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Solvothermal synthesis of vanadium phosphate catalysts for *n*-butane oxidation

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ABSTRACT

In this paper, we have developed a simple, low-cost, template-free and surfactant-free solvothermal process for synthesis of vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) with well defined crystal size. The synthesis was performed by reaction of $VPO_4{\cdot}2H_2O$ with an aliphatic alcohol (isobutyl alcohol, 1-pentanol, 1-hexanol, 1-heptanol or 1-decanol). This afforded well crystallized $VOHPO_4{\cdot}0.5H_2O$ by solvothermal methods at 120 °C temperature. 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. By varying the reducing agent, the solvothermal evolution process from layered tetragonal phase $VOPO_4{\cdot}2H_2O$ to orthorhombic phase $VOHPO_4{\cdot}0.5H_2O$ was observed. It was found that the length of carbon chain in an alcohol in the solvothermal condition had a great impact on chemical and physical properties of resulting catalysts. Interestingly, there was no trace of $VO(H_2PO_4)_2$ an impurity noted to be readily formed under solvothermal preparation condition. Therefore, this study introduces a more facile synthetic pathway to V(III) compounds. In addition, the microwave-synthesized catalysts exhibited some properties superior to those of conventionally synthesized catalyst such as better stability, crystallinity, and catalytic activity in the production of maleic anhydride. The characterization of both precursors and calcined catalysts was carried out using X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometer (ICP-AES), N_2 physisorption, temperature programmed reduction (H_2-TPR) and scanning electron microscopy (SEM). The XRD pattern of the active catalyst prepared by this solvothermal method confirmed the presence of smaller crystal size (between 6 and 13 nm along 0 2 0 planes) of vanadium phosphate catalyst with higher specific surface area. Finally, the yield of maleic anhydride was significantly increased from 29% for conventional catalyst to 44% for the new solvothermal catalyst.

1. Introduction

Catalysts are well-known in industry for their ability to speed up reactions and they provide pathways by which the selectivity of the reaction maybe improved. This increased selectivity is the most important factor in catalysis, because a required product is obtained, rather than a mixture with side products of little value. The selective oxidation of *n*-butane continues to receive considerable research attention. In this respect, vanadium phosphate catalysts have been extensively investigated and to date they represent the sole example of a commercial catalyst for the selective oxidation of an alkane [1–4]. The most interesting of these materials is considered to be vanadyl pyrophosphate $(VO)_2P_2O_7$, which is derived from a stable precursor material, *i.e.*, vanadyl hydrogen phosphate hemihydrate, $VOHPO_4{\cdot}0.5H_2O$, via a topotactic transformation [3]. Hence, the preparation route and precursor morphology is of importance in determining the eventual catalyst morphology [4–14], and the performance following *in situ* activation in *n*-butane/air to form the final catalyst [4,5].

Various synthesis methods have been developed in order to obtain vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) with controlled catalytic properties. Among them, three widely used techniques are (i) VPA method which was used in the early literature [15] with water as the solvent, (ii) VPO method which is considered to be the standard preparation method and is used in most academic studies [16,17] and (iii) VPD method which was first disclosed by Horowitz et al. [17] and further described by Johnson et al. [16] and has subsequently been investigated in detail [10,18,19]. Previously these catalysts have been synthesized by slow hydrothermal synthesis requiring the presence of templates at 150 °C for 144 h [20,21]. The method described in this work, is termed solvothermal because of the use of organic media in place of oxalic acid dehydrate, surfactants and water for hydrothermal reactions [22–25].

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Recently the solvothermal technique has attracted much interest in the synthesis of novel and essential materials. While, there have been very few studies focused on the preparation of vanadium phosphate catalyst using solvothermal synthesis at lower temperatures. In this paper, we report the successful preparation of crystalline vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$) via this new technique. The synthesis is carried out in an aliphatic alcohol (such as $C_5H_{12}O$, $C_6H_{14}O$, $C_7H_{16}O$ and $C_{10}H_{22}O$) as the solvent and $VOPO_4{\cdot}2H_2O$ as precursor without employing any template or surfactant. We have been exploring a controlled solvothermal synthesis of orthorhombic phase $VOHPO_4{\cdot}0.5H_2O$ by easily varying reducing agents. We previously tried to modify the preparation procedure $VOHPO_4{\cdot}0.5H_2O$ synthesis under reflux conditions at ambient pressure in either isobutanol or ethylene glycol and water [26–28]. In this study however, we have improved the preparation method using 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 such as (i) producing no impurity phase $[VO(H_2PO_4)_2]$ in resulted catalyst, (ii) applying a simple and low-cost technique (template and water free method), (iii) utilizing lower amount of reducing agent, (iv) producing a higher active surface area catalyst, and (v) synthesizing of catalyst at shorter time as compared to conventional method. In this study, vanadium phosphate catalysts were prepared by two different methods namely (i) conventional VPD and (ii) solvothermal synthesis method. The information presented by this work, provides a basis for development of an improved solvothermal method for the synthesis of VPO catalyst.

2. Experimental

2.1. Catalysts 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.

2.1.1. $VOPO_4{\cdot}2H_2O$

Vanadyl phosphate dihydrate ($VOPO_4{\cdot}2H_2O$, VPD) was prepared according to the procedure described by Johnson et al. [16] at ambient pressure which has subsequently been improved by using different reducing agents and promoters [19,26–29]. Details of preparation and characterization of $VOPO_4{\cdot}2H_2O$ can be found in Rownaghi et al. [26–28] and are omitted here for brevity.

