Chemical Engineering Journal 165 (2010) 328–335

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Innovative process for the synthesis of vanadyl pyrophosphate as a highly selective catalyst for *n*-butane oxidation

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ARTICLE INFO

Article history:
Received 6 February 2010
Received in revised form 5 September 2010
Accepted 10 September 2010

Key words:
Vanadyl hydrogen phosphate hemihydrate
Vanadyl pyrophosphate catalysts
Solvothermal synthesis
High-pressure autoclave
n-Butane oxidation

ABSTRACT

Vanadyl pyrophosphate (VPO) catalysts are used for the selective oxidation of light alkanes, which are based on vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) as the precursor. Catalyst precursor with well-defined crystal size has been successfully synthesized for the first time, using a simple one-step high-pressure autoclave that was surfactant-free and water-free method with significantly lower temperature and shorter reaction time. $VOHPO_4{\cdot}0.5H_2O$ was prepared from V_2O_5 using an isobutanol, 1-pentanol, 1-heptanol and 1-dectanol as both solvent and reducing agent at elevated temperatures (100, 120, and 150 °C). This new method significantly reduced the preparation time and lowered production temperature (50%) of catalyst precursor ($VOHPO_4{\cdot}0.5H_2O$) when compared to conventional hydrothermal synthesis methods. $VOHPO_4{\cdot}0.5H_2O$ can be obtained at temperature far below 150 °C. It was found that the presence of 1-heptanol and 1-decanol in the reaction mixtures is crucial for obtaining a well-defined crystal size of precursor phase and solely generated impurity $[VO(H_2PO_4)_2]$. Our findings show that both the phase composition and morphology of vanadium phosphate can be influenced by the use of different reducing agents and temperatures during the preparation process. This new methodology produces catalysts with a much higher surface area (*ca.* 23 $m^2\,g^{-1}$) compared with those materials prepared by slow hydrothermal synthesis (*ca.* 9.5 $m^2\,g^{-1}$). Finally, the yield of maleic anhydride was significantly increased from 21.3% for conventional catalyst to 37.9% for the new solvothermal catalyst.

1. Introduction

Vanadyl pyrophosphate catalysts have been studied extensively for selective oxidation of *n*-butane to maleic anhydride. Vanadium phosphates have also shown promising results as heterogeneous catalysts in the selective oxidation of propane and of pentane to acrylic acid, maleic and pthalic anhydride, respectively and in the oxidative dehydrogenation of ethane, propane, etc. [1–5]. Vanadium phosphates exist in a wide range of structural forms because of their variable oxidation states as well as the large diversity in the bonding of the VO*n* polyhedra (tetrahedra, square pyramids, and distorted and regular octahedra) and the PO_4 tetrahedra [3,4]. The association of different vanadium oxidation states (V, IV, and III) with their various polyhedra leads to a large diversity of the resulting structures and properties [1,2]. Most attention has focused on the vanadyl hydrogen phosphate hydrate phase, $VOHPO_4{\cdot}0.5H_2O$ [6]. The topotactic transformation from the vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) to the final vanadyl pyrophosphate catalysts $[(VO)_2P_2O_7]$ is well documented [7,8]. Various synthesis methods have been developed in order to obtain vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) with controlled catalytic properties. Initial catalyst preparations [9] used water as solvent but most studies, in recent years, have concentrated on the use of alcohols as they can exhibit the duel role of solvent and reducing agent. In previous studies [10–13] we have shown that very active catalysts can be prepared using an organic (VPO) and dihydrate (VPD) method. The alcohol plays a role in establishing the morphology of the vanadyl hydrogen phosphate hydrate which, since the transformation to the final catalyst is topotactic, controls the morphology of the final catalyst [8]. We have recently reported a high-pressure solvothermal process to synthesise high crystalline catalyst precursor, $VOHPO_4{\cdot}0.5H_2O$ [11,14]. It was found that the alcohol used as a reducing agent can control the morphology and the best results are obtained using primary alcohols. However, precursor can be synthesized in alcohols at temperatures lower than that required by

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doi:10.1016/j.cej.2010.09.043

Table 1
Preparation condition of the VPO catalyst.

Precursor	Catalyst	Preparation condition	Precursor heating
VHPA1	VPOA1	$V_2O_5 + H_3PO_4$ + isobutanol + 100 °C	Microwave
VHPA2	VPOA2	$V_2O_5 + H_3PO_4$ + isobutanol + 120 °C	Microwave
VHPA3	VPOA3	$V_2O_5 + H_3PO_4$ + isobutanol + 150 °C	Microwave
VHPB1	VPOB1	$V_2O_5 + H_3PO_4$ + 1-pentanol + 100 °C	Microwave
VHPB2	VPOB2	$V_2O_5 + H_3PO_4$ + 1-pentanol + 120 °C	Microwave
VHPB3	VPOB3	$V_2O_5 + H_3PO_4$ + 1-pentanol + 150 °C	Microwave
VHPC1	VPOC1	$V_2O_5 + H_3PO_4$ + 1-heptanol + 100 °C	Microwave
VHPC2	VPOC2	$V_2O_5 + H_3PO_4$ + 1-heptanol + 120 °C	Microwave
VHPC3	VPOC3	$V_2O_5 + H_3PO_4$ + 1-heptanol + 150 °C	Microwave
VHPD1	VPOD1	$V_2O_5 + H_3PO_4$ + 1-decanol + 100 °C	Microwave
VHPD2	VPOD2	$V_2O_5 + H_3PO_4$ + 1-decanol + 120 °C	Microwave
VHPD3	VPOD3	$V_2O_5 + H_3PO_4$ + 1-decanol + 150 °C	Microwave
VHP1	VPO1	VPO method ($V_2O_5 + H_3PO_4$ + benzyl alcohol + isobutanol)	Microwave
VHP2	VPO2	VPD method ($VOPO_4{\cdot}2H_2O$ + isobutanol)	Microwave

slow hydrothermal synthesis requiring the presence of surfactants as the template agent at 150 °C for 144 h [15,16].

