

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231391362>

Novel Synthesis Techniques for Preparation of Ultrahigh-Crystalline Vanadyl Pyrophosphate as a Highly Selective Catalyst for n-Butane Oxidation

ARTICLE in INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JANUARY 2010

Impact Factor: 2.59 · DOI: 10.1021/ie902011a

CITATIONS

7

READS

21

2 AUTHORS:



Ali Rownaghi

Georgia Institute of Technology

26 PUBLICATIONS 235 CITATIONS

SEE PROFILE



Yun Hin Taufiq-Yap

Putra University, Malaysia

265 PUBLICATIONS 2,009 CITATIONS

SEE PROFILE

Novel Synthesis Techniques for Preparation of Ultrahigh-Crystalline Vanadyl Pyrophosphate as a Highly Selective Catalyst for *n*-Butane Oxidation

Ali Asghar Rownaghi^{*,†} and Yun Hin Taufiq-Yap[‡]

Department of Chemical Engineering, Monash University, Victoria 3800, Australia, and Department of Chemistry, Universiti Putra Malaysia, 43400, Selangor, Malaysia

The vanadyl hydrogen phosphate hemihydrate ($\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$), with well-defined crystal size, has been successfully synthesized for the first time, using a simple one-step solvothermal process that was free of surfactants and water and had a short reaction time and low temperature. The synthesis was performed via the reaction of V_2O_5 and H_3PO_4 with an aliphatic alcohol (1-propanol or 1-butanol) at high temperatures (373, 393, and 423 K) in a high-pressure autoclave. The mixture of reactions directly gave the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, which is a valuable commercial catalyst precursor for the selective oxidation of *n*-butane to maleic anhydride. The catalyst precursors were dried by microwave irradiation. The reaction conditions (by varying the reducing agent and reaction temperature) were used further for optimization of the crystallite size, surface area, morphology, and activity of the nanostructure of vanadium phosphate oxide $[(\text{VO})_2\text{P}_2\text{O}_7]$ catalyst. This new method significantly reduced the preparation time and lowered the production temperature (50%) of catalyst precursor ($\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$), when compared to conventional hydrothermal synthesis methods. The as-prepared $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst under various conditions exhibited remarkably different physical and chemical properties, indicating the potential of the suggested method in tuning the crystalline structure and surface area of $(\text{VO})_2\text{P}_2\text{O}_7$ to improve its catalytic performance. It was found that the length of the carbon chain in an alcohol and reaction temperature in the solvothermal condition had a great impact on the chemical and physical properties of resulting catalysts. Interestingly, there was no trace of $\text{VO}(\text{H}_2\text{PO}_4)_2$, which is an impurity noted to be readily formed under solvothermal preparation conditions. The precursors and catalysts were characterized using a combination of powder X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area measurement, scanning electron microscopy (SEM), and temperature-programmed reduction in hydrogen (H_2 -TPR). A correlation between the surface area of the catalyst and the activity was observed. Finally, the yield of maleic anhydride was significantly increased from 21% for conventional catalyst to 38% for the new solvothermal catalyst.

1. Introduction

Vanadyl pyrophosphate catalyst (VPO) is well-known as a commercial catalyst for the selective oxidation of *n*-butane to maleic anhydride, and experimental studies have shown that vanadium phosphates are also effective catalysts for propane and pentane partial oxidation.^{1–4} Most of the attention has focused on the vanadyl hydrogen phosphate hydrate phase ($\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$), which is transformed under reaction conditions to give a complex mixture of V^{4+} and V^{5+} phases.⁵ The preferred industrial catalyst is synthesized from $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ to form an active catalyst comprised of $(\text{VO})_2\text{P}_2\text{O}_7$ with α -, γ -, and δ - VOPO_4 by *in situ* activation in *n*-butane/air.⁶ Although many preparation methods have been cited, virtually all are based on the reaction between a vanadium compound (typically V_2O_5), a phosphorus compound (typically H_3PO_4), and a reducing agent/solvent (typically an alcohol).⁷ The alcohol is intercalated into the layer structure of the VPO compounds, and the subsequent removal on heat treatment plays a central role in establishing the final surface area of the catalyst. The alcohol can also play a role in establishing the morphology of the vanadyl hydrogen phosphate hydrate, which, because the transformation to the final catalyst is topotactic, controls the morphology of the final catalyst.⁸ Therefore, the solvent clearly plays a valuable and identifiable function in the preparation of VPO materials. When the alcohol is used as a reducing agent,

it is oxidized to form an aldehyde or ketone.⁷ Most researchers agree that it is essential that the desired precursor $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ is produced in a form that is as pure as possible. In particular, it is known that the material $\text{VO}(\text{H}_2\text{PO}_4)_2$ can be deleterious when present as an impurity in the catalyst precursor, because it reduces the surface area of the activated catalyst and, consequently, these catalysts display poorer catalyst performance.^{8,9} Various synthesis methods have been developed to obtain vanadyl hydrogen phosphate hemihydrate ($\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$) with controlled catalytic properties. Among them are four widely used techniques: (i) the VPA method, which was used in the early literature¹⁰ with water as the solvent; (ii) the VPO method, which is considered to be the standard preparation method and is used in most academic studies;^{7,12} (iii) the VPD method, which was first disclosed by Horowitz and co-workers¹² and further described by Johnson et al.,⁷ and has subsequently been investigated in detail;^{5,13,14} and (iv) the hydrothermal method, by which these catalysts have been synthesized by slow hydrothermal synthesis, requiring the presence of surfactants as the template agent at 423 K for 144 h.^{15,16}

Recently, the solvothermal technique has attracted much interest in the synthesis of novel and essential materials.^{17,18} However, the literature reveals no studies focused on the preparation of vanadium phosphate catalyst using solvothermal synthesis at lower high temperatures (373, 393, and 423 K). We will show that $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ can be crystallized in alcohols at temperatures lower than that required by hydrothermal conversion. In this paper, we report the successful preparation of crystalline vanadyl hydrogen phosphate hemihydrate ($\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$) via this new technique. The direct (one-

* To whom correspondence should be addressed. Tel.: +613 9905 3147. Fax: +613 9905 5689. E-mail addresses: ali.rownaghi@eng.monash.edu.au, alia.rownaghi@gmail.com.

[†] Department of Chemical Engineering, Monash University.

[‡] Department of Chemistry, University Putra Malaysia.

Table 1. Preparation Condition and Methods of the VPO Catalysts

precursor	catalyst	preparation condition	precursor heating
VPHA1	VPOA1	V_2O_5 + o - H_3PO_4 + 1-propanol + 373 K	microwave
VPHA2	VPOA2	V_2O_5 + o - H_3PO_4 + 1-propanol + 393 K	microwave
VPHA3	VPOA3	V_2O_5 + o - H_3PO_4 + 1-propanol + 423 K	microwave
VPHB1	VPOB1	V_2O_5 + o - H_3PO_4 + 1-butanol + 373 K	microwave
VPHB2	VPOB2	V_2O_5 + o - H_3PO_4 + 1-butanol + 393 K	microwave
VPHB3	VPOB3	V_2O_5 + o - H_3PO_4 + 1-butanol + 423 K	microwave
VPH1	VPO1	VPO method (V_2O_5 + o - H_3PO_4 + benzyl alcohol + isobutanol)	microwave
VPH2	VPO2	VPD method ($VOPO_4 \cdot 2H_2O$ + isobutanol)	microwave

step) synthesis is performed in an aliphatic alcohol (such as 1-propanol or 1-butanol) as the solvent and V_2O_5 and H_3PO_4 as starting materials without employing any high cost template or surfactant. We have been exploring a controlled solvothermal synthesis of orthorhombic phase $VOHPO_4 \cdot 0.5H_2O$ via a simple variation of reducing agents. We previously attempted to modify the preparation procedure for $VOHPO_4 \cdot 0.5H_2O$ synthesis under reflux conditions at ambient pressure in either isobutanol or ethylene glycol and water.^{19–21} In this study, however, we have developed a preparation method using a high-pressure technique. The vanadium phosphate catalysts were synthesized in an autoclave system under higher reaction temperature and pressure. This synthesis strategy provides some substantial advantages, including the following: (i) product is obtained in excellent yield in a one-pot synthesis, using a self-assembly strategy; (ii) the technique is simple and low cost (free of surfactants and water); (iii) no impurity-phase $VO(PO_3)_2$ is produced in the resultant catalyst; (iv) a lower amount of reducing agent is used; (v) a higher active surface area catalyst is produced as compared to conventional methods; (vi) preparation time is reduced by 50%; and (vii) reaction temperature is significantly reduced.