2.1.2. $VOHPO_4{\cdot}0.5H_2O$

Two different techniques for $VOPO_4{\cdot}2H_2O$ synthesis at ambient and high pressure conditions were carried out as follows:

- *Standard isobutanol method*: Vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$, VHP) was synthesized by the reduction of $VOPO_4{\cdot}2H_2O$ in isobutanol. The detailed description of precursor production was reported in our previous published studies [26–28].
- *Standard high pressure autoclave (solvothermal method)*: In a typical solvothermal synthesis process, the same amount of vanadyl phosphate dihydrate [$VOPO_4{\cdot}2H_2O$ (2.0 g)] was reacted with an alcohol (30 ml) in a 50 ml capacity Teflon-lined stainless steel autoclave and then alcohol was added to fill the autoclave up to about two thirds of the total volume and the autoclave was sealed. In the next step, the autoclave was heated and maintained at 120 °C for typically 72 h. After that, the system was allowed to cool down to ambient temperature naturally. The resulting precipitate (blue solid) was then recovered by filtration and washed with hot distilled water and acetone repeatedly to remove the residual reactants and by-products. Finally, a blue powder was obtained after drying of products by both microwave heating and oven for 5 min and 12 h, respectively. All precursors synthesized by both heating methods contained $VOHPO_4{\cdot}0.5H_2O$ which were 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 *n*-butane/air mixture environment.

Table 1
Preparation condition of precursor and VPO catalyst.

Precursor	Catalyst	Preparation condition	Precursor heating
VHPA1	VPOA1	VPD1 + isobutyl alcohol + reflux	Microwave
VHPA2	VPOA2	VPD2 + isobutyl alcohol + reflux	Conventional
VHPB1	VPOB1	VPD1 + 1-pentanol + autoclave	Microwave
VHPB2	VPOB2	VPD2 + 1-pentanol + autoclave	Conventional
VHPC1	VPOC1	VPD1 + 1-hexanol + autoclave	Microwave
VHPC2	VPOC2	VPD2 + 1-hexanol + autoclave	Conventional
VHPD1	VPOD1	VPD1 + 1-heptanol + autoclave	Microwave
VHPD2	VPOD2	VPD2 + 1-heptanol + autoclave	Conventional
VHPE1	VPOE1	VPD1 + 1-decanol + autoclave	Microwave
VHPE2	VPOE2	VPD2 + 1-decanol + autoclave	Conventional

2.2. Catalyst characterization

2.2.1. X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of catalyst. It was conducted 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 was scanned at a rate of 2.0°/min in the range $2\theta = 10–60°$.

2.2.2. Inductively coupled plasma-atomic emission spectrometer (ICP-AES)

The bulk chemical composition was determined by using a sequential scanning inductively coupled plasma-atomic emission spectrometer (ICP-AES) PerkinElmer Emission Spectrometer Model Plasma 1000.

2.2.3. N_2 physisorption

The specific surface area of catalysts was determined using Sorptomatic 1990 series nitrogen adsorption/desorption analyzer. In this technique (the Brunauer–Emmett–Teller (BET) equation) was employed to calculate the specific surface area based on nitrogen uptake at liquid-nitrogen temperature by the single point method.

2.2.4. Redox titration

Redox titration was carried out using the method of Niwa and Murakami [30] to estimate the average oxidation number of vanadium.

2.2.5. Scanning electron microscope (SEM)

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

2.2.6. Temperature-programmed reduction in H_2 (H_2-TPR)

Temperature-programmed reduction in H_2 (H_2-TPR) was performed in order to observe the reducibility of the VPO catalyst by using a ThermoFinnigan TPDRO 1110 apparatus utilizing a thermal conductivity detector (TCD). H_2-TPR experiment was carried out using a quartz reactor tube (4 mm i.d.), in which a ~25 mg sample was mounted on loosely packed quartz wool. Prior to H_2-TPR measurement, catalyst was pretreated in N_2 at 473 K (heating rate of 10 K min^{-1} and hold time 30 min) and then cooled down under He gas flow. The reduction gas was composed of 5 vol% H_2 in Ar. The reaction temperature was programmed to rise at a constant rate of 10 K min^{-1}. A thermocouple in contact with the catalyst allowed the control of the temperature. The amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD). The effluent H_2O formed during H_2-TPR was adsorbed by a 5 A molecular sieve adsorbent. The error on the peak temperature was found to be ±15 °C.

2.3. Catalytic test

The oxidation of *n*-butane to maleic anhydride was carried out in a fixed-bed flow microreactor 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 give particles with 250–300 μm diameter. *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 to an on-line gas chromatography 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. Phase transformation under solvothermal condition

XRD patterns of solvothermal and conventional catalyst precursors prepared in different alcohols with various carbon chain lengths ($C_mH_{2m+1}OH$, $m = 4–10$) are shown in Fig. 1. Different solvents used in solvothermal synthesis largely affect the phase composition during the solvothermal treatment [31]. In the present research, all precursors display the same pattern corresponding to vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$, JCPDS 37-0269), identified with peaks at $2\theta = 15.48°$, 19.56°, 24.14°, 27.00° and 30.34° and confirmed to be $VOHPO_4{\cdot}0.5H_2O$ [32]. The patterns of the precursors synthesized in the conventional reflux (VPD method) as well as those of the precursors prepared in the autoclave (solvothermal method) do not reveal any extra phases. There was no obvious variation in the type of phase formation with respect to the type of solvent used. As expected, the hemihydrate precursor $VOHPO_4{\cdot}0.5H_2O$ was the only product formed at 393 K. XRD patterns of the precursors (Fig. 1) prepared throughout both standard VPD method and solvothermal route represent almost identical crystals in (1 3 0) plane and good exposure of different crystallographic plane (0 0 1). Interestingly, no characteristic peak was observed for $VO(H_2PO_4)_2$ impurities [11,33].