In this paper, we extend this earlier work and present a detailed study of the morphology and structure of vanadyl pyrophosphate catalysts. The direct (one step) synthesis is carried out in a long chain aliphatic alcohol (such as isobutanol, 1-pentanol, 1-heptanol and 1-decanol) 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 $VOHPO_4{\cdot}0.5H_2O$ by simple variation of reducing agents. Meanwhile for comparison, vanadyl pyrophosphate catalysts were prepared by three different methods, namely (i) conventional VPO, (ii) conventional VPD, and (iii) the new solvothermal synthesis method. The information presented by this work provides a basis for the improved high-pressure solvothermal method for the preparation of the catalyst precursor.

2. Experimental

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 at ambient and high-pressure conditions were carried out. The detailed descriptions of precursor production by VPO and VPD have been reported in previous studies by Rownaghi et al. [17,18] and are omitted here for brevity.

2.1.1. 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 pre-treatment, and primary long chain aliphatic alcohol (isobutanol, 1-pentanol, 1-heptanol and 1-decanol) was 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 elevated temperatures (100, 120 and 150 °C) 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 by-products. The resulting hot blue solid was recovered by vacuum filtration, and washed with hot distilled water. The obtained blue solid was then heated for 5 min in the microwave (MW). The heating conditions were a frequently of 2450 MHz and an output power of 300 W.

All precursors synthesized by the three methods indicated above contained $VOHPO_4{\cdot}0.5H_2O$, which was identified by powder X-ray diffraction. The calcination of obtained precursors was carried out 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 Shimadzu diffractometer model XRD 6000 employing CuK_α ($\lambda = 1.54439$ Å) radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The spectra were scanned at a rate of 2.0°/min in the range $2\theta = 10–60°$.

2.2.2. BET surface area

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

2.2.3. Redox titration

Redox titration was carried out using the method of Niwa and Murakami [19] to estimate the average oxidation number of vanadium.

2.2.4. Scanning electron microscope (SEM)

Surface morphology of the catalysts was observed under a scanning electron microscope (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.

2.3. Catalytic test

The oxidation of *n*-butane to maleic anhydride was carried out in a fixed-bed flow microreactor under standard reaction condition containing a standard mass of catalyst (0.25 g) at 673 K with 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 diameter (to avoid mass transfer limitations) 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 on-line gas chromatograph for *in situ* analysis. The