In this study, vanadium phosphate catalysts were prepared via three different methods, namely, (i) conventional VPO, (ii) conventional VPD, and (iii) the new solvothermal method synthesis method. The information presented by this work provides a basis for the development of an improved solvothermal method for the synthesis of VPO catalyst.

The effects of the carbon number, polarity, and viscosity of the alcohol and the drying of vanadyl hydrogen phosphate hemihydrate by microwave (MW) heating on the physicochemical properties and morphology of the solid solution and catalytic reactivity for n -butane oxidation are discussed.

2. Experimental Section

2.1. Catalyst Preparation. V_2O_5 and H_3PO_4 (85%) were purchased from Fluka and Merck suppliers, respectively. All alcohols were purchased from BDH Chemical and were used without any further purification. Preparation conditions under which the samples were synthesized are listed in Table 1. Three different techniques for $VOHPO_4 \cdot 0.5H_2O$ synthesis under ambient and high-pressure conditions were performed: the VPO method, the VPD method, and the proposed new solvothermal method (called VPS).

2.1.1. The VPO Method. The VPO method is considered to be the standard preparation method and is used in most academic studies. In this method, V_2O_5 was refluxed with H_3PO_4 with an alcohol, and a blue precursor was obtained as a precipitate. This precipitate was composed almost exclusively of the hemihydrate $VOHPO_4 \cdot 0.5H_2O$.⁷ A detailed description of precursor production has been reported in previous studies by Rownaghi and Taufiq-Yap²² and by other research teams.^{23–25} The light blue solid was recovered by filtration and dried for 5

min using a microwave irradiation method (this solid is denoted as VHP1). The heating conditions were a frequency of 2450 MHz and an output power of 300 W.

2.1.2. The VPD Method. Vanadyl phosphate dihydrate ($VOPO_4 \cdot 2H_2O$, VPD) was prepared according to the procedure described by Johnson et al.,⁷ at ambient pressure; this process has subsequently been improved using different reducing agents and promoters.^{14,19–21} Details regarding the preparation and characterization of $VOPO_4 \cdot 2H_2O$ can be found in Rownaghi et al.²³ and are omitted here for the sake of brevity. The reduction of $VOPO_4 \cdot 2H_2O$ with alcohols at ambient pressure produced $VOHPO_4 \cdot 0.5H_2O$, which is a valuable commercial catalyst precursor for the oxidation of n -butane to maleic anhydride.²³ The resulting blue solid (which is denoted as VHP2) was recovered by filtration and then heated for 5 min in a microwave, as mentioned previously.

2.1.3. The Proposed New Solvothermal Method (VPS). In this research, we report the excellent yield in a one-pot synthesis by a self-assembly strategy of crystalline vanadyl hydrogen phosphate hemihydrate ($VOHPO_4 \cdot 0.5H_2O$) via this technique. Vanadium(V) pentoxide (V_2O_5) and *ortho*-phosphoric acid (o - H_3PO_4) were used as the reactants without any pretreatment, and primary aliphatic alcohols (1-propanol and 1-butanol) were added as the solvent and reducing agent. The autoclave (50-mL capacity, Teflon-lined stainless steel) was filled to about two-thirds of the total volume and then sealed. In the next step, the autoclave was heated and maintained at high temperatures (373, 393, and 423 K) for typically 72 h. The system was then allowed to cool to ambient temperature. The resulting precipitate (blue solid) was then recovered by filtration and repeatedly washed with hot distilled water and acetone to remove the residual reactants and byproduct. The resulting hot blue solid was recovered by vacuum filtration, and washed with hot distilled water. The obtained blue solid was then subjected to 5 min of MW heating, as mentioned previously. All precursors synthesized via the three heating methods previously indicated contained $VOHPO_4 \cdot 0.5H_2O$, which was identified by powder X-ray diffraction (XRD). The calcination of obtained precursors was conducted in a furnace. The precursors were heated at the rate of 2 °C/min at 733 K for 6 h under a flow of 1.5% n -butane/air mixture.

2.2. Catalyst Characterization. **2.2.1. X-ray Diffraction (XRD).** XRD was performed to determine the bulk crystalline phases of the catalysts using a diffractometer (Shimadzu, Model XRD 6000) employing Cu K α radiation ($\lambda = 1.54439$ Å) to generate diffraction patterns from powder crystalline samples at ambient temperature. The spectra were scanned at a rate of 2.0°/min in the 2θ range of 10°–60°.

2.2.2. BET Surface Area. The total surface area of catalysts was measured by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption at 77 K. The experiment was performed using a nitrogen adsorption/desorption analyzer (Sorptomatic 1990 series).

2.2.3. Redox Titration. Redox titration was performed using the method of Niwa and Murakami²⁶ to estimate the average oxidation number of vanadium.

2.2.4. Scanning Electron Microscopy (SEM). Surface morphology of the catalysts was observed under scanning electron microscopy (SEM), using a LEO operated at accelerating voltages of 15 kV. The samples were prepared by dispersing the catalyst powder on a metallic sample holder, using double-sided tape to keep them on the holder. The samples were coated with a thin layer of gold using BIO-RAS sputter coater. Micrographs were recorded at various magnifications.

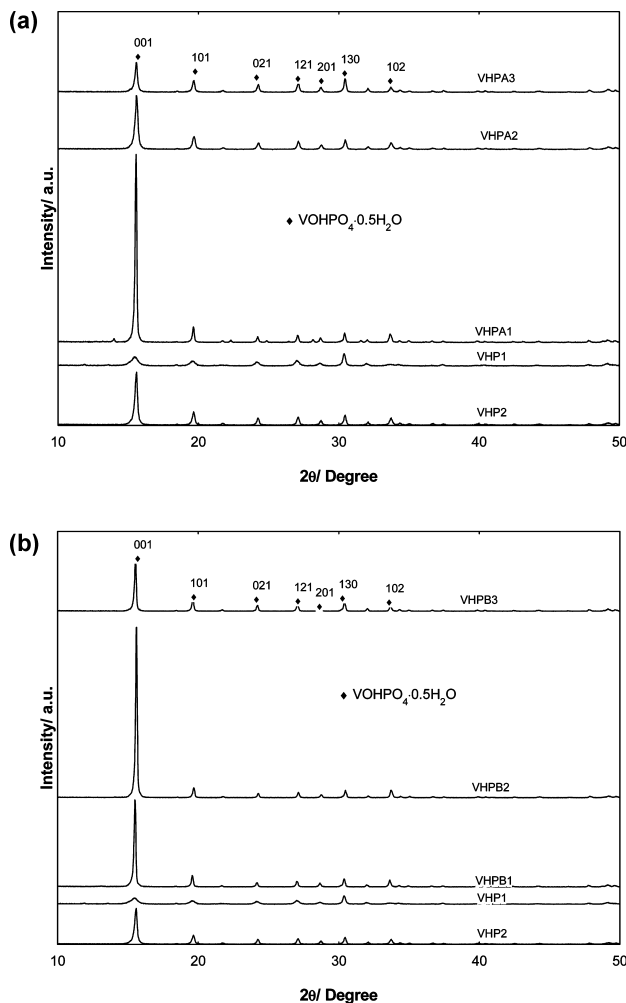


Figure 1. (a) Powder XRD patterns of vanadyl hydrogen phosphate hemihydrate (VOHPO₄·0.5H₂O, VHP) derived by solvothermal reaction in 1-propanol for 72 h at 373 (VHPA1), 393 (VHPA2), and 423 K (VHPA3), as well as via conventional VPO and VPD methods. ((001) and (130) are the main peaks for VOHPO₄·0.5H₂O.) (b) Powder XRD patterns of vanadyl hydrogen phosphate hemihydrate (VOHPO₄·0.5H₂O, VHP) derived by solvothermal reaction in 1-butanol for 72 h at 373 (VHPB1), 393 (VHPB2), and 423 K (VHPB3), as well as via conventional VPO and VPD methods. ((001) and (130) are the main peaks for VOHPO₄·0.5H₂O.)