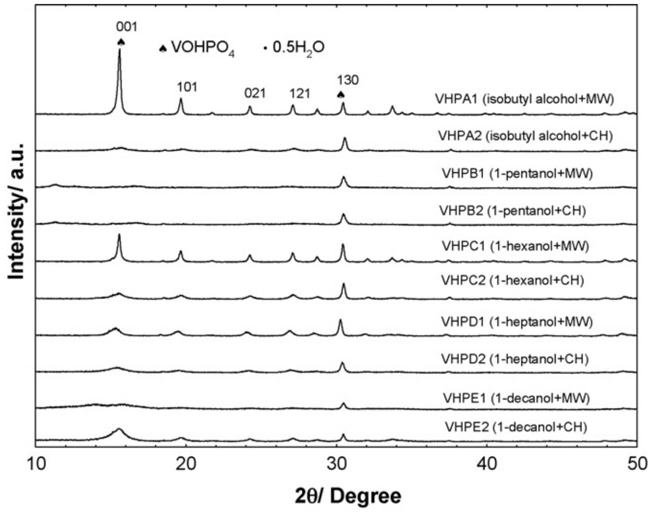

Fig. 1. X-ray powder diffraction patterns of solvothermal and conventional of vanadyl hydrogen phosphate hemihydrate ($VOHPO_4{\cdot}0.5H_2O$, VHP) precursors heated by microwave and conventional; (0 0 1) and (1 3 0) main peaks for $VOHPO_4{\cdot}0.5H_2O$.

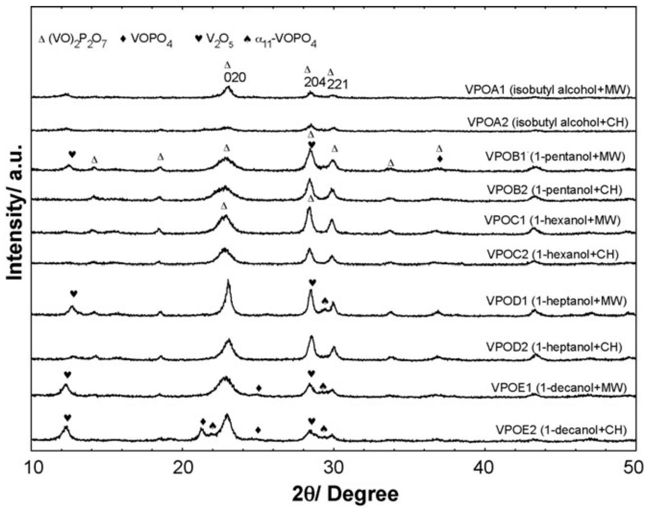

Fig. 2. X-ray powder diffraction patterns of solvothermal and conventional vanadium phosphorous oxide ($(VO)_2P_2O_7$, VPO) catalysts; (0 2 0) and (2 0 4) main peaks for $(VO)_2P_2O_7$.

Fig. 2 shows the XRD patterns of catalysts treated by calcination in *n*-butane at 460 °C. As evident from Fig. 2, the XRD patterns of catalysts correspond to the $(VO)_2P_2O_7$ phase (JCPDS 34-1381) with the main peaks at $2\theta = 22.6°$, 28.2° and 29.7°. These peaks are related to (0 2 0), (2 0 4), and (2 2 1) reflections, respectively and indicate the transformation of $VOHPO_4{\cdot}0.5H_2O$ to $(VO)_2P_2O_7$, with variations in relative intensity and peak broadness depending on the reducing agent used [11,33]. Based on the peak intensities observed in XRD patterns, microwave samples are much more crystalline than the conventionally prepared ones. Furthermore, for catalyst prepared solvothermally, some additional weak peaks emerged at $2\theta = 12.2°$ and 28.2° (JCPDS No. 45-1074) and $2\theta = 21.6°$ and 25° (JCPDS 27-0948), which correspond to the V_2O_5 and $VOPO_4$ phases, respectively.

The new phases such as V_2O_5, $VOPO_4$ and $(VO)_2P_2O_7$ were found to be the main phases when 1-pentanol, 1-hexanol and 1-decanol were used as reducing agents. In the case of VPOB1 and VPOC1, which were heated by microwave, V_2O_5 was the only phase accompanied with $(VO)_2P_2O_7$ phase. However, in the case of VPOE2, $VOPO_4$ simultaneously was appeared in the catalyst when the VHPE2 precursor was heated conventionally. Lower peak intensities at 22.2° and 29.1° were observed for solvothermal catalyst synthesized by 1-heptanol and 1-decanol as organic media representing the presence of small amount of V^{5+} phase from α_{II}-$VOPO_4$.

The average crystallite size of the samples was calculated from FWHM (full width at half maximum) of (0 2 0) and (2 0 4) peaks (the most intense peaks), using the Sherrer equation [34]. The average crystallite size value is larger for conventionally prepared cata-

Table 2
XRD data of solvothermal and conventional nanostructure VPO catalysts.