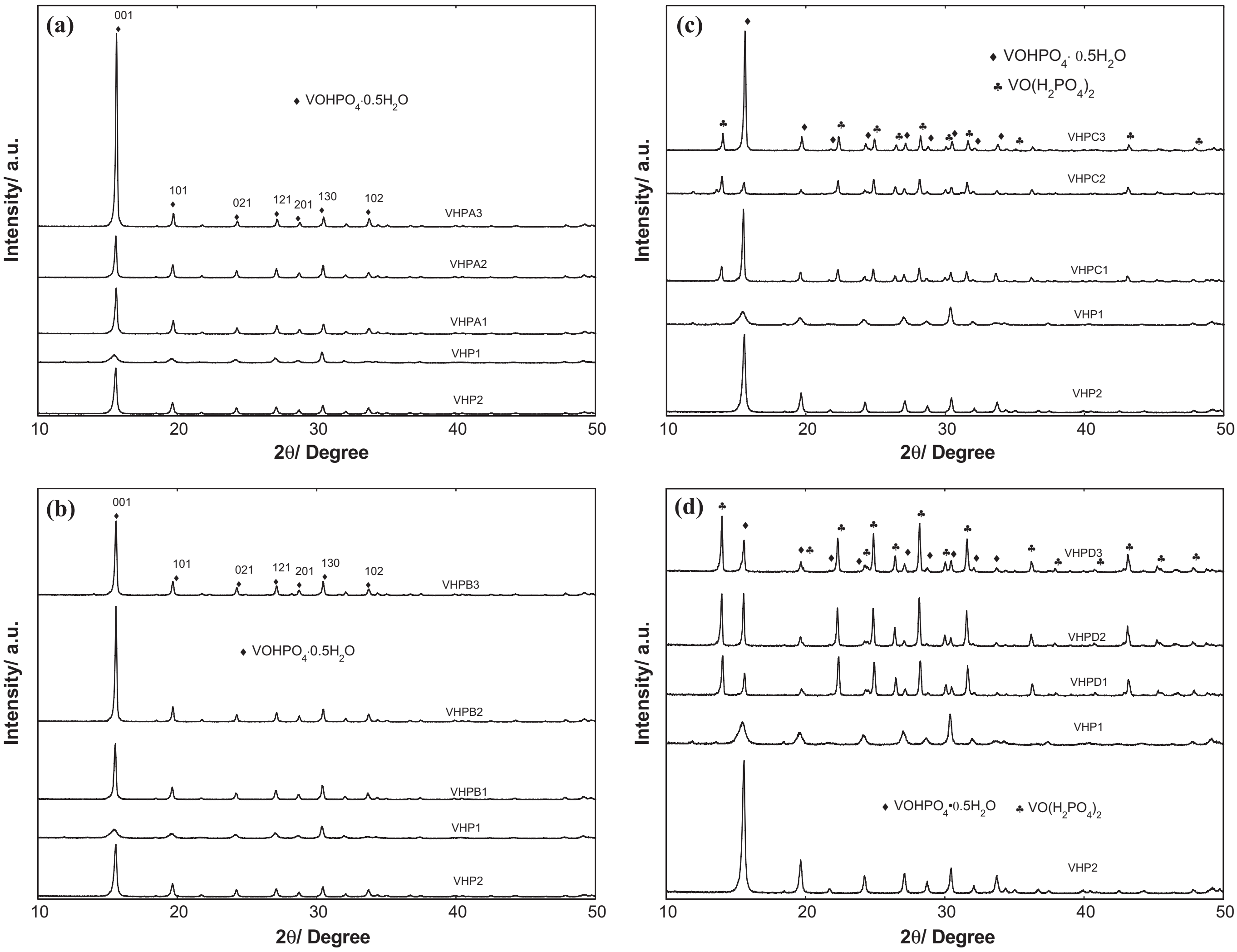

Fig. 1. (a) Powder XRD patterns of vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$, VHP) derived by solvothermal reaction in isobutanol for 72 h at 100 °C (VHPA1), 120 °C (VHPA2), 150 °C (VHPA3) and conventional VPO and VPD methods: (0 0 1) and (1 3 0) main peaks for $VOHPO_4{\cdot}0.5H_2O$. (b) Powder XRD patterns of vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$, VHP) derived by solvothermal reaction in 1-pantanol for 72 h at 100 °C (VHPB1), 120 °C (VHPB2), 150 °C (VHPB3) and conventional VPO and VPD methods: (0 0 1) and (1 3 0) main peaks for $VOHPO_4{\cdot}0.5H_2O$. (c) Powder XRD patterns of vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$, VHP) derived by solvothermal reaction in 1-heptanol for 72 h at 100 °C (VHPC1), 120 °C (VHPC2), 150 °C (VHPC3) and conventional VPO and VPD methods: (0 0 1) and (1 3 0) main peaks for $VOHPO_4{\cdot}0.5H_2O$. (d) Powder XRD patterns of vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$, VHP) derived by solvothermal reaction in 1-decanol for 72 h at 100 °C (VHPD1), 120 °C (VHPD2), 150 °C (VHPD3) and conventional VPO and VPD methods: (0 0 1) and (1 3 0) main peaks for $VOHPO_4{\cdot}0.5H_2O$.

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. The influence of alcohols and reduction temperature on microstructures of precursors and catalysts

The vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) was produced isothermally by solvothermal processing, at 100, 120 and 150 °C. Diffraction patterns for the precursor and for VPO catalysts are shown in Figs. 1 and 2. The catalyst precursors obtained solvothermally (isobutanol and 1-pentanol) show the same hydrated phase ($VOHPO_4{\cdot}0.5H_2O$) as conventional VPO and VPD. The crystallinity of precursor and catalyst is strongly dependent on the reducing agent and reduction temperature. In Figs. 1(a) and 2(a), for example, it is observed that diffraction peaks for the 0 0 1 and 0 2 0 plane narrow and intensify with increasing reduction temperature. Fig. 1(a) shows the XRD patterns of the $VOHPO_4{\cdot}0.5H_2O$ prepared by the conventional VPO and VPD methods, and using isobutanol in the solvothermal method. The diffractions at $2\theta = 15.48°$, 19.56°, 24.14°, 27.00° and 30.34° are identical to $VOHPO_4{\cdot}0.5H_2O$ precursors (JCPDS 37-269) and no traces of the impurity $VO(H_2PO_4)_2$ [20,21]. Similar trends were observed for the entire precursor studied but the method at the evaluated temperatures leads to intensity at peaks of $2\theta = 15.5°$ and 30.4° indexed to the 0 0 1 and 1 3 0 planes. The same intensity was obtained from the 1 3 0 plane for all the precursors prepared by the solvothermal method at different temperatures and the conventional VPO and VPD methods. However, as can be seen from the XRD patterns shown in Fig. 1(a), the intensity of 0 0 1 plane significantly increases as the temperature increases from 100 to 150 °C at $2\theta = 15.5°$ (four to five-fold) as compared to the same peak of the precursor prepared by the conventional VPO (VHP1) and VPD (VHP2) methods. The peak intensities reflect the total scattering from the each plane in the phase's crystal structure, and are directly dependent on the distribution of particular atoms in the structure. Thus intensities are ultimately related to both the structure and composition of the phase. The different preparation methods