2.2.5. Temperature-Programmed Reduction in H₂ (H₂-TPR). Temperature-programmed reduction in H₂ (H₂-TPR) was performed to observe the reducibility of the VPO catalyst, using an apparatus (ThermoFinnigan, Model TPDRO 1110) utilizing a thermal conductivity detector (TCD). H₂-TPR experiments were conducted using a quartz reactor tube (4 mm inner diameter), in which an ~25-mg sample was mounted on loosely packed quartz wool. Prior to H₂-TPR measurement, each catalyst was pretreated in N₂ at 473 K (at a heating rate of 10 K min⁻¹ and a hold time of 30 min) and then cooled under helium gas flow. The reduction gas was composed of 5 vol % H₂ in argon. The reaction temperature was programmed to increase at a constant rate of 10 K min⁻¹. A thermocouple in contact with the catalyst allowed the temperature to be controlled. The amount of H₂ uptake during the reduction was measured by a thermal conductivity detector (TCD). The effluent H₂O that formed during H₂-TPR was adsorbed by a 5A molecular sieve adsorbent. The error on the peak temperature was determined to be ±15 °C.

2.3. Catalytic Test. The oxidation of *n*-butane to maleic anhydride was performed in a fixed-bed flow microreactor containing a standard mass of catalyst (0.25 g) at 673 K with

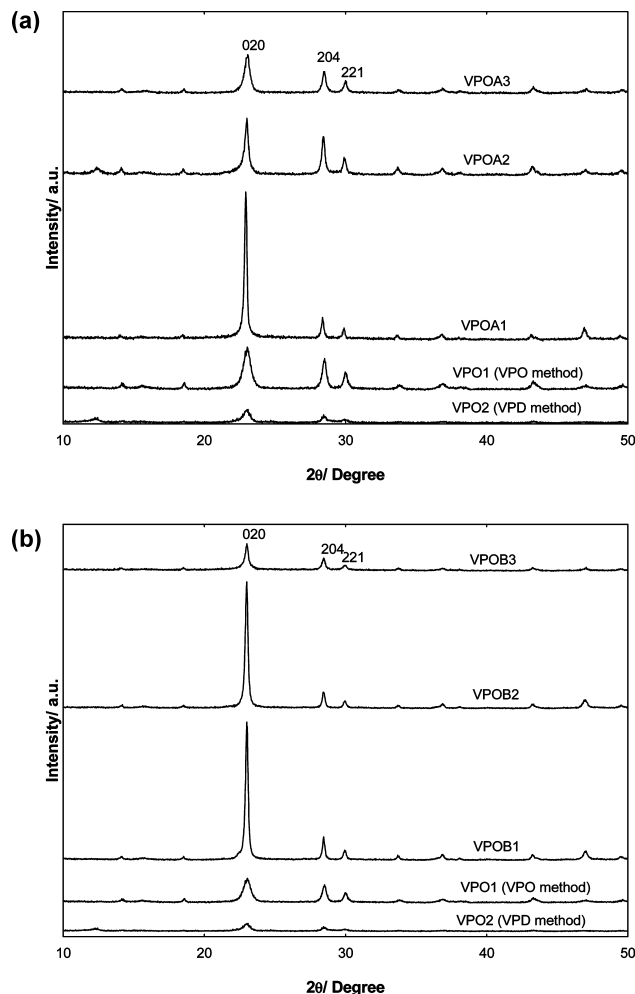


Figure 2. (a) Powder XRD patterns of vanadium phosphorus oxide ((VO)₂P₂O₇, VPO) derived by solvothermal reaction in 1-propanol for 72 h at 373 K (VPOA1), 393 K (VPOA2), and 423 K (VPOA3), as well as via conventional VPO (VPO1) and VPD (VPO2) methods. ((020) and (204) are the main peaks for (VO)₂P₂O₇.) (b) Powder XRD patterns of vanadium phosphorus oxide ((VO)₂P₂O₇, VPO) derived by solvothermal reaction in 1-butanol for 72 h at 373 K (VPOB1), 393 K (VPOB2), and 423 K (VPOB3), as well as conventional VPO (VPO1) and VPD (VPO2) methods. ((020) and (204) are the main peaks for (VO)₂P₂O₇.)

gas hourly space velocity (GHSV) of 2400 h⁻¹. Prior to use, the catalysts were pelleted and sieved to produce particles with 250–300 μm in diameter, and *n*-butane and air were fed to the reactor via calibrated mass flow controllers to give a feedstock composition of 1.7% *n*-butane in air. The products were injected into an online gas chromatograph for *in situ* analysis. The reactor is composed of stainless steel tube with the catalyst held in place by plugs of quartz wool. A thermocouple was located in the center of the catalyst bed and temperature difference was typically ±1 K. Carbon mass balances of ≥95% were typically observed.

3. Results and Discussion

3.1. X-ray Diffraction (XRD). The solid solution of VOHPO₄·0.5H₂O was produced isothermally by solvothermal processing at temperatures of 373, 393, and 423 K. Figure 1a shows the XRD patterns of the VOHPO₄·0.5H₂O solid solution prepared via the conventional VPO and VPD methods, and using 1-propanol in the solvothermal method. The diffractions at 2θ = 15.48°, 19.56°, 24.14°, 27.00°, and 30.34° are identical to

Table 2. XRD Data of Solvothermal and Conventional Nanostructure VPO Catalysts

catalyst	fwhm ^a (Å)		crystallite size ^b (nm)	
	020 phase	204 phase	020 phase	204 phase
VPOA1	0.200	0.188	40.1	43.1
VPOA2	0.308	0.120	26.0	67.5
VPOA3	0.450	0.310	17.8	26.1
VPOB1	0.236	0.277	33.9	29.2
VPOB2	0.231	0.215	34.7	37.7
VPOB3	0.277	0.267	28.9	30.3
VPO1	0.891	0.462	9.0	17.5
VPO2	0.574	0.455	14.0	17.8

^a Full width at half-maximum (fwhm) of the 020 or 204 reflection.

^b Crystallite sizes were calculated accordingly to the Debye–Scherrer equation.³⁰

VOHPO₄·0.5H₂O precursors (JCPDS File Card No. 37-269) and show no traces of the impurity VO(H₂PO₄)₂.^{27,28}

Similar trends were observed for the entire precursor studied, but the method at the evaluated temperatures lead to intensity at the peaks of $2\theta = 15.5^\circ$ and 30.4° being indexed to the 001 and 130 planes, respectively.²⁷ However, the 001 peak at $2\theta = 15.5^\circ$ for the solvothermal precursor (VHPA1) was shown to be significantly more intense (4-fold to 5-fold), compared to the same peak of the precursor prepared by the conventional VPO (VHP1) and VPD (VHP2) methods. It is known that the 001 plane of the VOHPO₄·0.5H₂O phase transforms to the topologically similar 020 plane of (VO)₂P₂O₇, which is believed to be responsible for the catalytic activity in *n*-butane oxidation.²⁹

The XRD patterns of the four catalysts that were prepared by calcination of the precursors at 723 K under the flow of *n*-butane/air are shown in Figure 2a. As can be seen, the catalyst prepared by the solvothermal method, (VO)₂P₂O₇ (JCPDS File Card No. 34-1381) was the only product formed. The catalyst prepared by the solvothermal method at 373 K gave highly crystalline structure and exposure of the crystallographic phase 020. The main peaks appeared at $2\theta = 22.9^\circ$, 28.4° , and 29.38° , which corresponded to the 020, 204, and 221 planes, respectively.