Catalysts	Crystallite size[a] (nm)	
	0 2 0	2 0 4
VPOA1	139.61	178.06
VPOA2	231.10	190.48
VPOB1	70.28	133.53
VPOB2	60.22	138.30
VPOC1	138.96	154.31
VPOC2	114.13	191.38
VPOD1	82.84	147.19
VPOD2	86.44	143.80
VPOE1	70.27	108.01
VPOE2	102.29	92.07

[a] Crystallite size were calculated accordingly to Scherrer equation [34].

lysts compared to that of the microwave synthesized samples of vanadium phosphate catalyst. The calculated values are listed in Table 2.

On the basis of the crystalline size results calculated from the Scherrer equation, catalysts synthesized by solvothermal method exhibited smaller particle size with higher line width compared to the catalysts prepared via the conventional VPD method (Fig. 3). For all the solvothermal catalysts, the crystals present in 0 2 0 and 2 0 4 phases displayed smaller size which thought to be due to the fact that the basal spacing is influenced by longer chain alcohols. As results show, by using 1-pentanol as organic media, the crystallite size of (0 2 0) was significantly decreased from 23.1 nm (VPOA2) to 6.0 nm (VPOB2). Previous studies [35,36] reported that the best method to improve the catalytic performance of VPO catalysts is to increase the relative exposure of the (0 2 0) plane of $(VO)_2P_2O_7$, since this plane effectively participates in the reaction of partial oxidation of *n*-butane to maleic anhydride.

3.2. Surface area, chemical analysis and average oxidation number determination

Table 3 summarizes the surface area, P/V atomic ratio, and oxidation number of *V* in the bulk of the catalysts. BET results indicated that surface area of catalyst prepared by solvothermal was larger than catalysts prepared under the standard dihydrate VPD method. The obtained surface area values were consistent with crystallite size data and SEM morphology. The surface area of the solvothermal catalyst synthesized by 1-pentanol and microwave drying (VPOB1) shown to be 40.3 $m^2 g^{-1}$. One of the important features of BET results was that the replacement of the 1-hexanol, 1-heptanol and 1-decanol by 1-pentanol, slightly reduced the surface area to 34.3, 19.7 and 24.8 $m^2 g^{-1}$, respectively.

Table 3
Physical and chemical properties of solvothermal and conventional VPO catalyst.

Catalyst	Surface area[a] ($m^2 g^{-1}$)	P/V ratio[b]	V^{5+} (%)	V^{4+} (%)	Average oxidation number of V in bulk[c]
VPOA1	32.3	1.08	27	73	4.27
VPOA2	26.9	1.04	25	75	4.25
VPOB1	40.3	1.07	15	85	415
VPOB2	39.7	1.07	13	87	4.13
VPOC1	34.3	1.08	21	79	4.21
VPOC2	24.6	1.06	16	84	4.16
VPOD1	19.7	1.06	15	85	4.15
VPOD2	18.3	1.04	10	90	4.1
VPOE1	24.7	1.05	17	83	4.17
VPOE2	23.6	1.04	21	79	4.21

[a] After pretreatment at 423 K in a vacuum.
[b] Estimated from ICP-AES.
[c] Average oxidation number of vanadium estimated by redox titration [30].

However, the surface area of the solvothermal catalyst was found to be significantly higher than that reported for the VPO catalyst prepared via hydrothermal [20,21], organic and dihydrate [16,36–38] methods. As mentioned, the BET surface area value is in agreement with the crystallite size distribution and obviously, larger crystals display lower surface area. From crystallite size results calculated by Scherrer equation, all catalyst prepared solvothermally showed smaller particle size with higher line width as compared to standard VPD method. However, the catalyst precursors dried by microwave irradiation, represented higher specific surface area as compared with conventional heating.

Thermal decomposition of $VOPO_4{\cdot}2H_2O$ mixtures in longer chain alcohols (C_5–C_{10}) gives rise to a nanocrystalline VPO catalyst with crystal size of 6–13 nm. Synthesis of VPO catalysts using various organic media modifies the morphology and surface area of the catalyst. The VPO catalyst prepared by 1-pentanol produces a solid solution of $(VO)_2P_2O_7$ which in turn, leads to smaller crystals with larger 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. In conclusion, as shown in Table 3, by introducing the longer chain alcohols, C_5–C_{10}, the surface area of solvothermal catalysts would be eventually decreased.

As discerned in Table 3, the P/V atomic ratios of the bulk obtained via chemical analysis using ICP and average oxidation number of vanadium were found, for all catalysts, to be near unity and 4.2, respectively. The preparation and drying processes of precursors were observed to be directly proportional to the average oxidation state of vanadium. The average charge on vanadium is slightly higher for the microwave catalyst. However, for catalyst prepared by solvothermal method, the average oxidation number was decreased with an increase in V^{4+} phase. Materials were mainly composed of phosphorus (P), vanadium (V), and oxygen. Some of the values slightly deviated from the nominal P/V atomic ratio value of 1:1; however, these values were still in the optimal P/V atomic ratio range for producing an active and selective $(VO)_2P_2O_7$ phase. The phosphorus content in the microwave prepared materials was slightly higher compared with that in the conventionally prepared catalysts. This is also well-agreed upon in numerous literature works, indicating that the V^{4+} species responsible for the activity of the respective catalyst could be stabilized by higher P/V atomic ratios [13]. 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 [39]. 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