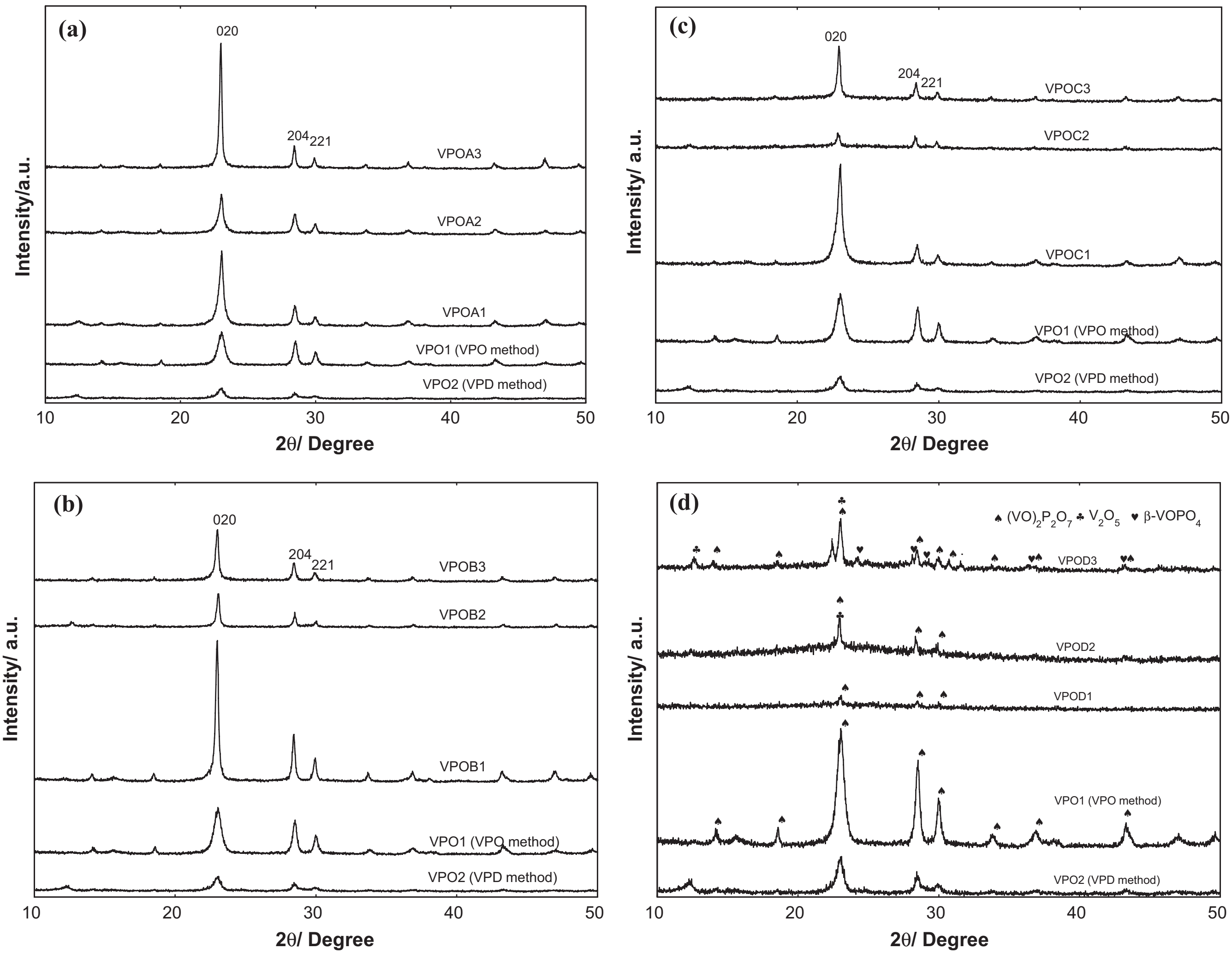

Fig. 2. (a) Powder XRD patterns of vanadyl pyrophosphate ($(VO)_2P_2O_7$, VPO) derived by solvothermal reaction in isobutanol for 72 h at 100 °C (VPOA1), 120 °C (VPOA2), 150 °C (VPOA3) and conventional VPO (VPO1) and VPD (VPO2) methods: (0 2 0) and (2 0 4) main peaks for $(VO)_2P_2O_7$. (b) Powder XRD patterns of vanadyl pyrophosphate ($(VO)_2P_2O_7$, VPO) derived by solvothermal reaction in 1-pantanol for 72 h at 100 °C (VPOB1), 120 °C (VPOB2), 150 °C (VPOB3) and conventional VPO (VPO1) and VPD (VPO2) methods: (0 2 0) and (2 0 4) main peaks for $(VO)_2P_2O_7$. (c) Powder XRD patterns of vanadyl pyrophosphate ($(VO)_2P_2O_7$, VPO) derived by solvothermal reaction in 1-heptanol for 72 h at 100 °C (VPOC1), 120 °C (VPOC2), 150 °C (VPOC3) and conventional VPO (VPO1) and VPD (VPO2) methods: (0 2 0) and (2 0 4) main peaks for $(VO)_2P_2O_7$. (d) Powder XRD patterns of vanadyl pyrophosphate ($(VO)_2P_2O_7$, VPO) derived by solvothermal reaction in 1-decanol for 72 h at 100 °C (VPOD1), 120 °C (VPOD2), 150 °C (VPOD3) and conventional VPO (VPO1) and VPD (VPO2) methods: (0 2 0) and (2 0 4) main peaks for $(VO)_2P_2O_7$.

and temperatures affect the distribution of particular atoms in the structure and composition of the phase. For the purposes of forming active catalysts with tetravalent vanadium, the precursors were calcined at 733 K under 1.5% *n*-butane/air mixtures. As can be seen from the XRD patterns shown in Fig. 2(a), the intensity of 0 2 0 phase significantly increases (four to five-fold) as the temperature increases from 100 to 150 °C at $2\theta = 22.9°$. However, the increasing synthesis temperature causes dramatic changes in the crystallinity of the $(VO)_2P_2O_7$ phase. As the synthesis temperature increases, the X-ray diffraction peaks sharpen and the surface area decreases (Fig. 2(a)). The same trend was observed as compared to the same peak of the catalyst prepared by the conventional VPO (VPO1) and VPD (VPO2) methods. The average crystallite size obtained in this step by the Debye–Scherrer equation [22] is shown in Table 2. The average particle size of the VPO catalyst prepared by the solvothermal method using isobutanol as a reducing agent was estimated to be ~38 nm. The average vanadium oxidation states of calcined samples are reported in Table 2. With VPOA1, VPOA2 and VPOA3, the oxidation states are 4.12, 4.2 and 4.10, respectively, indicating that pentavalent vanadium (highly oxidized) is prevalent in the all solvothermal catalysts. As shown by XRD, the only crystalline

Table 2
XRD data of solvothermal and conventional nanostructure catalyst.

Catalyst	FWHM[a] (Å)		Crystallite size[b] (nm)	
	0 2 0	2 0 4	0 2 0	2 0 4
VPOA1	0.522	0.464	15.3	17.5
VPOA2	0.355	0.306	22.5	26.5
VPOA3	0.207	0.204	38.7	39.8
VPOB1	0.236	0.221	33.9	36.7
VPOB2	0.227	0.210	35.2	38.6
VPOB3	0.493	0.480	16.3	16.9
VPOC1	0.387	0.304	20.7	26.6
VPOC2	0.282	0.256	28.4	31.7
VPOC3	0.229	0.230	35.0	35.2
VPOD1	0.220	0.240	36.4	33.7
VPOD2	0.230	0.191	34.8	42.3
VPOD3	0.469	0.490	17.1	16.5
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 0 2 0 and 2 0 4 reflection.

[b] Crystallite size was calculated according to Debye–Scherrer equation [22].

phase detected in all materials is the pyrophosphate $(VO)_2P_2O_7$ [23,24], where vanadium is tetravalent, which is the phase that is considered to be the most active one for *n*-butane partial oxidation reactions [25].