Peak broadening in the 020 phase was significantly smaller for the catalyst prepared via the solvothermal method (VPOA1) at 373 K than the catalyst prepared via the conventional VPO (VPO1) and VPD (VPO2) methods (see Figure 2a), because of the faster crystal growth in the solvothermal method at 373 K. The peaks became narrower in the 020 phase, yet the *d*-spacing (the 2θ position) of each peak was fixed.

The average crystallite size of an individual phase can be estimated by applying peak broadening analysis to the corresponding XRD diffraction using the Debye–Scherrer equation.³⁰ Therefore, from the results obtained in this study (shown in Table 2), the average particle size of the VPO catalyst prepared by the solvothermal method (VPOA) and using 1-propanol as a reducing agent was estimated to be ~40 nm.

In view of the well-established role of the 020 plane of the (VO)₂P₂O₇ phase in catalyzing the selective oxidation of butane to maleic anhydride, the synthesis of phases with preferential exposure of this plane would be of great significance in increasing the activity of (VO)₂P₂O₇ catalyst.

The XRD patterns for the precursors and catalyst using 1-butanol as a reducing agent and prepared by the solvothermal and conventional VPO and VPD methods are shown in Figures 1b and 2b, respectively. As can be seen from the figures, by using 1-butanol, the same trend as 1-propanol was observed. However, the 001 peak at $2\theta = 15.5^\circ$ for solvothermal precursor (VHPB2) was shown to be significantly more intense (4-fold

Table 3. Physical and Chemical Properties of Solvothermal and Conventional Catalysts

catalyst	surface area ^a (m ² g ⁻¹)	[V ⁵⁺] (%)	[V ⁴⁺] (%)	average oxidation number of vanadium in bulk ^b
VPOA1	34	17	77	4.17
VPOA2	29	10	90	4.10
VPOA3	22	8	92	4.08
VPOB1	23	10	90	4.10
VPOB2	21	5	95	4.05
VPOB3	7	21	79	4.21
VPO1	17	27	73	4.27
VPO2	24	21	79	4.21

^a After pretreatment at 423 K in a vacuum. ^b Estimated by redox titration.²⁶

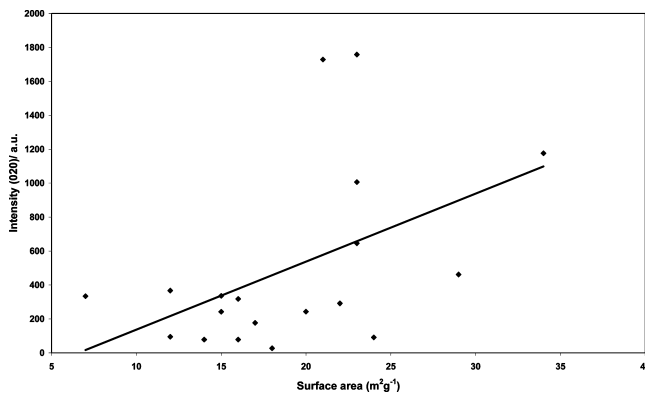


Figure 3. Relationship between intensity of the 020 plane and catalyst surface area for the VPO catalyst derived by solvothermal reaction for 72 h at 373, 393, and 423 K.

to 5-fold), compared to the same peak of the precursor prepared by the conventional VPO (VHP1) and VPD (VHP2) methods. The catalyst prepared by the solvothermal method at 373 and 393 K gave a highly crystalline structure and exposure of the crystallographic plane 020. The average crystallite size, relative to the corresponding XRD diffraction using the Debye–Scherrer equation³⁰ obtained in this study (Table 2) and the average particle sizes of VPO catalyst prepared by the solvothermal method (VPOB) and using 1-butanol as a reducing agent, was estimated to be ~30 nm.

Figures 1b and 2b show the XRD patterns of precursors and catalyst with 1-butanol as reducing agent. As can be seen in the XRD patterns, the same trend as that observed for 1-propanol was observed. However, the 001 peak at $2\theta = 15.5^\circ$ for the solvothermal precursor (VHPB2) was shown to be significantly more intense (4-fold to 5-fold), compared to the same peak of the precursor prepared via conventional VPO (VHP1) and VPD (VHP2) methods. The catalyst prepared by the solvothermal method at 373 and 393 K gave a highly crystalline structure and exposure of the crystallographic 020 phase. The average crystallite size obtained in this step by the Debye–Scherrer equation³⁰ is shown in Table 2. The XRD patterns for the results obtained were conducted isothermally at 373, 393, and 423 K; a reaction time of 72 h shows that the chain of alcohol (number of carbons) plays an important role in the phase content and the particle size the orthorhombic structure³¹ of the VOHPO₄·0.5H₂O phase and the (VO)₂P₂O₇ catalyst.

3.2. BET Surface Area Measurement and Redox Titration. The BET surface areas of the catalysts prepared by the solvothermal method at different isothermal temperatures are shown in Table 3. BET results indicated that the surface area of the catalyst prepared via solvothermal methods is higher than those reported for the VPO catalyst prepared via the hydrothermal method.¹⁵ The obtained surface area values were

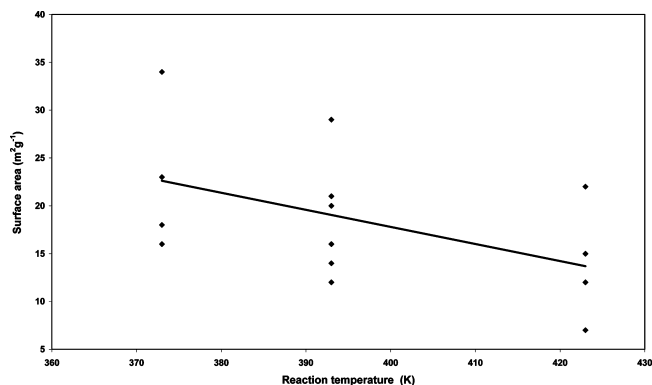


Figure 4. Relationship between catalyst surface area and reaction temperature for the VPO catalyst derived by solvothermal reaction for 72 h at 373, 393, and 423 K.

consistent with crystallite size data and SEM morphology. However, the values obtained (depending on the chain of alcohol) were slightly higher than those for the organic and dihydrate methods, respectively.^{7,12} Increases in the rate crystal growth at any temperature affect the crystallize structure, and

the XRD peaks become narrower with reduced peak broadening. The relationship between surface area and intensity in the 020 phases (Figure 3) shows the same trend as that observed for the catalyst prepared by the solvothermal method; the intensity of the 020 plane increases as the surface area increases. In Figure 4, the surface area of the catalyst obtained by the solvothermal method is plotted against the reaction temperature. The results show that, with the increase in the reaction temperature, the surface area of the catalyst gradually decreases. This can be attributed to this fact that catalysts synthesized at higher temperatures have bigger size (due to occurring of agglomeration of particles) with more amorphous structure than catalysts obtained at lower temperatures with rosette structure.