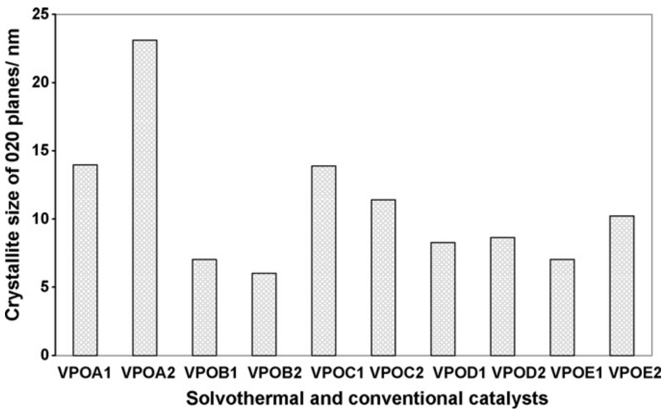

Fig. 3. Crystallite size of (0 2 0) planes for solvothermal and conventional catalysts.

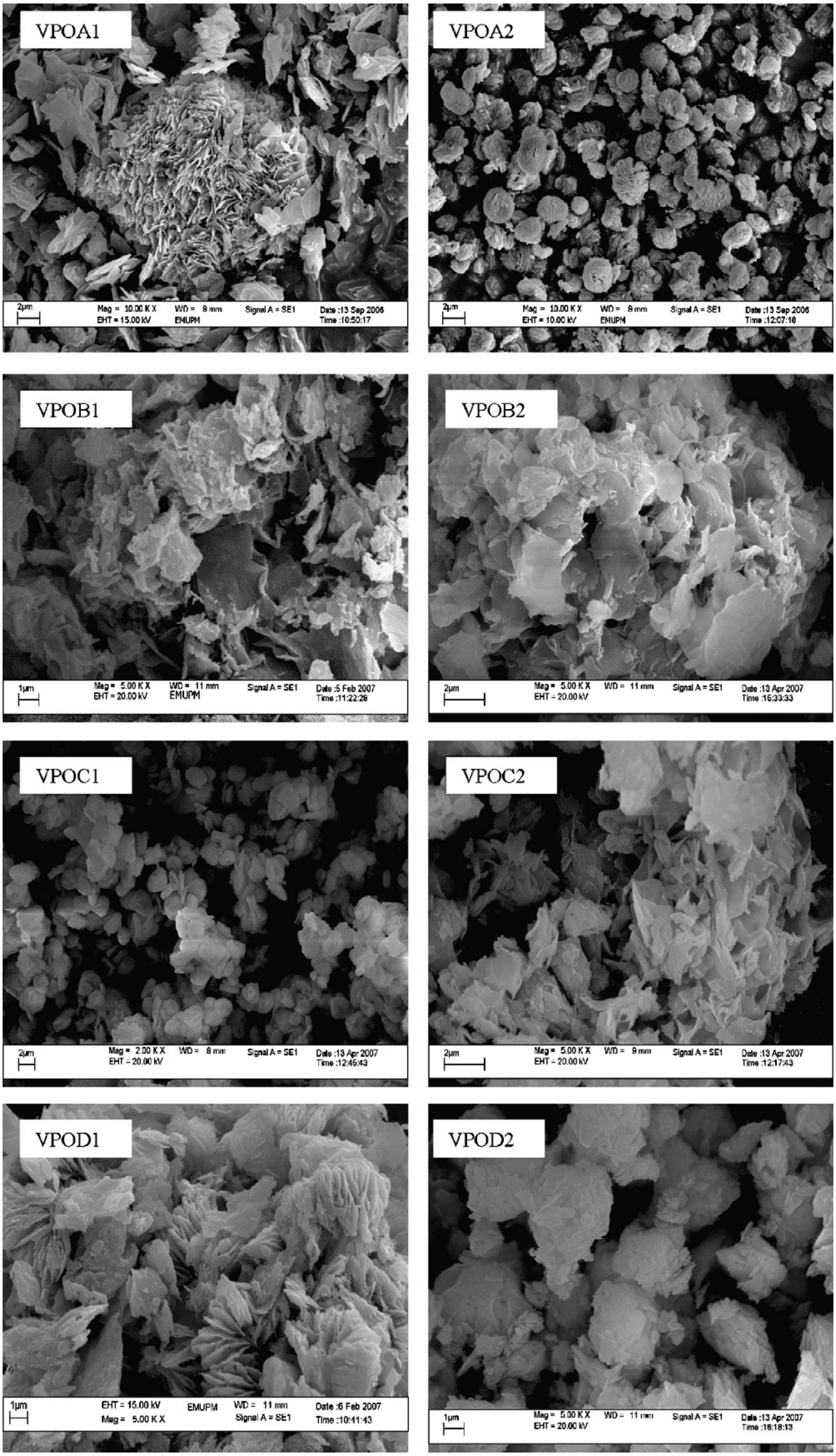

Fig. 4. Scanning electron micrographs (SEM) of VPO catalysts prepared by conventional isobutyl alcohol (VPOA) and solvothermal 1-pentanol (VPOB), 1-hexanol (VPOC), 1-heptanol (VPOD) and 1-decanol (VPOE) catalysts.