In view of the well-established role of the 0 2 0 plane of the $(VO)_2P_2O_7$ 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 $(VO)_2P_2O_7$ catalyst. The catalyst prepared by the solvothermal method at 100 °C, is shown to be significantly more intense (four to eleven-fold) as compared to the same peak of the catalyst prepared by the conventional VPO (VPO1) and VPD (VPO2) methods. The intensity of the plane 0 2 0 is used to determine the preferential exposure of the surface 0 2 0 planes proposed to contain the active and selective catalytic sites for selective oxidation of butane to maleic anhydride [26].

The XRD patterns of the precursor and catalyst obtained using 1-pentanol as a reducing agent by the solvothermal method are shown in Figs. 1(b) and 2(b). The results show similar 2θ diffraction as compared to the isobutanol. The XRD patterns of the precursors show that the strong peak of 0 0 1 phase significantly increases as the temperature increases from 100 to 120 °C at $2\theta = 15.5°$. The same trend was observed in the 0 0 1 plane intensity increase (four to five-fold) as compared to the same peak of the precursors prepared by the conventional VPO (VHP1) and VPD (VHP2) methods. XRD patterns of the catalyst are shown in Fig. 2(b). Interestingly, the intensity of 0 2 0 plane significantly decreases (four to five-fold) as the temperature increases from 100 to 150 °C at $2\theta = 22.9°$. The catalyst prepared by the solvothermal method in this step, also shows the higher crystallite structure in 0 2 0 plane as compared to the same peak of the catalyst prepared by the conventional VPO (VPO1) and VPD (VPO2) methods. The average crystallite size of VPO catalyst obtained by the Debye–Scherrer equation [22], prepared by solvothermal method (VPOD) and using 1-pentanol as a reducing agent was estimated to be ∼30 nm. Interestingly, for the catalyst prepared by the solvothermal method, the intensity of 0 2 0 plane and particle size significantly decrease as the temperature increases.

Fig. 1(c) shows XRD patterns of the precursors obtained from 1-heptanol. When 1-heptanol was used as a reducing agent, the product partly transformed from orthorhombic $(VOHPO_4{\cdot}0.5H_2O)$ into the tetragonal $VO(H_2PO_4)_2$ phase. A new phase, $VO(H_2PO_4)_2$ and $VOHPO_4{\cdot}0.5H_2O$ were the main phase of the precursors. As shown in Fig. 1(c), by changing the environment, with increase in the temperatures from 100 to 150 °C, the tetragonal $VO(H_2PO_4)_2$ phase is present and thermodynamically stable. With the increase in the reaction temperature from 100 to 120 °C, first the diffraction peaks became shorter, and then with increase in the temperature to 150 °C, the diffraction peaks became progressively sharp, the crystallite size being enlarged. As can be seen from the XRD patterns shown in Fig. 2(c), a main phase of $(VO)_2P_2O_7$ (JCPDS 34-1381) appeared in the catalyst. Interestingly, the trend observed for the catalyst prepared by 1-heptanol is reduced 0 2 0 intensity by increasing the preparation temperature from 100 to 150 °C. Fig. 2(c) shows that with increased reaction temperature, the diffraction 0 2 0 plane became weak.

However, the effect of 1-decanol on the XRD patterns of precursors prepared by the solvothermal method was different. As Fig. 1(d) shows, using 1-decanol as a reducing agent, the fraction of tetragonal phase $VO(H_2PO_4)_2$ increases with a decrease in the orthorhombic $(VOHPO_4{\cdot}0.5H_2O)$ phase [26]. Interestingly, the results obtained in this trend were reversed when 1-decanol was replaced with light primary alcohols. However, the result shows an impurity and a slight decrease in the diffraction peaks as compared with the catalyst obtained by conventional VPO and VPD methods. The XRD patterns of the catalyst are shown in Fig. 2(d). $VOPO_4$ (JCPDS 27-948) was the only other phase accompanied with $(VO)_2P_2O_7$ phase, but V_2O_5 (JCPDS 45-1074) simultaneously appeared in the VPOD catalyst. This probably illuminated that the used long chain carbon alcohol leads to the formation of some $VO(H_2PO_4)_2$ and changed in the crystallinity of the $(VO)_2P_2O_7$. The catalyst prepared by the solvothermal method in this step, shows the poor crystallites structure in the 0 2 0 plane as compared with the same peak of the catalyst prepared by the conventional VPO (VPO1) and VPD (VPO2) methods and a decrease in the particle size as increase in reaction temperature (Table 2). The average particle sizes prepared by the solvothermal method (VPOD) and using 1-decanol as a reducing agent were estimated to be ∼30 nm. The X-ray diffraction patterns for the results obtained were carried out isothermally at 100, 120 and 150 °C a reaction time of 72 h show the chain of alcohol (number of carbon) plays an important role on the phase content and the particle size the orthorhombic structure [27] of the $VOHPO_4{\cdot}0.5H_2O$ phase and the $(VO)_2P_2O_7$ catalyst.

Table 3
Surface area, average oxidation states and percentage of V^{4+} and V^{5+} oxidation states present in solvothermal and conventional VPO catalyst.

Catalyst	Surface area[a] ($m^2\,g^{-1}$)	Oxidation state of vanadium[b]		
		V^{5+} (%)	V^{4+} (%)	Average
VPOA1	16	12	88	4.12
VPOA2	12	20	80	4.20
VPOA3	12	10	90	4.10
VPOB1	23	13	87	4.13
VPOB2	20	20	80	4.20
VPOB3	15	16	84	4.16
VPOC1	18	10	90	4.10
VPOC2	16	17	83	4.17
VPOC3	15	15	85	4.15
VPOD1	11	20	80	4.20
VPOD2	13	15	85	4.15
VPOD3	14	10	90	4.10
VPO1	17	27	73	4.27
VPO2	24	21	79	4.21

[a] After pretreatment at 423 K in a vacuum.