However, the thermal decomposition of mixtures of V_2O_5 and H_3PO_4 in primary alcohols (C_3 – C_4) shows a nanocrystalline VPO catalyst with a catalyst crystallite size of 20–40 nm and large BET surface areas, compared to the catalyst prepared by hydrothermal methods. The VPO catalyst prepared in 1-propanol produces ultrahigh-quality $(VO)_2P_2O_7$ crystallites and leads to large surface areas and small crystallite sizes. In conclusion, as can be seen in Table 1 and Figure 4, the surface area of the catalyst prepared by the solvothermal method had a linear

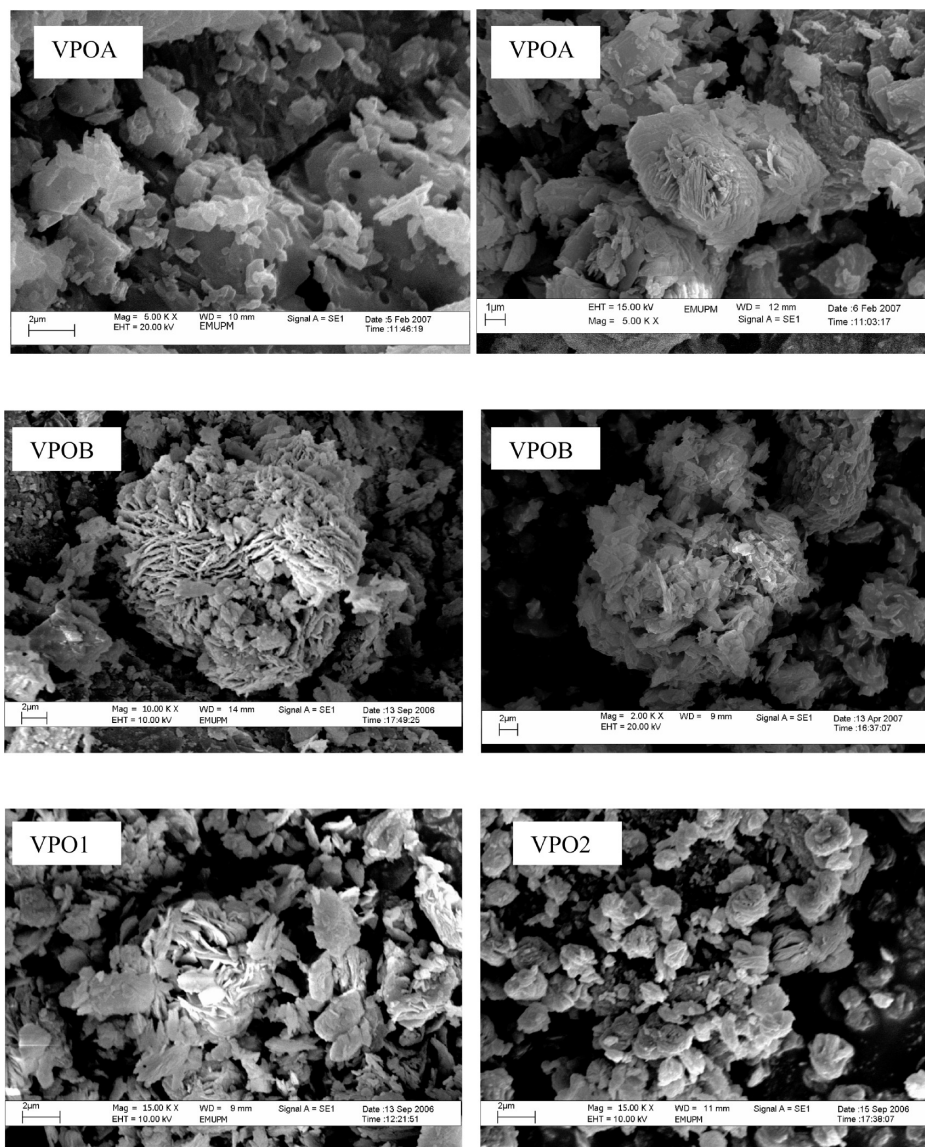


Figure 5. Scanning electron microscopy (SEM) micrographs of VPO catalyst derived by solvothermal reaction for 72 h in 1-propanol (VPOA1), 1-butanol (VPOB), and conventional VPO (VPO) and VPD (VPO2) methods.

relationship with temperature and reaction media: the longer the chain alcohols and the higher the reaction temperature, the smaller the surface area.

The average oxidation number of vanadium and percentage of V^{4+} and V^{5+} oxidation states are also summarized in Table 3. It is widely accepted that the valence state of vanadium plays an important role in the selective oxidation of *n*-butane to MA.³² The average oxidation number for vanadium in the microwave catalysts is higher than conventionally made catalysts. The calculated values are presented in Table 3. This difference might influence the catalytic properties of vanadium phosphate catalyst in oxidation reactions and could be attributed to the formation of a V^{5+} phase ($VOPO_4$) during solvothermal synthesis. Therefore, the polarity and the type of the alcohol used as reducing agent exhibit stronger impact on catalysts properties.

3.3. Scanning Electron Microscopy (SEM). The SEM micrographs of the solvothermal and conventional VPO and VPD catalysts are shown in Figure 5. The crystallites clearly are not single-crystal faces, because the surfaces are marked with many indentations. SEM images reveal a novel morphology of solvothermal–MW-prepared catalysts. Among the characteristic vanadium phosphate rosette-shaped particles, solvothermal catalysts displayed a platelike structure with an average particle size of $<2\ \mu\text{m}$. SEM images confirmed that the solvothermal synthesis was highly dependent on the type of reducing agent. Solvents with different physical and chemical properties can influence the solubility, reactivity, and diffusion behavior of the reactants; in particular, the polarity and coordinating ability of the solvent can change the morphology and the crystallization behavior of the final products. The particle size was found to be nearly the same for both conventional and MW-assisted solvothermal treatment of VPO catalyst and significantly smaller than conventional VPO- and VPD-derived catalysts. The presence of the lengthy alkyl chain dramatically increases the hydrophobic nature, which leads to a lower diffusion rate of ions in the solvent and, finally, to the formation of smaller particles. The SEM micrographs of $VOHPO_4 \cdot 0.5H_2O$ synthesized via conventional VPO (VPO1) and VPD (VPO2) methods, showed rosette structures with platelets characterized by an XRD pattern with a dominant 020 reflection.^{11,13} All catalysts exhibited rosette-shape species, adhered to the aggregated particles, which were recognized as the $(VO)_2P_2O_7$ phase, which is one of the most typical morphologies observed. The SEM micrographs of solvothermal catalysts (VPOA) synthesized by 1-propanol, show that the crystals are not single-crystal faces, because the surfaces are marked with many indentations, thereby exposing more of the surface plane. The VPOA catalyst represents nanostructure plates with a secondary platelet morphology. In the case of VPOB, by replacing 1-butanol with 1-propanol, a very different morphology was observed. The structure is mainly composed of platelike crystals, which are arranged into the characteristic rosette-shape clusters with homogeneous dispersion. Hence, the use of organic media as a reducing agent in the preparation of $VOHPO_4 \cdot 0.5H_2O$ controls the morphology of the crystallites and the surface area. Comparing the series allows one to conclude that solvothermal synthesis produces the nanostructure platelet structure with a secondary platelet morphology.