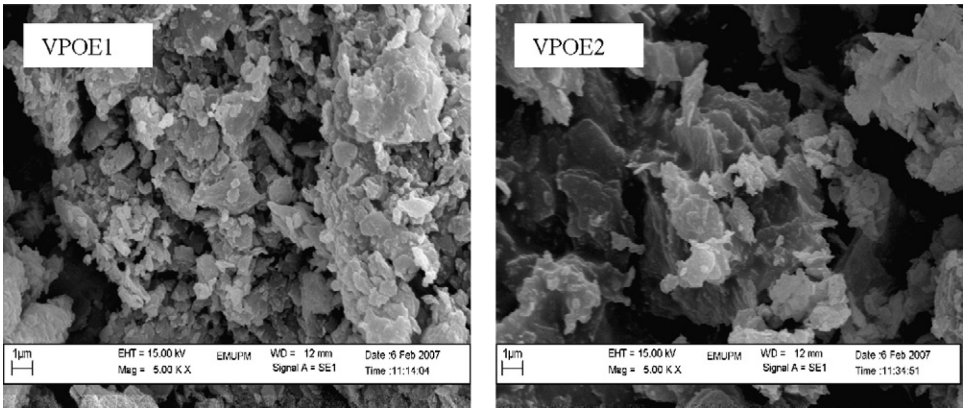

Fig. 4. (*Continued*).

in oxidation reactions and could be attributed to the formation of a V^{5+} phase ($VOPO_4$) during solvothermal synthesis, as shown in the XRD diffraction patterns (Fig. 2). Therefore, the polarity and the type of the alcohol used as reducing agent exhibit stronger impact on catalysts properties (Figs. 2 and 3).

3.3. Scanning electron microscopy

Fig. 4 shows SEM micrographs of the VPO catalysts. SEM images reveal a novel morphology of solvothermal-microwave prepared catalysts. Among the characteristic vanadium phosphate rosette shaped particles, solvothermal catalysts displayed a plate-like structure with the average particle size of less than 2 μm. The thin-plate morphology was found in all microwave catalyst structure. The solvent plays an important role in determining the crystal morphology. 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 microwave-assisted solvothermal treatment of VPO catalyst and significantly smaller than conventional VPD catalyst. 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. SEM images confirmed that the solvothermal synthesis was highly dependent on the type of reducing agent. The SEM micrographs of $VOHPO_4{\cdot}0.5H_2O$ synthesized by refluxing of $VOPO_4{\cdot}2H_2O$ with isobutyl alcohol showed rosette structures with platelets as characterized by an XRD pattern with the (0 2 0) reflection dominant [10,18]. All catalysts exhibited rosette-shape species, adhered to the aggregated particles which were recognized as $(VO)_2P_2O_7$ phase, one of the most typical morphologies observed. The SEM micrographs of solvothermal catalysts (VPOB) synthesized by 1-pentanol, show that the crystals are not single crystal faces since the surfaces are marked with many indentations, thereby exposing more surface plane. The VPOB catalyst represents nanostructure plats with secondary platelet morphology. In the case of VPOC, by replacing 1-hexanol with 1-pentanol, a quite different morphology was observed. The structure is mainly composed of plate-like crystals, which are arranged into the characteristic rosette-shape clusters with homogeneous dispersion. On the other hand, as with conventional heated catalyst shown in Fig. 4, the catalysts lost their secondary rosette-shape structure and provided shear forces which allowed the crystal platelets to slide away from one another. In contrast, the SEM images vanadium phosphate catalyst prepared by 1-heptanol as reducing agent and conventional heating, revealed the existence of spherical particles with a high tendency to agglomerate in a random configuration causing a decrease in surface area of the catalyst. SEM of VPOE 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-decanol was replaced by 1-pentanol. These amorphous parts reduce the particle size and

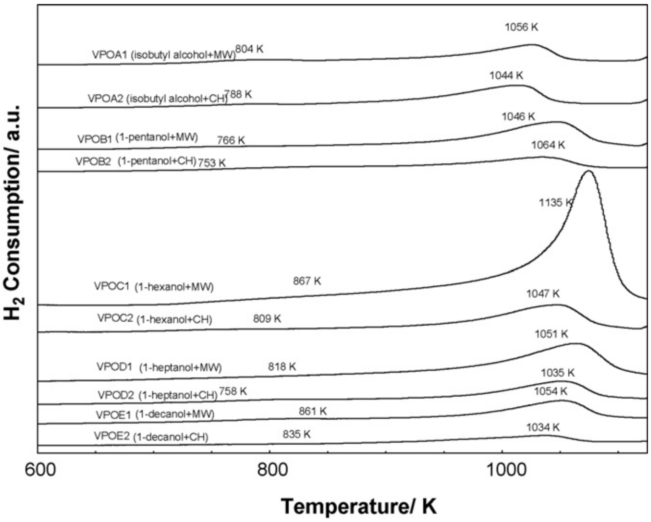

Fig. 5. Temperature programmed reduction (H_2-TPR) profiles of VPO catalysts prepared by conventional isobutyl alcohol (VPOA) and solvothermal 1-pentanol (VPOB), 1-hexanol (VPOC), 1-heptanol (VPOD) and 1-decanol (VPOE) catalysts.