[b] Average oxidation number of vanadium estimated by redox titration [19].

3.2. BET surface area measurement and average oxidation number determination

Table 3 shows the effect of the reaction conditions and organic media on the BET surface area, oxidation state of vanadium as well as percentage of V^{4+} and V^{5+} present in the catalysts. It is found that the surface area for the 1-pentanol obtained catalysts (VPOB1) increased from 16 $m^2\,g^{-1}$ (VPOA1–isobutnaol) to 23 $m^2\,g^{-1}$ and then further decreased to 18 $m^2\,g^{-1}$ for the VPOC1 catalyst (1-heptanol). The surface area however was drastically reduced to 11 $m^2\,g^{-1}$ for the VPOD1 catalyst. BET results indicated that surface area of catalyst prepared by solvothermal (depended on chain alcohol) was significantly higher than those reported for VPO catalyst prepared via the hydrothermal method [15]. The obtained surface area values were consistent with crystallite size data and SEM morphology. Increases in the rate crystal growth at any temperature, affect crystallite structure and the X-ray diffraction peaks become narrower with reduced peak broadening. The results show that with the increase in the reaction temperature, the surface area of the catalyst gradually decrease.

However, the thermal decomposition of mixtures of V_2O_5, H_3PO_4 in longer chain alcohols (C_4–C_{10}) shows, nanocrystalline VPO catalyst with crystallite size of catalyst (20–40 nm) and large BET surface areas as compared the catalyst prepared by hydrothermal. The VPO catalyst prepared in isobutanol produces ultrahigh crystallite of $(VO)_2P_2O_7$ and leads to large surface areas and small crystallite sizes. Interestingly, the result obtained by 1-decanol had

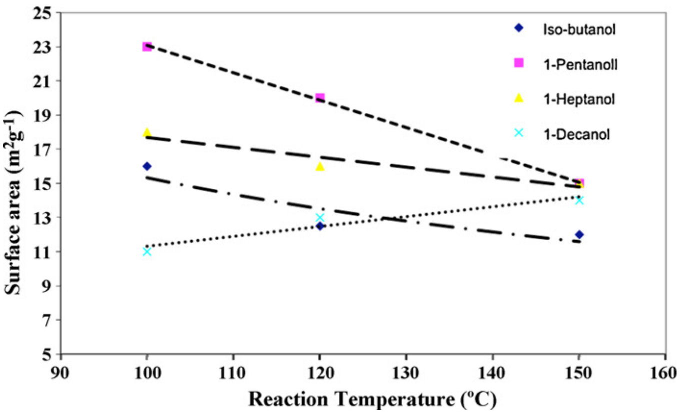

Fig. 3. Relationship between preparation reaction temperature with catalyst surface area for the VPO catalyst derived by solvothermal reaction for 72 h at 100, 120 and 150 °C.

mixed of the $(VO)_2P_2O_7$ and impurity gave a small surface area. Moreover, in the case of 1-decanol, the combination of $(VO)_2P_2O_7$ with $VOPO_4$ phase resulted in lower surface area. The preparation temperature is very important in the solvothermal synthesis of vanadium phosphate catalysts. In Fig. 3, the surface area of the catalyst obtained by the solvothermal method is plotted against the preparation reaction temperature. As the reaction temperature increased over the range 100–150 °C, the surface area of the catalyst gradually decreased, except for 1-decanol. In conclusion, as can be seen in Table 1 and Fig. 3, the surface area of the catalyst prepared by solvothermal, had linear relation with temperature and reaction media, which is increase the longer chain alcohols (except 1-decanol) and reaction temperature, the surface area will be decreased.

The average vanadium oxidation number of the solvothermal catalysts was found lower (~4.15) compared to the conventional VPO (4.21) and VPD (4.27) catalysts. This was due to an increment of V^{4+} oxidation state from ~75% to ~85%. However, the amount of the V^{4+} was increased to 90%, corresponding to a decrease in the average vanadium oxidation state to 4.10 for the VPOA3, VPOC1 and VPOD3 catalysts. 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. It is widely accepted that the valence state of vanadium plays an important role in the selective oxidation of *n*-butane to MA [28]. Therefore, the polarity and the type of the alcohol used as reducing agent exhibit stronger impact on catalysts properties.

3.3. *Effect of alcohol on vanadyl pyrophosphate catalyst morphology when using the solvothermal route*

Fig. 4 reports SEM micrographs of the catalysts prepared in an organic media by solvothermal, VPO and VPD method. SEM images reveal a novel morphology of solvothermal prepared catalysts. Among the characteristic vanadium phosphate rosette shaped particles, solvothermal catalysts displayed a platelike structure with the average particle size of less than 2 μm. In contrast to other solvothermal catalysts, catalyst prepared in an isobutanol solvent clearly shows a lamellar morphology with well-formed plate-like crystals in agreement with XRD results. 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 presence of the lengthy alkyl chain dramatically increases the hydrophobic nature, leads to lower diffusion rate of ions in the solvent, and finally to the formation of smaller particles. The SEM micrographs synthesized by conventional VPO (VPO1) and VPD (VPO2) methods showed rosette structures as characterized by the XRD pattern with the 0 2 0 reflection dominant [10,13,17]. VPOA shows particles of different shapes and sizes agglomerated together. Mainly flat smooth needle-like particles are aggregated in a concentric secondary structure.

SEM of VPOB reveals the presence of amorphous parts in the form of small and flat particles with a secondary structure of primary platelets (due to high chain alcohol), below 1 μm mean diameter, when 1-pentanol was replaced by isobutanol. These amorphous parts reduce the particle size and therefore increase the specific surface area. In contrast, vanadium phosphate prepared using 1-heptanol as a reducing agent (VPOC) has smaller pieces of crystal platelets in a random configuration, thus providing an explanation for the higher measured surface area observed. Some of the micrographs from the VPOD catalyst show flat rounded particles that reveal the existence of small spherical particles (about 2 μm in diameter). Hence, the use of organic media as reducing agent in the preparation of $VOHPO_4{\cdot}0.5H_2O$, controls the morphology of the crystallites and surface area. Comparing the series allows to conclude that solvothermal synthesis produces the nanostructure platelet structure with a secondary platelet morphology.