3.4. Influence of Reducing Agent (Catalyst Microstructure) on the Amount and Nature of the Oxygen Species. To investigate the effect of solvent on the redox properties, as well as the amount and nature of the oxygen species of the catalysts, temperature-programmed reduction in H_2/Ar (H_2 -TPR) experiments were performed on the solvothermal and conventional

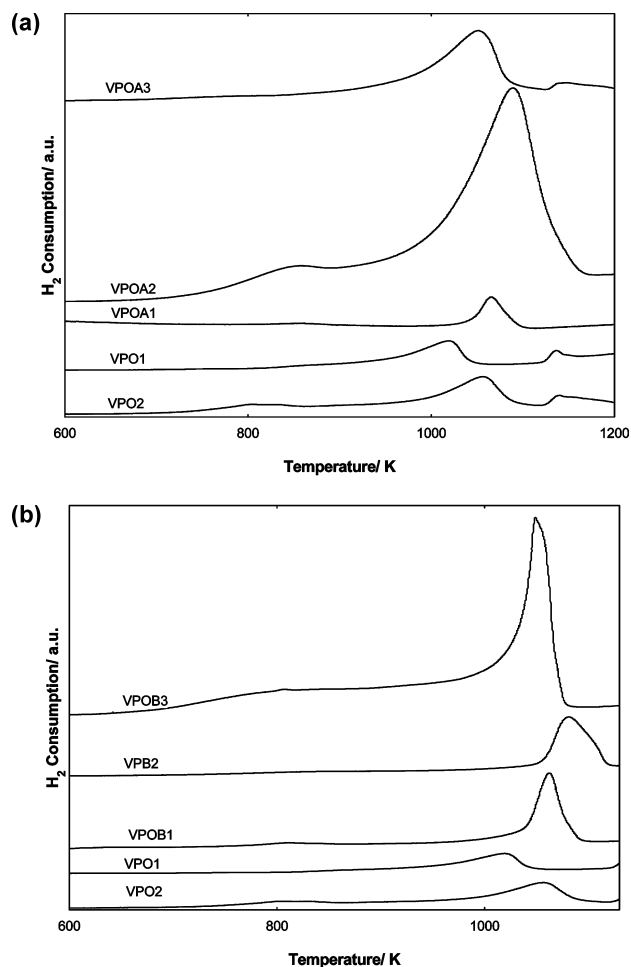


Figure 6. (a) Temperature-programmed reduction (H_2 -TPR) profiles of vanadium phosphorus oxide catalyst derived by solvothermal reaction in 1-propanol for 72 h at 373 K (VPOA1), 393 K (VPOA2), and 423 K (VPOA3), as well as via conventional VPO (VPO1) and VPD (VPO2) methods. (b) Temperature-programmed reduction (H_2 -TPR) profiles of vanadium phosphorus oxide catalyst derived by solvothermal reaction in 1-butanol for 72 h at 373 K (VPOA1), 393 K (VPOA2), and 423 K (VPOA3), as well as via conventional VPO (VPO1) and VPD (VPO2) methods.

VPO and VPD catalysts. The H_2 -TPR patterns of solvothermal catalysts are compared in Figure 6, while the temperatures of the maximum hydrogen consumption (T_{Max}) and the amount of oxygen removed from the catalyst in the H_2 -TPR experiments are shown in Table 4. As can be seen in the results obtained from the TPR patterns, all the catalysts undergo two reduction stages. The reduction of vanadium in the oxide form $(VO)_2P_2O_7$ to the trivalent form (V^{3+}) involves a two-step reduction: first, the reduction of V^{5+} to V^{3+} and then the subsequent reduction of $(VO)_2P_2O_7$ to V^{3+} .³³

Figure 6a shows that the first peak at low temperature (between $\sim 790\ \text{K}$ and $860\ \text{K}$) was assigned to the removal of oxygen species associated with V^{5+} whereas the latter peak at high temperature (between $\sim 1000\ \text{K}$ and $\sim 1140\ \text{K}$) is due to the removal of the oxygen species associated with the V^{4+} phase. Investigations of the electrical conductivity of this catalyst suggest that O^{2-} is associated with the V^{5+} phase, whereas O^- is associated with the V^{4+} phase.^{34–36} It is apparent that reduction of vanadium components (V^{4+} , as well as V^{5+}) is more difficult, compared to the VPO catalyst prepared by the solvothermal method and conventional VPO and VPD methods.

The metal particle size has an influence on the reduction behavior of the vanadium phosphate catalyst, resulting in the

Table 4. Total Amounts of Oxygen Removed and the Ratio of Oxygen Removed of V^{5+}/V^{4+} , Estimated by Temperature-Programmed Reduction in H_2/Ar for Catalysts

peak ^a		Total Amount of Oxygen Removed		
VPO2 Catalyst	T_{\max} (K)	($\times 10^{-3}$ mol g ⁻¹)	($\times 10^{21}$ atom g ⁻¹)	ratio of oxygen removal for V ⁵⁺ /V ^{4+b}
VPOA1 Catalyst				
1	861	0.18	0.11	0.21
2	1066	0.86	0.52	
total amount of oxygen atoms removed		1.05	0.63	
VPOA2 Catalyst				
1	856	1.18	0.71	0.17
2	1089	7.81	4.70	
total amount of oxygen atoms removed		8.99	5.41	
VPOA3 Catalyst				
1	788	0.04	0.02	0.02
2	1050	1.69	1.02	
total amount of oxygen atoms removed		1.73	1.04	
VPOB1 Catalyst				
1	811	0.16	0.10	0.10
2	1062	1.71	1.03	
total amount of oxygen atoms removed		1.87	1.13	
VPOB2 Catalyst				
1	823	0.04	0.02	0.03
2	1081	1.24	0.75	
total amount of oxygen atoms removed		1.28	0.77	
VPOB3 Catalyst				
1	811	0.53	0.32	0.32
2	1052	1.64	0.99	
total amount of oxygen atoms removed		2.17	1.31	
VPO1 Catalyst				
1	799	0.24	0.14	0.18
2	1007	1.30	0.78	
total amount of oxygen atoms removed		1.54	0.92	
VPO2 Catalyst				
1	804	0.62	0.37	0.38
2	1056	1.61	0.97	
total amount of oxygen atoms removed		2.23	1.34	

^a After pretreatment at 473 K in nitrogen gas and cooling under helium. ^b Estimated from H_2 -TPR.

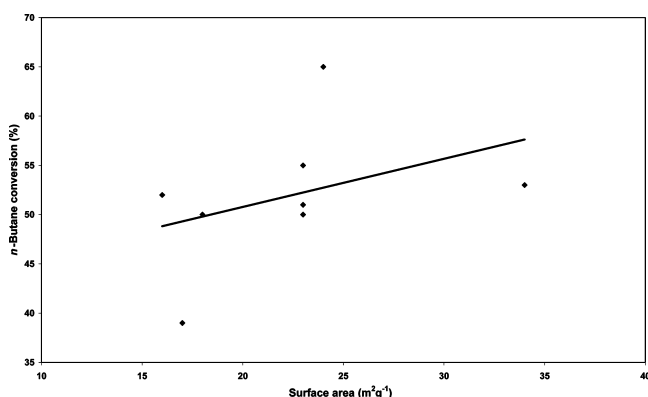
observation of different locations of the TPR peaks. The H_2 -TPR profiles of the solvothermal catalyst were different from that of the VPO catalyst prepared via conventional VPO and VPD methods in which the reduction peaks have a tendency to shift to higher temperatures. Figure 6a shows that the temperature required to reduce the catalyst prior to reaction was 790 K for the conventional methods. For the solvothermal method, the reduction temperature was higher. As can be seen in Figure 6a, the amounts of oxygen removed from both peaks of the solvothermal catalyst, which used 1-propanol at a reaction temperature of 393 K (VPOA2), are 0.71×10^{21} and 4.7×10^{21} atom g⁻¹, respectively, with an oxygen ratio for V^{5+}/V^{4+} of 0.17. The conventional catalysts (VPO1 and VPO2) show similar reduction profiles to those from the solvothermal method, but the total amount of oxygen removed from the solvothermal catalyst (VPOA2) is significantly higher than that for the conventional catalysts. These results show that, with the use of 1-propanol as an organic media and 393 K for a reaction temperature, with decreased particle size (Table 2) and increased surface area (Table 3), the reduction temperature for hydrogen consumption (TPR peaks) shifts to a lower temperature and the total oxygen removed from the conventional catalyst is significantly higher than for the conventional catalyst. Although space limitations preclude discussion of further results, similar trends were obtained for other reducing agents (1-butanol), as shown in Figure 6b.