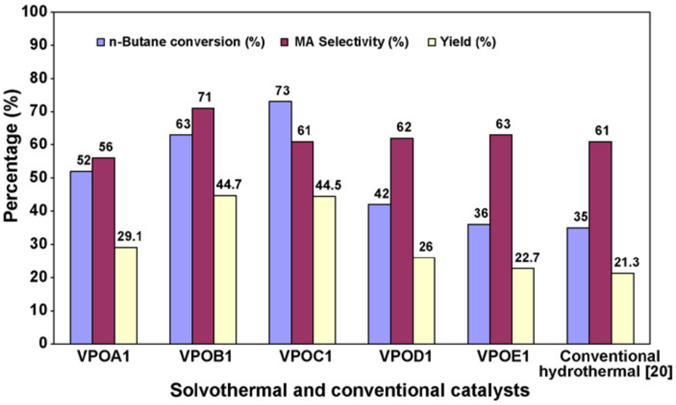

Fig. 6. *n*-Butane conversion, MA selectivity and yield for different catalysts.

therefore increase the specific surface area, while for VPOE2 catalyst dried by conventional heating, agglomeration occurs and a new secondary structure forms. Comparing the series allows to conclude that solvothermal synthesis produces the nanostructure platelet structure with a secondary platelet morphology.

3.4. Influence of reducing agent (catalyst microstructure) on amount and nature of the oxygen species

The partial oxidation of *n*-butane on vanadium phosphate catalyst is known to proceed via a redox mechanism [40]. Therefore, the reduction property of a catalyst is a key factor accounting for reaction behavior. The reduction behavior of a catalyst can be examined by means of temperature-programmed reduction (TPR) technique. For partial oxidation of *n*-butane, the redox cycle of vanadium only involves the reduction of V^{4+} and V^{5+} and the further reduction of V^{3+} is not the main concern of this study. Therefore, the adopted temperature range (from RT to ~1050 K) for H_2-TPR is usually sufficient for the reduction of V^{4+} and V^{5+} according to previous studies [41,42]. Fig. 5 shows the TPR profiles of catalysts. It can be observed that the consumption of H_2 starts at around 750 K but the major reduction process of V^{4+} in $(VO)_2P_2O_7$ phase was completed as the temperature raised to ~1150 K. After being held in reducing atmosphere at ~1050 K for ~45 min, the reduction of V^{4+} was nearly completed. On the other hand, as Fig. 5 shows, employing isobutyl alcohol as reducing agent, slightly decreased the reduction temperature of both peaks by ~20 K as compared with VPOA results. The total amount of oxygen removed from both microwave and conventional heated catalysts were shown to be 1.34×10^{21} and 1.10×10^{21} atom g^{-1}, respectively, with an oxygen ratio of 0.38 to 0.25 for V^{5+} to V^{4+}.

Based on H_2-TPR data obtained (Table 4), catalysts synthesized by solvothermal method, represent two reduction peaks at lower temperatures with lower oxygen ratio of V^{5+} to V^{4+} than conventional catalysts. However, utilization of 1-pentanol in the synthesis of catalysts, reduced the reduction temperature to 753 K (VPOB2) along with the amount of oxygen removed from both peaks to 1.25×10^{21} and 0.91×10^{21} for microwave and conventional heated catalysts, respectively, with an oxygen ratio of 0.04 to 0.07 for V^{5+} to V^{4+}. The 1-hexanol shows similar reduction pro-

Table 4

Total amount of oxygen removed and ratio for oxygen removed of V^{5+}/V^{4+} obtained by temperature programmed reduction in H_2/Ar (H_2-TPR).

Catalysts	Peaks[a]	T_{max} (K)	Total amount of oxygen remowed × 10^{-3} (mol g^{-1})	Total amount of oxygen removed × 10^{21} (atom g^{-1})	[b]Ratio of oxygen removal of V^{5+}/V^{4+}
VPOA1	1	804	0.62	0.37	0.38
	2	1056	1.61	0.97	
Total oxygen atoms removed			2.23	1.34	
VPOA2	1	788	0.36	0.22	0.25
	2	1044	1.47	0.88	
Total oxygen atoms removed			1.83	1.10	
VPOB1	1	776	0.09	0.05	0.04
	2	1046	1.99	1.20	
Total oxygen atoms removed			2.08	1.25	
VPOB2	1	753	0.10	0.06	0.07
	2	1064	1.42	0.85	
Total oxygen atoms removed			1.52	0.91	
VPOC1	1	867	0.60	0.36	0.11
	2	1135	5.36	3.23	
Total oxygen atoms removed			5.96	3.59	
VPOC2	1	809	0.09	0.05	0.05
	2	1047	1.45	0.87	
Total oxygen atoms removed			1.54	0.92	
VPOD1	1	818	0.25	0.15	0.18
	2	1051	1.35	0.81	
Total oxygen atoms removed			1.60	0.96	
VPOD2	1	758	0.01	0.01	0.02
	2	1035	1.12	0.67	
Total oxygen atoms removed			1.13	0.68	
VPOE1	1	861	1.11	0.67	0.63
	2	1054	1.78	1.07	
Total oxygen atoms removed			2.89	1.74	
VPOE2	1	835	0.67	0.40	0.83
	2	1034	0.80	0.48	
Total oxygen atoms removed			1.47	0.88	

[a] After pretreatment at 473 K in a N_2 and cooling down under He.

[b] Estimated from H_2-TPR.

Table 5
Catalytic performance of conventional VPD, solvothermal and conventional hydrothermal method for the oxidation of *n*-butane to maleic anhydride[a].

Catalyst	*n*-Butane conversion (%)	Selectivity (%)			Yield[b] (%)
		MA	CO	CO_2	
VPOA1	52	56	32	12	29.1
VPOB1	63	71	16	13	44.7
VPOC1	73	61	22	17	44.5
VPOD1	42	62	23	15	26.0
VPOE1	36	63	21	16	22.7
Conventional hydrothermal method[c]	35	61	22	17	21.3

[a] Reaction condition, 673 K, 1.7% *n*-butane in air, GHSV: 2400 h^{-1}.
[b] Yield (%) = *n*-butane conversion (%) × MA selectivity (%).
[c] Taufiq-Yap et al. [20].

files as 1-pentanol. Moreover, it was found that the 1-hexanol catalyst slightly increased the reduction temperature. However, interestingly, the total amount of oxygen removed from VPOC1 was 3.59×10^{21} atom g^{-1}, with an oxygen ratio of 0.01 for V^{5+} to V^{4+}.