3.4. *Influence of catalyst microstructure on selectivity in the selective oxidation of n-butane*

Table 4 and Fig. 5 demonstrate the effect of both catalyst synthesis method (solvothermal, conventional VPO, VPD and hydrothermal) and reducing agent on *n*-butane conversion and maleic anhydride selectivity. The catalysts were evaluated *in situ* in the laboratory microreactor with 1.7% *n*-butane in air at 673 K. The catalyst performance data at steady state condition are shown in Table 4. Under the conditions applied, in all catalysts, the conversions increased slowly with time online, steadily approaching complete conversion over a 300 min period, although the catalysts that were synthesized solvothermally in 1-pentanol (VPOB1) seem to stabilize more rapidly and stabilize first. The most active catalysts for maleic anhydride synthesis were VPOB1 and VPO2 which gave almost identical performance with surface area of 23 and 24 $m^2\,g^{-1}$, respectively. The crystals along 0 2 0 phases (Table 2) display smaller size and hence higher surface area (Table 3). Furthermore, higher amounts of surface lattice oxygen (oxygen species associated with $V^{4+}(O^-)$) which act as active species, are also contributed to improved catalyst activity [31–33]. Maleic anhydride (MA) selectivity profiles for all catalysts do not change significantly with time. The MA selectivities remained higher than 60% for all cat-

Table 4
Catalytic performance of solvothermal, conventional VPO, VPD and hydrothermal methods for the oxidation of *n*-butane to maleic anhydride.[a]

Catalyst	*n*-Butane conversion (%)	Selectivity (%)			Yield[b] (%)
		MA	CO	CO_2	
VPOA1	52	*66*	15	19	34.3
VPOB1	55	*69*	14	17	37.9
VPOC1	51	*64*	16	20	32.6
VPOD1	50	*61*	17	22	30.5
VPO1	39	62	19	19	24.2
VPO2	65	54	20	26	35.1
[c]Conventional hydrothermal (VPH)	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] Taufiq-Yap et al. [15].

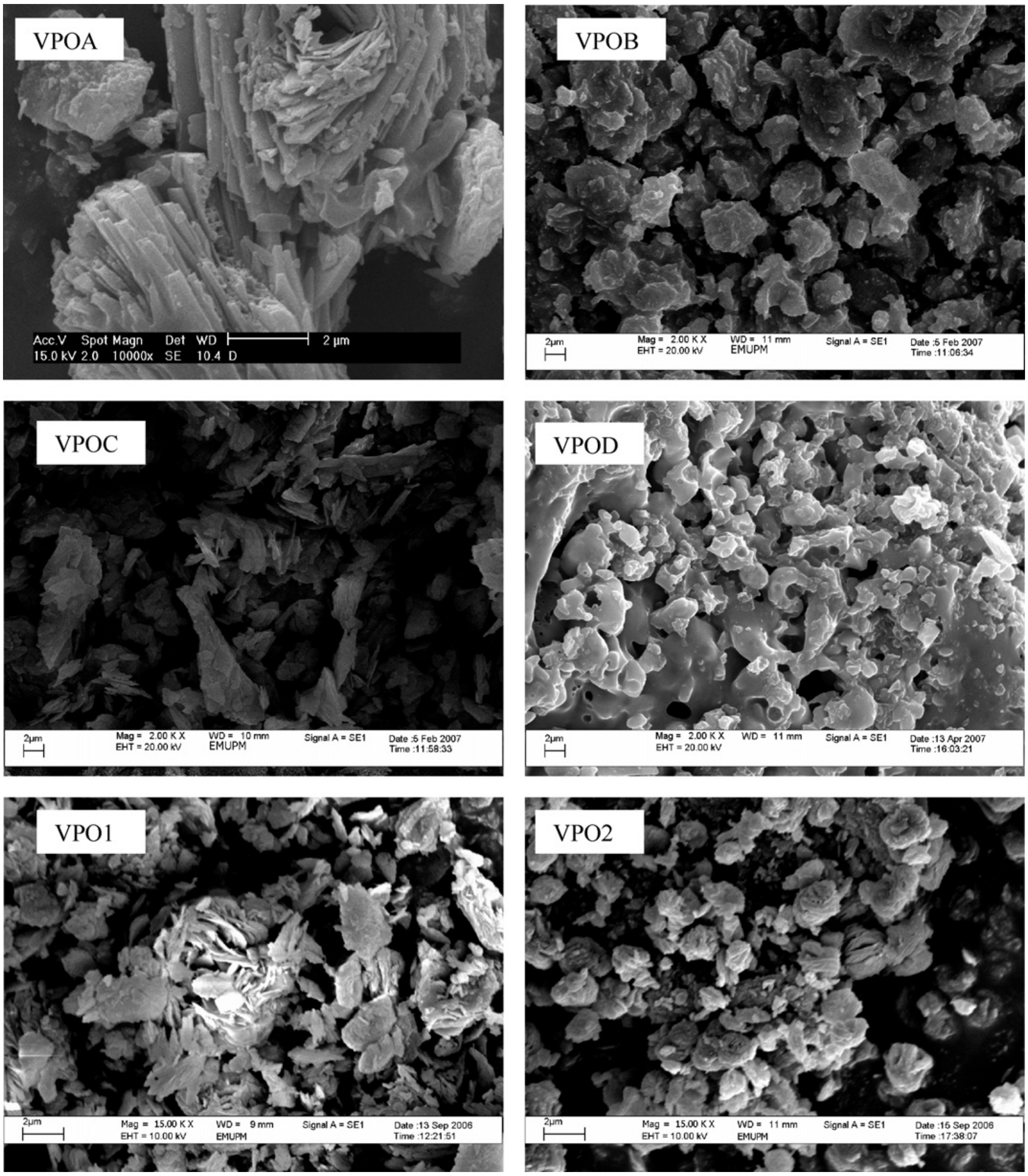

Fig. 4. Scanning electron microscope (SEM) of VPO catalyst derived by solvothermal reaction for 72 h in isobutanol (VPOA), 1-pentanol (VPOB), 1-heptanol (VPOC), 1-decanol (VPOD) and conventional VPO (VPO) and VPD (VPO2) methods.

alysts, except conventional VPO1 catalyst (see Fig. 5). The highest value was 69% (at 55% conversion), with VPOB1. The CO_x selectivities vary between 31% and 39% for the solvothermal catalysts and 38–46% for the conventional VPO and VPD catalysts.