However, the catalysts prepared via conventional VPO and VPD methods are easier to reduce than those obtained via the solvothermal method. This is consistent with the effect on the reduction temperature of vanadium, relative to a higher particle size. As can be seen in the results, the catalyst prepared via the solvothermal method does not show the same trend for each organic medium and reaction temperature. However, there are important differences in the T_M values and the amount of hydrogen consumption for the catalysts prepared via the solvothermal and conventional VPO and VPD methods.

3.5. Influence of Catalyst Microstructure on Selectivity in the Selective Oxidation of *n*-Butane. The catalysts were evaluated *in situ* in the laboratory microreactor with 1.7% *n*-butane in air at 673 K. During this time, the catalyst performance for the formation of maleic anhydride steadily improved. The catalyst performance data, when the steady state was achieved, are shown in Table 5, and data are also given for the catalysts prepared using the conventional VPO, VPD, and hydrothermal methods. It is apparent that the catalysts derived from the solvothermal method can produce high surface area, resulting in high-activity and high-selectivity catalysts, which have performance comparable to that of the catalysts prepared using the standard VPO, VPD, and hydrothermal methods. When the V_2O_5 and H_3PO_4 solvent-based methods (solvothermal) are contrasted with the conventional VPO, VPD, and hydrothermal methods of preparation, it is clear that the

Table 5. Catalytic Performance of Solvothermal, Conventional VPO, VPD, and Hydrothermal Methods for the Oxidation of *n*-Butane to Maleic Anhydride^a

catalyst	<i>n</i> -butane conversion (%)	Selectivity (%)			yield ^b (%)
		MA	CO	CO ₂	
VPOA1	53	65	15	20	34.4
VPOB1	50	63	16	21	31.5
VPO1	39	62	19	19	24.2
VPO2	65	54	20	26	35.1
conventional hydrothermal ^c	35	61	17	22	21.3

^a Reaction conditions: 673 K, 1.7% *n*-butane in air, GHSV: 2400 h⁻¹.^b Yield (%) = *n*-butane conversion (%) × MA selectivity (%). ^c Data taken from Taufiq-Yap et al.¹⁵**Figure 7.** Relationship between *n*-butane conversion (expressed as a percentage) and catalyst surface area.

new methods produce much-higher-surface-area catalysts and, in particular, surface areas that are comparable to those prepared using VPO, VPD, and hydrothermal methods. The enhancement in activity is considered to be due in part to the high-pressure solvothermal method producing high pure crystallites for these preparations where the impurity VO(H₂PO₄)₂ is absent. Figure 7 shows *n*-butane conversion, selectivity and yield to MA data.

The catalysts show similar conversion, indicating that the surface area of the catalyst is the most important parameter for these catalysts. This is further demonstrated by a plot of the *n*-butane conversion based on the surface area of catalyst (see Figure 7). Clearly, the activity is primarily dependent upon the catalyst surface area. The higher number of active sites (V⁴⁺) and oxygen species are responsible for the activation of *n*-butane and enhancement of the catalyst activity. Moreover, the availability and behavior of the oxygen species play an important role in determining the catalytic activity and support the idea that the mobility of active oxygen species (O⁻) in the catalyst is the main determining step for *n*-butane activation.^{33–35} The selectivity to MA observed for the solvothermal-derived catalysts was slightly higher than other VPO catalysts reported in the literature. At present, the surface area achieved for active catalyst is typically 15–30 m² g⁻¹. However, this is significantly higher than that previously reported for conventional hydrothermal preparation.¹⁵ Although it is considered likely that the solvothermal method would be used for the synthesis of commercial VPO catalyst, the present study shows that relatively high surface area catalysts can be achieved using this method. At present, our initial experiments have used high autoclave temperatures of 373 K, 393 K, and 423 K and a three-day preparation time. Meanwhile, it can be expected that significant improvements can be expected for the catalyst surface area if the reaction conditions are optimized with different solvents, temperature, and time. Our present study also shows that surfactant-free and water-free methods can also be developed

using the autoclave methodology, and this may be of value in the synthesis of new formulations or the promotion of VPO catalysts.

4. Conclusions

In the present study, we have explored a novel, alternative route for the preparation of pure orthorhombic form of VOHPO₄·0.5H₂O. This can be achieved in the presence of different organic media via a simple one-step solvothermal method, which is free of water and surfactant, using a low amount of reducing agent in a closed autoclave at higher temperature (373, 393, and 423 K) and on a relatively short time scale (72 h). Based on the aforementioned solvothermal process, ultracrystalline vanadyl hydrogen phosphate hemihydrate could be obtained. This new methodology produces catalysts with a much higher surface area (ca. 30 m² g⁻¹), compared to previous surfactant- and water-based hydrothermal methods that give rise to low-surface-area catalysts (ca. 9.5 m² g⁻¹).

These catalysts exhibit catalytic activities and selectivities that are comparable to vanadium phosphate catalysts prepared using conventional standard VPO, VPD, and hydrothermal methods. The catalysts show an approximately linear relationship between the conversion of *n*-butane and the surface area. In particular, for the VPO catalyst, the number of active sites (V⁴⁺) and oxygen species also play important roles in the catalytic activity, in addition to the catalyst surface area. The study shows that carbon chain reducing agent (C₃–C₄) and high temperature are not required for the production of highly active and selective catalysts. In summary, the solvothermal method represents a simple, efficient, and low-cost technique for the synthesis of VPO catalyst with improved catalytic performance in the selective oxidation of C₄-hydrocarbon.

Literature Cited

- Centi, G.; Cavani, F.; Trifirò, F. *Selective Oxidation by Heterogeneous Catalysis*; Fundamental and Applied Catalysis Series; Springer: New York, 2001.
- Griesel, L.; Bartley, J. K.; Wells, R. P. K.; Hutchings, G. J. Preparation of vanadium phosphate catalysts from VOPO₄·2H₂O: Effect of VOPO₄·2H₂O preparation on catalyst performance. *J. Mol. Catal. A: Chem.* **2004**, *220*, 113.
- Ballarini, N.; Cavani, F.; Cortelli, C.; Ligi, S.; Pierelli, F.; Trifirò, F.; Fumagalli, C.; Mazzoni, G.; Monti, T. VPO catalyst for *n*-butane oxidation to maleic anhydride: A goal achieved, or a still open challenge. *Top. Catal.* **2006**, *38*, 147.
- Trifirò, F. Key properties of V–P mixed oxides in selective oxidation of C₄ and C₅ *n*-Paraffins. *Catal. Today* **1993**, *16*, 91.
- Kiely, C. J.; Burrows, A.; Hutchings, G. J.; Bere, K. E.; Volta, J. C.; Tuel, A.; Abon, M. Structural transformation sequences occurring during the activation of vanadium phosphorus oxide catalysts. *J. Chem. Soc., Faraday Discuss.* **1996**, *105*, 103.
- Hutchings, G. J.; Desmartin Chomel, A.; Olier, R.; Volta, J. C. Role of the product in the transformation of a catalyst to its active state. *Nature* **1994**, *368*, 41.
- Johnson, J. W.; Johnston, D. C.; Jacobsen, A. J.; Brody, J. F. Preparation and characterization of vanadyl hydrogen phosphate hemihydrate and its topotactic transformation to vanadyl pyrophosphate. *J. Am. Chem. Soc.* **1984**, *106*, 8123.
- Hutchings, G. J. Heterogeneous catalysts—Discovery and design. *J. Mater. Chem.* **2009**, *19*, 1222.
- Bartley, J. K.; Kiely, C. J.; Wells, R. P. K.; Hutchings, G. J. Vanadium(V) phosphate prepared using solvent-free method. *Catal. Lett.* **2001**, *72*, 99.
- Centi, G. Vanadyl Pyrophosphate—A Critical Overview. *Catal. Today* **1993**, *16*, 5.
- Ellison, I. J.; Hutchings, G. J.; Sananes, M. T.; Volta, J. C. Control of the composition and morphology of vanadium phosphate catalyst precursors from alcohol treatment of VOPO₄·2H₂O. *J. Chem. Soc., Chem. Commun.* **1994**, 1093.

