. Dr. Law Ah Theem
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16. Prof. Dr. Md. Nordin Hj. Lajis
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17. Prof. Dr. Sheikh Omar Abdul Rahman
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18. Prof. Dr. Mohamed Shariff Mohamed Din
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19. Prof. Dr. Tengku Azmi Tengku Ibrahim
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20. Prof. Dr. Abdul Hamid Mahmood
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22. Prof. Dr. Nik Muhammad Nik Abd. Majid
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