It is apparent that the reducing agent and preparation reaction temperature are very important parameters in the solvothermal synthesis of vanadium phosphate catalysts. As the carbon chain increased over the range C_4–C_{10}, both conversion and selectivity of VPO catalyst in *n*-butane to maleic anhydride reaction decreased. However, the catalyst prepared with solvothermal method is more active and more selective compared to conventional VPO synthesized by hydrothermal routes (Fig. 5).

The catalysts derived from solvothermal method can provide high surface area resulting in high activity and selectivity with comparable performance to those prepared by conventional methods such as standard VPO, VPD and hydrothermal routes [5,12,15–17]. 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 (Fig. 6). It is clear

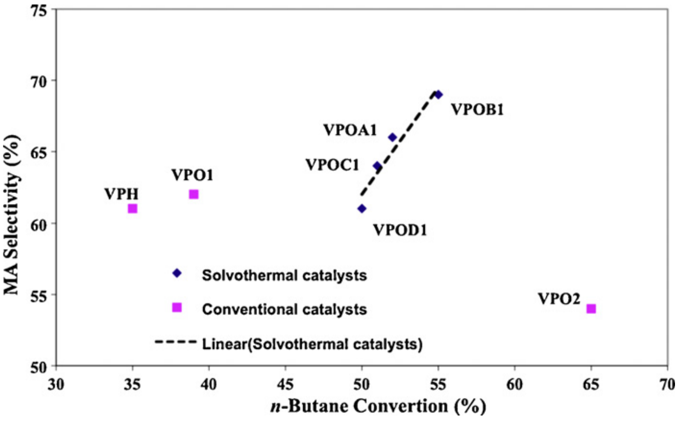

Fig. 5. MA selectivity as a function of the *n*-butane conversion (T = 673 K).

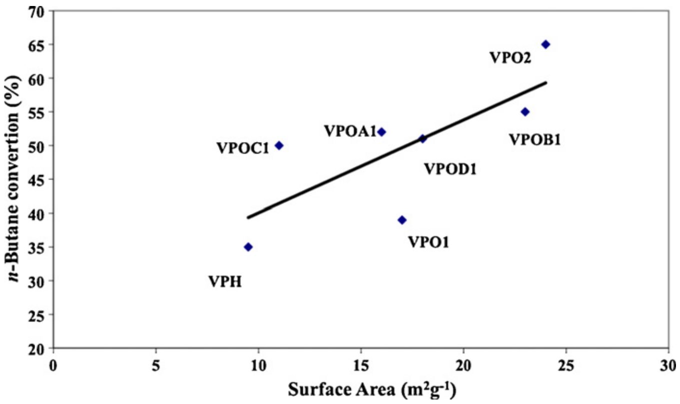

Fig. 6. Relationship between *n*-butane conversions (%) with catalyst surface area.

that the activity is primarily dependent upon the catalyst surface area. The higher number of active sites (V^{4+}) and oxygen species are responsible for activation of *n*-butane and enhancement of 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 [29–33]. However, this is significantly higher than for conventional hydrothermal preparation previously reported [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.

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, time and promoters. 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

The use of high-pressure autoclave during the reaction of H_3PO_4 and V_2O_5 with alcohols has been shown to be effective not only in altering the crystalline and morphology of the precursors and catalyst, but it can also induce certain phase transformation. The use of a simple one-step solvothermal method, which is water- and surfactant-free by using low amount of reducing agent in these preparations shows that the rate of catalyst precursors formation can be increased. On the basis of the above solvothermal process, the excess carbon chain leads to the formation of some $VO(H_2PO_4)_2$; however, changing synthesis reaction temperature also causes dramatic changes in the crystallinity of $VOHPO_4{\cdot}0.5H_2O$ phase. As the carbon chain and synthesis reaction temperature increased, the X-ray diffraction peaks sharpened (higher crystalline size in 0 2 0 phase) and the surface area decreased. Current results confirmed the linear relationship between surface area and crystalline size along the 0 2 0 phase. Moreover, as the carbon chain increased over the range C_5–C_{10}, the activity of the catalysts as well as selectivity for the *n*-butane to maleic anhydride decreased.

This solvothermal method has proved beneficial in the formation of high surface area catalyst (*ca.* 23 $m^2\,g^{-1}$) and significantly higher conversion (*ca.* 55%) for the partial oxidation of *n*-butane to MA. This method of preparation consistently yields high surface area materials compared to previous surfactant- and water-based hydrothermal method that give rise to low surface area catalysts (*ca.* 9.5 $m^2\,g^{-1}$) that would have a (*ca.* 35%) on conversion of *n*-butane. The study shows that long carbon chain reducing agent (C_6–C_{10}) and high temperature are not required for the production of highly active and selective catalysts. In general, the catalysts prepared via solvothermal method give very similar conversion and selectivity for *n*-butane to maleic anhydride, under the same reaction conditions. The highest MA selectivity (69%) with 1.7% *n*-butane in the feed was associated with a 1-pentanol solvothermal catalyst (VPOB1). In summary, the solvothermal method represents a simple, efficient and low-cost technique for the synthesis of VPO catalyst with improved catalytic performance in selective oxidation of *n*-butane.

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