- (12) Horowitz, H. S.; Blackstone, C. M.; Sleight, A. W.; Teufer, G. VPO catalysts for oxidation of butane to maleic anhydride. Influence of $(VO)_2H_4P_2O_9$ precursor morphology on catalytic properties. *Appl. Catal.* **1988**, 38, 193.
- (13) Sananes, M. T.; Ellison, I. J.; Sajip, S.; Burrows, A.; Kiely, C. J.; Volta, J. C.; Hutchings, G. J. *n*-Butane oxidation using catalysts prepared by treatment of $VOPO_4 \cdot 2H_2O$ with octanol. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 137.
- (14) Taufiq-Yap, Y. H.; Rownaghi, A. A.; Hussein, M. Z.; Irmawati, R. Preparation of vanadium phosphate catalysts from $VOPO_4 \cdot 2H_2O$: Effect of microwave irradiation on morphology and catalytic property. *Catal. Lett.* **2007**, 119, 64.
- (15) Taufiq-Yap, Y. H.; Hasbi, M. A. R.; Hussein, M. Z.; Hutchings, G. J.; Bartley, J. B.; Dummer, N. Synthesis of vanadium phosphate catalysts by hydrothermal method for selective oxidation of *n*-butane to maleic anhydride. *Catal. Lett.* **2006**, 106, 177.
- (16) Torardi, C. C.; Calabrese, J. C. Ambient- and low-temperature crystal structure of vanadyl hydrogen phosphate, $(VO)_2H_4P_2O_9$. *Inorg. Chem.* **1984**, 23, 1308.
- (17) Demazeau, G. Solvothermal reactions: An original route for the synthesis of novel materials. *J. Mater. Sci.* **2008**, 43, 2104.
- (18) Rownaghi, A. A.; Taufiq-Yap, Y. H.; Rezaei, F. Solvothermal synthesis of vanadium phosphate catalysts for *n*-butane oxidation. *Chem. Eng. J.* **2009**, 155, 514.
- (19) Rownaghi, A. A.; Taufiq-Yap, Y. H.; Tang, W. J. Influence of the ethylene glycol, water treatment and microwave irradiation on the characteristics and performance of VPO catalysts for *n*-butane oxidation to maleic anhydride. *Catal. Lett.* **2009**, 130, 593.
- (20) Rownaghi, A. A.; Taufiq-Yap, Y. H.; Rezaei, F. Influence of rare-earth and bimetallic promoters on various VPO catalysts for partial oxidation of *n*-butane. *Catal. Lett.* **2009**, 130, 504.
- (21) Rownaghi, A. A.; Taufiq-Yap, Y. H.; Rezaei, F. High surface area vanadium phosphate catalysts for *n*-butane oxidation. *Ind. Eng. Chem. Res.* **2009**, 48, 7517.
- (22) Rownaghi, A. A.; Taufiq-Yap, Y. H. An improved process to produce high surface area nanoparticle vanadium phosphorus oxide catalyst and product derives thereof, International Patent WO/2009/061167, 2009.
- (23) Volta, J. C. Vanadium phosphorus oxides, a reference catalyst for mild oxidation of light alkanes: A review. *C. R. Acad. Sci., Series IIc: Chim.* **2000**, 3, 717.
- (24) Kiely, C. J.; Burrows, A.; Sajip, S.; Hutchings, G. J.; Sananes, M. T.; Tuel, A.; Volta, J. C. Characterisation of variations in vanadium phosphate catalyst microstructure with preparation route. *J. Catal.* **1996**, 162, 31.
- (25) Ellison, I. J.; Hutchings, G. J.; Sananes, M. T.; Volta, J. C. Control of the composition and morphology of vanadium phosphate catalyst precursors from alcohol treatment of $VOPO_4 \cdot 2H_2O$. *J. Chem. Soc., Chem. Commun.* **1994**, (9), 1093.
- (26) Niwa, M.; Murakami, Y. Reaction Mechanism of Ammoxidation of Toluene IV. Oxidation State of Vanadium Oxide and Its Reactivity for Toluene Oxidation. *J. Catal.* **1982**, 76, 9.
- (27) Albonetti, S.; Cavani, F.; Venturoli, P.; Galestani, G.; Lopez Granados, M.; J. Fierro, L. G. A Comparison of the Reactivity of "Nonequilibrated" and "Equilibrated" V-P-O Catalysts: Structural Evolution, Surface Characterization, and Reactivity in the Selective Oxidation of *n*-Butane and *n*-Pentane. *J. Catal.* **1996**, 160, 52.
- (28) Sajip, S.; Bartley, J. K.; Burrows, A.; Rhodes, C.; Volta, J. C.; Kiely, C. J.; Hutchings, G. J. Structural transformation sequence occurring during the activation under *n*-butane air of a cobalt-doped vanadium phosphate hemihydrate precursor for mild oxidation to maleic anhydride. *Phys. Chem. Chem. Phys.* **2001**, 3, 2143.
- (29) Igarashi, H.; Tsuji, K.; Okuhara, T.; Misono, M. Effects of consecutive oxidation on the production of maleic anhydride in butane oxidation over four kinds of well-characterized vanadyl pyrophosphates. *J. Phys. Chem.* **1993**, 97, 7065.
- (30) Patterson, A. L. The Scherrer Formula for X-Ray Particle Size Determination. *Phys. Rev.* **1939**, 56, 978.
- (31) Bordes, E. Crystallochemistry of V-P-O phases and application to catalysis. *Catal. Today* **1987**, 1, 499.
- (32) Abon, M.; Bere, K. E.; Tuel, A.; Delichere, P. Evolution of a VPO Catalyst in *n*-Butane Oxidation Reaction during the Activation Time. *J. Catal.* **1995**, 156, 28.
- (33) Abon, M.; Herrmann, J. M.; Volta, J. C. Correlation with the redox V^{5+}/V^{4+} ratio in vanadium phosphorus oxide catalysts for mild oxidation of *n*-butane to maleic anhydride. *Catal. Today* **2001**, 71, 121.
- (34) Pierini, B. T.; Lombardo, E. A. Structure and properties of Cr promoted VPO catalysts. *Mater. Chem. Phys.* **2005**, 92, 197.
- (35) (a) Taufiq-Yap, Y. H.; Goh, C. K.; Hussein, M. Z.; Hutchings, G. J.; Bartley, J. B.; Dummer, N. Effects of mechanochemical treatment to the vanadium phosphate catalysts derived from $VOPO_4 \cdot 2H_2O$. *J. Mol. Catal. A: Chem.* **2006**, 260, 2. (b) Herrmann, J. M. Heterogeneous photocatalysis: State of the art and present applications. *Top. Catal.* **2005**, 34, 49.
- (36) Havecker, M.; Mayer, R. W.; Knop-Gericke, A.; Bluhm, H.; Kleimenov, E.; Liskowski, A.; Su, D.; Follath, R.; Requejo, F. G.; Ogletree, D. F.; Salmeron, M.; Lopez-Sanchez, J. A.; Bartley, J. K.; Hutchings, G. J.; Schlögl, R. In situ investigation of the nature of the active surface of a vanadyl pyrophosphate catalyst during *n*-butane oxidation to maleic anhydride. *J. Phys. Chem. B* **2003**, 107, 4587.

Received for review December 19, 2009
 Revised manuscript received January 16, 2010
 Accepted January 22, 2010

IE902011A