In contrast, for conventionally made catalysts, replacement of 1-pentanol by 1-heptanol slightly reduced the total amount of oxygen removed to 0.68×10^{21} atom g^{-1}. As with VPOE1 which was produced by C_{10} alcohol and microwave irradiation, the first reduction peak was shifted to a higher temperature, *i.e.*, 866 K, while, the second reduction peak was appeared at lower temperature, *i.e.*, 1045 K on contrary to conventional reflux catalyst (VPOA1). In addition, the removal of oxygen was 1.35×10^{21} atom g^{-1} with an oxygen ratio of 0.63 for V^{5+} to V^{4+}. The catalyst subjected to solvothermal synthesis with 1-decanol as the reducing agent represented almost identical amount of oxygen removal to V^{5+}, *i.e.*, 0.91×10^{21} atom g^{-1} compared to the case with other organic solvents used in solvothermal method.

Furthermore, as Table 4 shows, drying of VPO catalysts by microwave irradiation rather than conventional heating, gives rise to the higher amount of oxygen removal in TPR experiments. In general, the solvothermal catalysts show similar reduction profiles to those of conventional reflux catalysts except with lower onset reduction temperature.

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

Table 5 summarizes the catalytic performance of catalysts at reaction temperature of 673 K and GSHV of 2400 h^{-1}. A significant improvement of catalytic performance was observed for *n*-butane conversion and maleic anhydride (MA) selectivity when VPO catalyst was synthesized using 1-pentanol as the solvent and reducing agent, and microwave as the heating media. Fig. 6 shows *n*-butane conversion, selectivity and yield to MA data. The VPOC1 catalyst was found to be the most active catalyst, while, VPOB1 catalyst was shown to exhibit the highest MA selectivity. The selectivity to MA of VPOB1 was reached to about 71% at 63% conversion. In addition, by using 1-heptanol and 1-decanol as the reducing agent, the *n*-butane conversion was reduced to 42% and 36% while the MA selectivity was enhanced to 62% and 63%, respectively. However, as shown in Fig. 6, all solvothermal catalysts (VPOB1, VPOC1, VPOD1, and VPOE1) displayed higher selectivity to MA than conventional VPOA1 catalysts. In particular, VPOC1 exhibited remarkably high conversion, reaching to 73% at low selectivity levels (61%) to MA. The *n*-butane conversion exhibited a 28% increase from 35% to 63% by using VPOB1 catalyst (produced by 1-pentanol). The higher surface area of solvothermal catalyst than conventional hydrothermal one significantly enhanced the catalytic conversion. The higher amount of active site (V^{4+}) and oxygen species are responsible for activation of *n*-butane and enhancement of catalyst activity. In general, the results revealed that using 1-pentanol and microwave irradiation in preparation of VPO catalysts can significantly improve catalytic performance, selectivity, and conversion of *n*-butane. Higher yields of VPOB1 and VPOC1 catalysts are due to higher surface area indicating the presence of highly reactive and labile oxygen species originated from V^{4+}, capable of increasing the breaking rate of C–H bonding. Therefore, the results show that the surface area of catalyst is one of the main factors affecting the catalyst activity. These results are in a good agreement with Hutchings findings [37] which suggested that the best performing catalyst had the higher surface area. Moreover, the availability and behavior the oxygen species play an important role in determining the catalytic activity and supports this idea that the mobility of active oxygen species (O^-) in the catalyst is the main determining step for *n*-butane activation [41–44]. As reported earlier, selective oxidation of *n*-butane over vanadium phosphate catalyst is carried out via a redox mechanism proposed by Mars and van Krevelen [45]. Furthermore, as shown in Table 2, the crystallite size of all solvothermal catalysts were significantly lower than conventional VPD catalyst providing the higher activity due to an increase in the amount of oxygen removed associated with V^{4+} phase. These results confirmed the previous results reported in literature [12]. Moreover, the results revealed the important role of high pressure solvothermal method in the catalytic performance, selectivity and especially conversion of *n*-butane.

4. Conclusion

In this work, $VOHPO_4{\cdot}0.5H_2O$ orthorhombic phase was selectively synthesized by a so-called “solvothermal method”. High surface area (*ca.* 40.3 $m^2\,g^{-1}$) catalysts comprising $(VO)_2P_2O_7$ and $VOPO_4$ can be prepared using a solvothermal method with an aliphatic alcohol acting as a solvent as well as a reducing agent for the synthesis of catalyst precursor ($VOHPO_4{\cdot}0.5H_2O$). We found that this method of preparation consistently yields high surface area materials compared to previous surfactant and water based methods (hydrothermal method) that give rise to low surface area catalysts (*ca.* 9.5 $m^2\,g^{-1}$). The catalysts synthesized by this technique exhibit activities and selectivities comparable to vanadium phosphate catalysts prepared using conventional VPD method. In summary, solvothermal method represents a simple, efficient and low-cost technique for the synthesis of VPO catalyst with improved catalytic performance in selective oxidation of C_4-hydrocarbon.

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